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First analysis of the $B^1\Sigma^+$ ($\upsilon=1$) Rydberg state in the lesser-abundant $^{12}C^{17}O$ isotopologue on the basis of the $1-\upsilon''$ progression of the Ångström band system

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ABSTRACT

So far unobserved in the $^{12}C^{17}O$ isotopologue, the $1-\upsilon''$ progression of the Ångström ($B^1\Sigma^+$–$A^1\Pi$) band system was recorded under high resolution in the 17,200–22,950 cm^{-1} spectral region as an emission spectrum using high-accuracy dispersive optical spectroscopy. The $^{12}C^{17}O$ molecules were formed and excited in two steps in a stainless steel hollow-cathode lamp with two anodes. The emission from the discharge was observed with a plane-grating spectrograph and recorded by a photomultiplier tube.

In the studied region, the full rotational structure of the 1–1 and 1–5 bands of the *B*–*A* system was observed, in total 114 spectral emission lines up to $J''=21$. All those lines were precisely measured with an estimated accuracy of about 0.0030 cm^{-1}, and rotationally analyzed. As a result, many molecular constants were determined for the $B^1\Sigma^+$ and $A^1\Pi$ states in the $^{12}C^{17}O$ isotopologue. In this paper we have also presented the results of calculations concerning RKR turning points, Franck–Condon factors, relative intensities, and *r*-centroids for the Ångström band system in the $^{12}C^{17}O$ molecule. We have also determined the value of the $\Delta G_{1/2}$ vibrational quantum, the isotope shifts, as well as the main, isotopically invariant parameters of the $B^1\Sigma^+$ Rydberg state in the CO molecule within the Born–Oppenheimer approximation.

For the $A^1\Pi$, $\upsilon=5$ state, considerable irregularities of the rotational structure have been observed and analyzed in detail. Suspected candidates responsible for these perturbations have been identified. The $B^1\Sigma^+$, $\upsilon=1$ state has been thoroughly analyzed in terms of possible perturbations and it emerged to be completely regular in the $^{12}C^{17}O$ molecule up to the observed maximum *J* value.

1. Introduction

Carbon monoxide is one of the most stable diatomic molecules and one of the most abundant to be identified in outer space. The presence of the CO molecule was discovered in planets, solar and stellar atmospheres, interstellar space, comet tails, supernova remnants as well as in the spectra of diverse cosmic objects [1–4]. Special attention is paid to the discoveries and quantification of different natural isotopologues of CO in order to model the evolution of interstellar clouds and stars [5–7]. The presence of all natural isotopologues of the CO molecule, also including a lesser-abundant $^{12}C^{17}O$, was found in the solar spectrum, recorded in high resolution with the ATMOS infrared Fourier transform interferometer [8]. Various isotopologues of CO are often used as tracers to determine the hydrogen-containing of molecular clouds to map the distribution of matter [9]. The carbon monoxide

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molecule together with its isotopologues also play a major role in other branches of science such as chemical physics, microbiology, molecular biology, environment of the earth, technology of new materials, metallurgy, engineering processes, etc. For the reasons mentioned above, a comprehensive and complex study of all natural isotopologues of CO, through which precise values of quantum-mechanical parameters and molecular constants of all excited states can be obtained, has become a momentous task for many branches of contemporary spectroscopy. In this respect, a high accuracy dispersive optical spectroscopy is extremely valuable, also applied in the research described in this paper.

For successive years laboratory research into the CO spectrum concentrated on its highly excited electron states, and especially on the Rydberg states. The first and the lowest placed state of this type is $B^1\Sigma^+$. A considerably greater part of such investigations was connected more with the ordinary $^{12}C^{16}O$ molecule than with the other isotopologues of CO [10–16]. Only vibrational levels $\upsilon=0$ and 1 are engaged in the emission transitions from the $B^1\Sigma^+$ state, however, the remaining existing vibrational levels exclusively take part in absorption transitions to the states: $B^1\Sigma^+(\upsilon=2)$ [11], $B^1\Sigma^+(\upsilon=3)$ [13] as well as $B^1\Sigma^+(\upsilon=6)$ [14]. A pioneering experimental study investigating the $B^1\Sigma^+(\upsilon=0)$ state in the rare $^{12}C^{17}O$ and $^{13}C^{17}O$ has been carried out by Hakalla et al. [17,18]. The first paper concerning the $B^1\Sigma^+(\upsilon=1)$ state in $^{13}C^{17}O$ has been published very recently by Hakalla et al. [19]. The $B^1\Sigma^+(\upsilon=1)$ state in the $^{12}C^{17}O$ molecule has remained unknown up to now. The first of the excited Rydberg states, $B^1\Sigma^+$, is accessible to study, for example, through analyses of the Ångström ($B^1\Sigma^+$–$A^1\Pi$) band system, located in the visible region, which is convenient for observation and analyses.

In this paper we present the results of the first analysis of the $B^1\Sigma^+$, $\upsilon=1$ Rydberg state in the $^{12}C^{17}O$ isotopologue on the basis of the 1–υ'' progression of the Ångström ($B^1\Sigma^+$–$A^1\Pi$) band system.

2. Experimental details

The measurement system has been described in detail in one of our previous studies [18], so in this section only details directly related to current research will be presented.

The spectrum of the $B^1\Sigma^+$–$A^1\Pi$ transition of $^{12}C^{17}O$ was excited in the water-cooled, hollow-cathode lamp with two anodes [20]. It was initially filled with a mixture of acetylene $^{12}C_2D_2$ (99.99% purity of ^{12}C) under pressure of about 6 Torr and helium carried gas under pressure of about 1 Torr. Next, electric current was passed through this mixture for about 130 h. After the deposition of an adequate amount of ^{12}C on the electrodes, this lamp was evacuated and molecular oxygen was let into this space including 70% of the $^{17}O_2$ isotope, as non-flowing gas under pressure of about 2 Torr. The electrodes were powered by direct current of the following parameters: 2×650 V and 2×40 mA. These experimental conditions were tested and considered as optimal to obtain the 1–υ'' progression bands of the Ångström system in the $^{12}C^{17}O$ isotopologue. In this way, the 1–1 and 1–5 bands of the *B*–*A* transition were successfully recorded.

A measurement system that enables us to obtain and record emission spectra using a high accuracy dispersive optical spectroscopy has been built in our laboratory (see Fig. 1 of Ref. [18]). The examined spectra were observed in the 5th order for 1–1 band and in the 4th order for 1–5 band of the Ångström system. The reciprocal dispersion was in the range of 0.10–0.12 nm/mm, and the theoretical resolving power was approximately 228,000 and 182,400 for the 1–1 and 1–5 bands, respectively. An atomic spectrum of thorium from a few overlapping orders was used as a calibration spectrum [21]. It was obtained in the water-cooled, hollow-cathode tube with the cathode lined with thin Th foil.

The peak positions of spectral lines were calculated by means of a least-squares procedure assuming a Gaussian line-shape for each spectral contour (30 points per line),

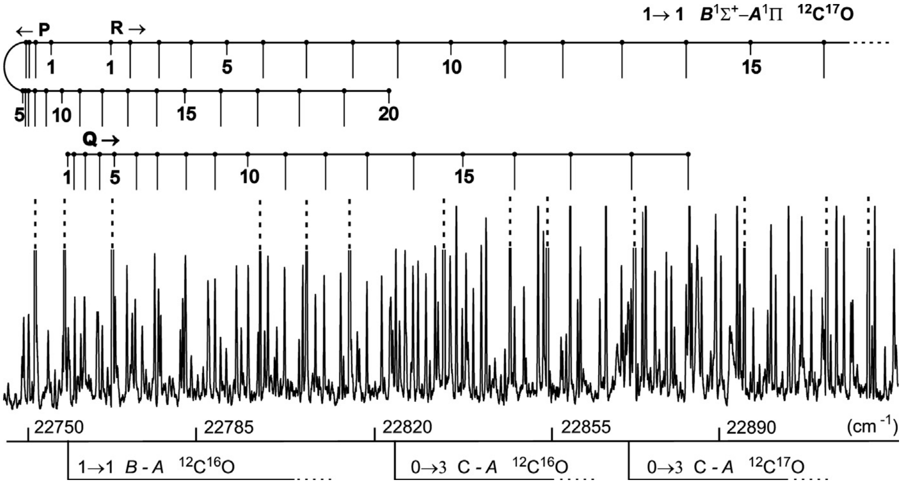

Fig. 1. Part of the rotational structure of the 1–1 band of the $B^1\Sigma^+\rightarrow A^1\Pi$ transition in $^{12}C^{17}O$. Peaks of the Th atomic lines used for calibrations are marked with broken lines. The positions of the band—head regions of the less intense 1–1 band of the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{16}O$ and for the first time recorded in $^{12}C^{17}O$ isotopologue the part of the 0–3 band of the $C^1\Sigma^+$–$A^1\Pi$ system, are displayed at the bottom of the figure.

with an uncertainty of the peak position for a single line of approximately 0.1–0.2 μm. In order to calculate the wavenumbers of the CO molecule, 4th- and 3th-order interpolation polynomials were used and the typical standard deviation of the least-squares fit for the 20–30 calibration lines was approximately $1.6\times10^{-3}\,\mathrm{cm}^{-1}$ and $6.6\times10^{-4}\,\mathrm{cm}^{-1}$ for the 1–1 and 1–5 bands, respectively. The spectral width of intense and single lines of CO was about $0.15\,\mathrm{cm}^{-1}$, and their maximum signal-to-noise ratio totalled about 60:1 and 40:1 for the 1–1 and 1–5 bands, respectively. The most intense lines produce the count rates of about 8000 photons/s and 4000 photons/s for the 1–1 and for 1–5 transitions, respectively. As a result, the measurements of strong and single lines of the examined spectrum are expected to be accurate to about $0.0030\,\mathrm{cm}^{-1}$. However, some of the weaker and blended lines were measured with lower accuracy, which amounted to $0.0060\,\mathrm{cm}^{-1}$. The summary of observations and analyses of the 1–υ'' progression of the Ångström band system ($B^1\Sigma^+$–$A^1\Pi$) for the $^{12}C^{17}O$ isotopologue is given in Table 1.

In total 114 emission lines belonging to the 1–1 and 1–5 bands of the $B^1\Sigma^+$–$A^1\Pi$ system in the $^{12}C^{17}O$ molecule have been measured and their wavenumbers are provided in Tables 2 and 3. Figs. 1 and 2 show a high quality, expanded view of the 1–1 and 1–5 bands of the Ångström (B–A) system in the $^{12}C^{17}O$ molecule together with their rotational assignments.

Table 1
Individual bands fits in the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{17}O$.

Band	σ_{head} (cm^{-1})	n[a]	J_{max}	f[b]	$\sigma\times10^3$ (cm^{-1})[c]
1–1	22,748.651	57	20	9	1.63
1–5	17,236.776	57	21	14	1.04

[a] Total number of observed lines.

[b] Number of degrees of freedom of the fit for the individual band-by-band analysis using the linear least-squares method proposed by Curl and Dane [22] and Watson [23].

[c] Standard deviation of the fit for the individual band analysis.

Table 2
Observed wavenumbers (cm^{-1}) and their rotational assignments for the 1–1 band of the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{17}O$. Values in parentheses denote observed minus calculated values in units of the last quoted digit. Asterisks denote the less accurate lines not used in the evaluation of individual rotational constants of $B^1\Sigma^+$ state.

J	$P_{11ee}(J)$		$Q_{11ef}(J)$		$R_{11ee}(J)$	
1	22,754.0612	*	22,757.8417	(0)	22,765.3065	(0)
2	22,751.7288	(−7)	22,759.2646	(0)	22,770.4707	(7)
3	22,750.0308	(−2)	22,761.3198	(0)	22,776.2667	(2)
4	22,749.0085	(−6)	22,764.0366	(0)	22,782.7391	(6)
5	22,748.6512	(−6)	22,767.4357	(0)	22,789.8741	(5)
6	22,748.9738	(−1)	22,771.4681	(0)	22,797.6863	(1)
7	22,749.9490	(0)	22,776.1855	(0)	22,806.1495	(−1)
8	22,751.5914	(2)	22,781.5649	(0)	22,815.2775	(−2)
9	22,753.9093	(19)	22,787.6112	(0)	22,825.0751	(−19)
10	22,756.8830	(15)	22,794.3372	(0)	22,835.5295	(−15)
11	22,760.5186	(−3)	22,801.7090	(0)	22,846.6450	(3)
12	22,764.8318	(4)	22,809.7603	(0)	22,858.4293	(−5)
13	22,769.7914	(4)	22,818.4630	(0)	22,870.8574	(−4)
14	22775.4307	(2)	22,827.8272	(0)	22,883.9609	(−3)
15	22781.7335	(−3)	22,837.8688	(0)	22,897.7239	(3)
16	22,788.6915	(38)	22,848.5920	(0)	22,912.1276	(−38)
17	22,796.3267	(−7)	22,860.0462	(0)	22,927.2201	(6)
18	22,804.6478	(0)	22,872.5923	(0)	22,942.9241	*
19	22,813.7087	(0)	22,884.5143	(0)		
20	22,823.6411	*				

Table 3
Observed wavenumbers (cm^{-1}) and their rotational assignments for the 1–5 band of the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{17}O$. Values in parentheses denote observed minus calculated values in units of the last quoted digit. Asterisks denote the less accurate lines not used in the evaluation of individual rotational constants of $B^1\Sigma^+$ state.

J	$P_{11ee}(J)$		$Q_{11ef}(J)$		$R_{11ee}(J)$	
1	17,240.4073	*	17,244.1605	(0)	17,251.6514	*
2	17,238.3552	(0)	17,245.8521	(0)	17,257.0832	*
3	17,237.1347	(−3)	17,248.3862	(0)	17,263.3708	(3)
4	17,236.7762	(−5)	17,251.7653	(0)	17,270.5065	(4)
5	17,237.2452	(−1)	17,255.9927	(0)	17,278.4671	(1)
6	17,238.5820	*	17,261.0654	(0)	17,287.2919	(0)
7	17,240.7452	(−9)	17,266.9721	(0)	17,296.9478	(10)
8	17,243.7697	(0)	17,273.7260	(0)	17,307.4458	*
9	17,247.6267	(1)	17,281.3277	(0)	17,318.7961	(−1)
10	17,252.3288	(0)	17,289.7673	(0)	17,330.9753	*
11	17,257.8809	(5)	17,299.0698	(0)	17,344.0058	(−4)
12	17,264.2693	(3)	17,309.1916	(0)	17,357.8671	(−3)
13	17,271.5304	(−1)	17,320.1697	(0)	17,372.5974	(1)
14	17,279.6314	(1)	17,331.9804	(0)	17,388.1618	(−2)
15	17,288.5739	(−20)	17,344.7211	(0)	17,404.5677	(20)
16	17,298.3866	(−2)	17,358.1854	(0)	17,421.8306	(2)
17	17,309.0260	(0)	17,372.5670	(0)		
18	17,320.5106	(0)	17,387.7645	(0)		
19	17,332.8221	(0)	17,403.8084	(0)		
20	17,345.9579	(0)	17,420.7656	(0)		
21	17,359.9810	(0)				

3. Analysis and results

Because of the extensive and multistate perturbation, which will be described in the next section, appearing in the $A^1\Pi$ state, a reduction of the wavenumbers of the examined molecular lines of the 1–1 and 1–5 bands of the B–A system in the $^{12}C^{17}O$ molecule to rovibronic parameters was performed by means of an individual band-by-band analysis, using the linear least-squares method proposed by Curl and Dane [22] and Watson [23]. This method is an efficient means of separating molecular information concerning the regular state of $B^1\Sigma^+(\upsilon'=1)$ from that which concerns the strongly perturbed state of $A^1\Pi(\upsilon''=1, 5)$. The $B^1\Sigma^+$ state in this method was represented by an effective Hamiltonian in the version proposed by Brown et al. [24] (the matrix elements of this Hamiltonian for a regular $^1\Sigma^+$ state are identical as energy level expansion in $J(J+1)$). In this way, we obtained two series of individual rotational molecular constants for the $B^1\Sigma^+(\upsilon=1)$ state, received from the independent fit of the 1–1 and 1–5 bands of the Ångström system and also the real (perturbed) $T(\upsilon;\,J)_{obs}$ term values for the $\upsilon''=1$ and 5 levels of the $A^1\Pi$ state in the $^{12}C^{17}O$ isotopologue.

In order to obtain final rotational constants for the $\upsilon=1$ level of the $B^1\Sigma^+$ Rydberg state, the calculations were performed by means of the least-squares merge fit method proposed by Albritton et al. [25] and Coxon [26] using the 1–1 and 1–5 bands, analyzed in this paper. The estimated

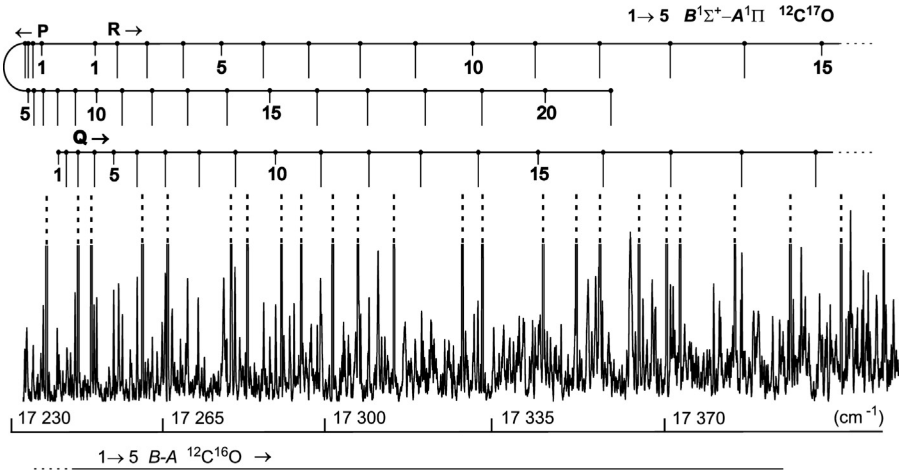

Fig. 2. Part of the rotational structure of the 1–5 band of the $B^1\Sigma^+ \rightarrow A^1\Pi$ transition in $^{12}C^{17}O$. Peaks of the Th atomic lines used for calibrations are marked with broken lines. The position of a fragment of the less intense 1–5 band of the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{16}O$ is shown at the bottom of the figure.

Table 4
Molecular constants (cm^{-1}) of the $B^1\Sigma^+$ and $A^1\Pi$ states of $^{12}C^{17}O$. Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. Values in square brackets were fixed during the fit.

υ	$B^1\Sigma^+$			$A^1\Pi$		
	B_υ	$D_\upsilon \times 10^6$	Description	B_υ	$D_\upsilon \times 10^6$	Description
1	1.874134 (33)	6.962 (78)	From 1 to 1 band[a]	1.539557 (34)	[6.950][b]	From 1 to 1 band[a]
	1.874148 (29)	6.909 (70)	From 1 to 5 band[a]			
	1.874146 (22)	**6.937 (52)**	Merged value[a,c]			
5				1.451773 (29)	[7.707][d]	From 1 to 5 band[a]

[a] This work.

[b] A constant taken from the work by Hakalla et al. [17] (0–υ'' progression of B–A in $^{12}C^{17}O$) because of too short bands of the 1–υ'' progression of the B–A transition, and the impossibility of determining a satisfactory D_1 constant during the analysis of the 1–1 band. This constant was constrained during the evaluation of the individual effective molecular constants in order to determine the rotational constants B_1 with greater precision.

[c] The estimated variance of the merging and the numbers of degrees of freedom were $\sigma_M^2=2.28$ and $f_M=2$, respectively.

[d] Obtained from the deperturbed molecular constants of the $^{12}C^{16}O$ molecule given by Field [34] by using standard isotope relations and constrained during the evaluation of the individual effective molecular constants in order to determine the rotational constants B_5 with greater precision.

variance of merging and the number of degrees of freedom were $\sigma_M^2=2.28$ and $f_M=2$, respectively. The results are presented in Table 4.

Next, by means of the linear least-squares method, in which both states involved in the transitions were represented by an effective Hamiltonian of Brown et al. [24], the individual rotational constants of the perturbed $A^1\Pi$ ($\upsilon=1, 5$) lower state and the 1–1 and 1–5 band origins of the Ångström system in the $^{12}C^{17}O$ molecule were calculated. In this fit the model representing irregular $A^1\Pi$ lower state was simplified to the version in which additional perturbing matrix elements were disregarded and only the wavenumbers of regular spectral lines were used. During this fit constants of the regular $B^1\Sigma^+(\upsilon'=1)$ upper state were constrained to very precise and well determined, merged molecular constants. All the results are presented in Table 4. The individual effective molecular constants for $A^1\Pi(\upsilon=5)$ in the $^{12}C^{17}O$ isotopologue are presented for the first time. The 1–1 and 1–5 band origins in the $^{12}C^{17}O$ molecule are highlighted in Table 5. Also, the first experimental values of the isotope shifts of the examined $^{12}C^{17}O$ isotopologue with regard to the ordinary $^{12}C^{16}O$ molecule (see Table 5) as well as the un-perturbed $T(v;\ J)_{calc}$ term values for the $A^1\Pi(\upsilon=1$ and $5)$ state were calculated.

Table 5
Band origins and isotope shifts (cm^{-1}) of the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{17}O$. Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

Band	Band origin	Isotope shift[a]
1–1	22,756.0278 (62)	9.142 (26)
1–5	17,241.8648 (18)	–54.028 (9)

[a] Calculated as $\sigma^{^{12}C^{16}O}_{band\ origin} - \sigma^{^{12}C^{17}O}_{band\ origin}$ experimental values. The $\sigma^{^{12}C^{16}O}_{band\ origin}$ were taken from [45] and [28] for the 1–1 and 1–5 bands, respectively.

An important result of this work is the possibility of determining for the first time the experimental vibrational and rotational equilibrium molecular constants in the lesser-abundant $^{12}C^{17}O$ molecule for the $B^1\Sigma^+$ state as well as for the $A^1\Pi$ state. It was performed by means of the weighted least-squares method on the basis of the merged and individual rovibronic constant values as well as the band origins determined in this paper and the data published in the [17] study, assuming their traditionally recognized polynomial dependence on the vibrational quantum number. The results are presented in Table 6. In order to determine the vibrational equilibrium constants with higher precision, the $\Delta G_{1/2}$ vibrational quantum for the regular $B^1\Sigma^+$ state was determined using rovibrational combination differences [27] on the basis of the data from the 1 to 1 bands (this work), as well as from 0 to 1 (Ref. [17]) of the B–A system in the $^{12}C^{17}O$ molecule. The value calculated amounts to

$$\Delta G_{1/2} = 2056.4865(12)\ \mathrm{cm}^{-1}.$$

Table 6
Equilibrium molecular constants (cm^{-1}) of the $B^1\Sigma^+$ and $A^1\Pi$ states of $^{12}C^{17}O$. Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. Values calculated within this work are given in bold. Values given in square brackets were constrained during the calculation.

Constant	State	
	$B^1\Sigma^+$	$A^1\Pi$
σ_e	**21,856.939 (39)**	
ω_e	**2124.92 (43)**[a] 2124.65[b]	**1498.64 (71)** 1497.60[b] 1498.65[c] 1497.94[d] 1501.18[e]
$\omega_e x_e$	**34.22 (22)**[a] 34.08[b]	[17.23][d]
$\omega_e y_e \times 10^2$		[7.43][d]
$\omega_e z_e \times 10^3$		[−8.82][d]
$Y_{50} \times 10^4$		[4.37][d]
B_e	**1.911250 (13)**	**1.57354 (45)** 1.57291[c] 1.57441[d] 1.57433[e]
$\alpha_e \times 10^2$	**2.4736 (23)**	**2.0559 (85)** 2.120[c] 2.172[d] 2.067[e]
$\gamma_e \times 10^3$		[−0.953][e]
$\varepsilon_e \times 10^4$		[2.862][e]
$\eta_e \times 10^5$		[−5.085][e]
$Y_{51} \times 10^6$		[5.1251][e]
$Y_{61} \times 10^7$		[−2.960][e]
$Y_{71} \times 10^9$		[8.846][e]
$Y_{81} \times 10^{10}$		[−1.106][e]
$D_e \times 10^6$	**6.174 (27)**	**6.67 (13)** 6.74[c] 6.97[d]
$\beta_e \times 10^7$	**5.09 (52)**	**1.89 (26)** 1.43[c]

[a] The value calculated on the basis of the derived $\Delta G_{1/2}$ vibrational quantum for the $^{12}C^{17}O$ molecule and all its already known values of other isotopologues of CO.

[b] The value evaluated from the $^{13}C^{17}O$ parameters given by Hakalla et al. [19] using Dunham's isotopic relationships.

[c] The value evaluated from the $^{13}C^{16}O$ parameters given by Kępa et al. [46] using Dunham's isotopic relationships.

[d] The value evaluated from the $^{12}C^{18}O$ parameters given by Beaty et al. [44] using Dunham's isotopic relationships.

[e] The value evaluated from the $^{12}C^{16}O$ parameters given by Field [34] using Dunham's isotopic relationships.

As a result of this calculation the value of the rotational $\Delta B = B_1 - B_0$ quantum was also obtained

$$\Delta B = -2.4644(36) \times 10^{-2}\ \mathrm{cm}^{-1}$$

On the basis of the derived $\Delta G_{1/2}$ value for the $B^1\Sigma^+$ state in $^{12}C^{17}O$ and using all its already known values for the $^{12}C^{16}O$ [28], $^{13}C^{16}O$ [29], $^{12}C^{18}O$ [30], $^{13}C^{17}O$ [19], $^{14}C^{16}O$ [30], $^{13}C^{18}O$ [31] and $^{14}C^{18}O$ [32] isotopologues, by means of the weighted least-squares method, the ω_e and $\omega_e x_e$ constants for the $B^1\Sigma^+$ Rydberg state in the $^{12}C^{17}O$ isotopologue were calculated. These values were constrained in the calculation of the vibrational equilibrium parameters. Because in the $^{12}C^{17}O$ molecule in the $B^1\Sigma^+$ state only two vibrational levels are known: the lowest $\upsilon=0$ [17] and the first excited $\upsilon=1$ (this work), so the rotational equilibrium constants for this state were determined from a fit of the data in which the amount of data equals the number of determined parameters. In that case

Table 7
Vibrational levels and RKR turning points for the $B^1\Sigma^+$ and $A^1\Pi$ states of the $^{12}C^{17}O$ isotopologue.[a]

	$B^1\Sigma^+$		$A^1\Pi$
	Y_{00}	−3.0373	−0.5915
	r_e	1.119780 (4) 1.1197 [b]	1.23410 (18) 1.233781 (25) [c] 1.233753 (86) [d]
$\upsilon=0$	**$G(\upsilon)+Y_{00}$**	**1053.9050**[e]	745.0190 [f]
	r_{min}	1.07546	1.18134 [f]
	r_{max}	1.17096	1.29494 [f]
$\upsilon=1$	$G(\upsilon)+Y_{00}$	3110.3850	2209.3857
	r_{min}	1.04629	1.14716
	r_{max}	1.21415	1.34590
$\upsilon=2$	$G(\upsilon)+Y_{00}$	5098.4250 [g]	3639.6969
	r_{min}	1.02748 [g]	1.12565
	r_{max}	1.24733 [g]	1.38477
$\upsilon=3$	$G(\upsilon)+Y_{00}$		5035.9751 [h]
	r_{min}		1.10926 [h]
	r_{max}		1.41897 [h]
$\upsilon=4$	$G(\upsilon)+Y_{00}$		6398.0309 [h]
	r_{min}		1.09582 [h]
	r_{max}		1.45066 [h]
$\upsilon=5$	$G(\upsilon)+Y_{00}$		7725.4636
	r_{min}		1.08435
	r_{max}		1.48086
$\upsilon=6$	$G(\upsilon)+Y_{00}$		9017.6605 [f]
	r_{min}		1.07428 [f]
	r_{max}		1.48086 [f]

[a] $G(\upsilon)$ and Y_{00} are in cm^{-1}; r_e, r_{min}, and r_{max} values are in Å.

[b] Value r_e calculated by Eidelsberg et al. [11] for the ordinary $^{12}C^{16}O$ molecule.

[c] Value r_e calculated by Field [34] for the ordinary $^{12}C^{16}O$ molecule.

[d] Value r_e calculated by Beaty et al. [44] for the $^{12}C^{18}O$ isotopologue.

[e] The bolded value is simultaneously the value of the $B^1\Sigma^+$ state zero-point energy in the $^{12}C^{17}O$ isotopologue.

[f] Values extrapolated for the $\upsilon=0$ and 6 vibrational levels of the $A^1\Pi$ state on the basis of equilibrium constants listed in Table 6.

[g] Values extrapolated for the $\upsilon=2$ vibrational level of the $B^1\Sigma^+$ state on the basis of equilibrium constants listed in Table 6.

[h] Values interpolated for the $\upsilon=3$ and 4 vibrational levels of the $A^1\Pi$ state on the basis of equilibrium constants listed in Table 6.

Table 8
Franck–Condon factors, relative intensities, and *r*-centroids for the $B^1\Sigma^+$–$A^1\Pi$ system of $^{12}C^{17}O$[a].

$A^1\Pi$ (υ)	$B^1\Sigma^+$ (υ)		
	0	1	2[b]
0[c]	9.0610×10^{-2} 3.8305 1.1855	0.2556 10.0000 1.2144	0.3305 10.0000 1.2454
1	0.1856 8.1489 1.1650	0.1709 6.2833 1.1903	4.0229×10^{-3} 0.1150 1.1812
2	0.2146 10.0000 1.1461	2.6320×10^{-2} 0.9514 1.1670	7.9990×10^{-2} 2.1546 1.2030
3[d]	0.1849 9.1050 1.1284	6.3825×10^{-3} 0.2450 1.1616	0.1128 2.8584 1.1794
4[d]	0.1326 6.8719 1.1116	5.9298×10^{-2} 2.4062 1.1381	4.1771×10^{-2} 1.1151 1.1590
5	8.3662×10^{-2} 4.5473 1.0954	0.1033 4.4107 1.1208	3.4831×10^{-4} 9.8290×10^{-3} 1.1190
6[c]	4.8308×10^{-2} 2.7441 1.0799	0.1116 4.9972 1.1047	1.9646×10^{-2} 0.5835 1.1307

[a] The values represented in sequence one under the other stand for the Franck–Condon factor, relative intensities ([energy/s] scaled to 10), and *r*-centroids ([Å]) for each band.

[b] Values extrapolated for the υ=2 vibrational level of the $B^1\Sigma^+$ state on the basis of equilibrium constants listed in Table 6.

[c] Values extrapolated for the υ=0 and 6 vibrational levels of the $A^1\Pi$ state on the basis of equilibrium constants listed in Table 6.

[d] Values interpolated for the υ=3 and 4 vibrational levels of the $A^1\Pi$ state on the basis of equilibrium constants listed in Table 6.

standard deviations of equilibrium parameters were calculated by means of the Gauss error propagation method.

Thus, equilibrium constants (from Table 6) allowed for determining parameters of the potential curve in the $^{12}C^{17}O$ molecule: the RKR turning points, Y_{00} Dunham's factor, zero point energy and the r_e equilibrium internuclear distance for the $B^1\Sigma^+$ as well as for the $A^1\Pi$ states, which is presented in Table 7. The Franck–Condon factors, relative intensities, and *r*-centroids for the Ångström band system in $^{12}C^{17}O$ are presented in Table 8.

4. Irregularities inside the Ångström band system of the $^{12}C^{17}O$ isotopologue

4.1. *Perturbations of the $A^1\Pi$ state in $^{12}C^{17}O$*

The electronic state $A^1\Pi$ in the CO molecule is intensely and extensively perturbed by many other electronic states located in its vicinity. They are: $I^1\Sigma^-$, $D^1\Delta$, $e^3\Sigma^-$, $a'^3\Sigma^+$, and $d^3\Delta_i$, as was described in our earlier works [17–19,33].

By means of the rovibronic term crossing diagram of the states situated in the region 66,000 cm^{-1}, the place of occurrence of rotational perturbations was theoretically estimated for vibrational level υ=5 of the $A^1\Pi$ state in the $^{12}C^{17}O$ molecule. The results are presented in Fig. 3.

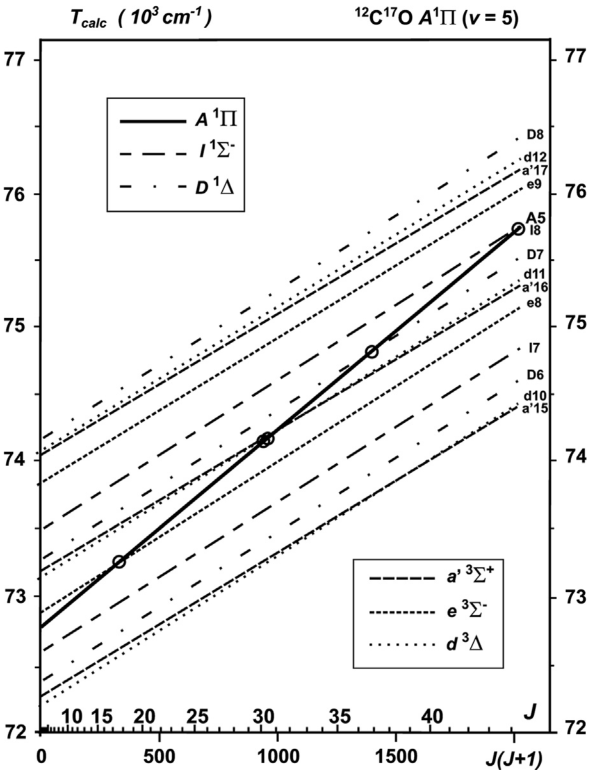

Fig. 3. Values of rovibronic terms of the perturbed $A^1\Pi$ (υ=5) level together with perturbing $I^1\Sigma^-$ (υ=7–8), $D^1\Delta$ (υ=6–8), $e^3\Sigma^-$ (υ=8–9), $a'^3\Sigma^+$ (υ=15–17), and $d^3\Delta_i$ (υ=10–12) states of $^{12}C^{17}O$ isotopologue. Points of intersection (marked by circles) show the regions for which the strongest perturbations are expected.

Necessary calculations were performed using molecular constants of the rovibronic structure of the $A^1\Pi$ (υ=5; J=0–45) state, determined in this paper, as well as on the basis of molecular constants of $I^1\Sigma^-$, $D^1\Delta$, $e^3\Sigma^-$, $a'^3\Sigma^+$, and $d^3\Delta_i$ states calculated by Field [34,35] and Kittrell and Garetz [36] in the $^{12}C^{16}O$ molecule and recalculated to the $^{12}C^{17}O$ molecule by means of standard isotopic relations [37]. Next, by means of the function introduced by Gerö [38] and Kovács [39]: $f_x(J)$ and $g_x(J)$ (where x=Q and $\overline{PR}$), experimental classification and analysis of the observed perturbations of the $A^1\Pi$ (υ=1, 5) state were carried out on the basis of wavenumbers of the 1–υ'' progression bands of the Ångström system in the $^{12}C^{17}O$ molecule. A non-linear function graph clearly indicates the location of the perturbation. Functions $f_Q(J)$ together with $f_{\overline{PR}}(J)$ and functions $g_Q(J)$ together with $g_{\overline{PR}}(J)$, showing perturbations of the *f*- and *e*-symmetry levels of the $A^1\Pi$ (υ=5) state are presented in Figs. 4 and 5, respectively. There is a negligible difference between the centrifugal distortion constants D' and D'' of the *B*–*A* system, so the f_x and g_x functions can be displayed simply as a function of *J*. Uncertainties of single measurements are negligibly small considering the scale of the graph used. A detailed description of the properties and applications of f_x and g_x functions was presented in our previous work [18].

Next, by means of the graphs presented in Figs. 4 and 5, and on the basis of the results of these calculations

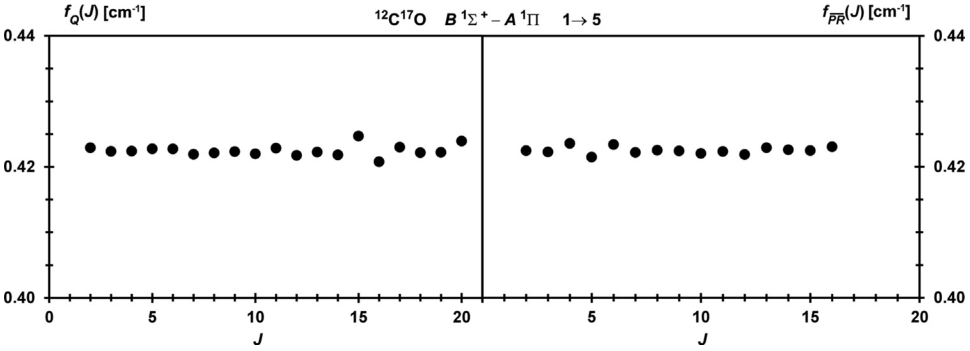

Fig. 4. Functions $f_x(J)$ of Kovács [39], where $x=Q$ or $\overline{PR}$ illustrating the perturbation of the $A^1\Pi$ ($\upsilon=5$) vibrational level. The graphs were plotted for the 1–5 band of the $B^1\Sigma^+ \rightarrow A^1\Pi$ transition in the $^{12}C^{17}O$ isotopologue.

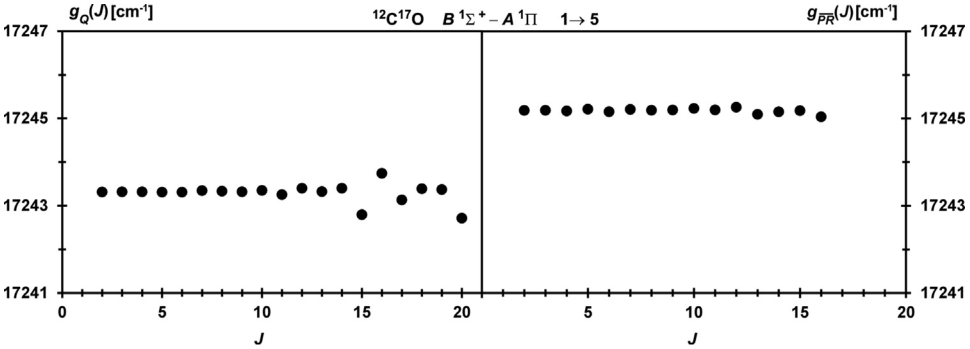

Fig. 5. Functions $g_x(J)$ of Kovács [39], where $x=Q$ or $\overline{PR}$ illustrating the perturbation of the $A^1\Pi$ ($\upsilon=5$) vibrational level. The graphs were plotted for the 1–5 band of the $B^1\Sigma^+ \rightarrow A^1\Pi$ transition in the $^{12}C^{17}O$ isotopologue.

Table 9
Comparison of the observed and calculated perturbations appearing in the $A^1\Pi$ ($\upsilon=5$) state of $^{12}C^{17}O$.

Maximum perturbation (J) of the-doubling component				Perturbing state	
f		e		Triplet component	Vibrational level
Obs.	Calc.	Obs.	Calc.		
		12[a]	14	F(1)	$e^3\Sigma^-$ ($\upsilon=8$)
15–16	17			F(2)	
		20–∗	20	F(3)	
∗	26–27	∗	26–27	F(3)	$d^3\Delta_i$ ($\upsilon=11$)
∗	30–31	∗	30–31	F(2)	
∗	34–35	∗	34–35	F(1)	
∗	27–28			F(1)	$a'^3\Sigma^+$ ($\upsilon=16$)
		∗	30–31	F(2)	
∗	33–34			F(3)	
∗	37	∗	37		$D^1\Delta$ ($\upsilon=7$)
∗	44–45				$I^1\Sigma^-$ ($\upsilon=8$)

∗ indicates regions experimentally unverified.
[a] Weak perturbation of a value lower than 0.1 cm^{-1} (see Fig. 6).

presented in the rovibronic term crossing diagram in Fig. 3 identification of perturbing states of the $A^1\Pi$ ($\upsilon=5$) state of the $^{12}C^{17}O$ molecule was carried out. A comparison of theoretical predictions and experimental observations is presented in Table 9.

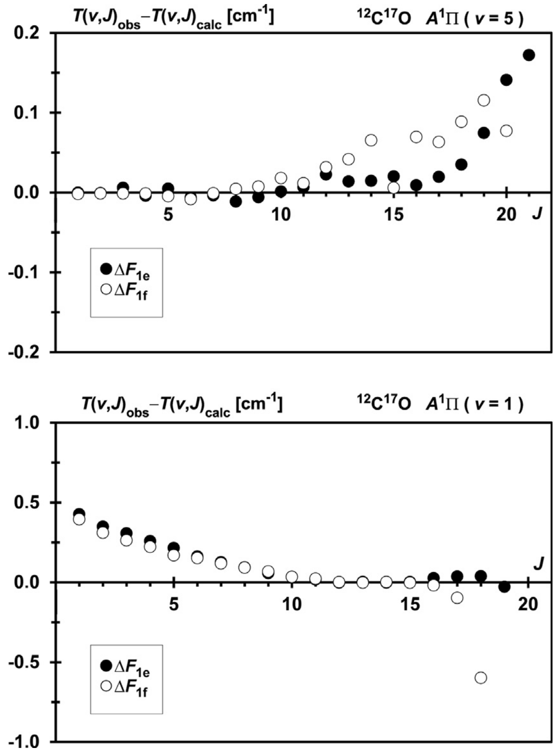

Fig. 6. Differences between the observed and calculated term values of the $\upsilon=5$ and 1 vibrational levels of the $A^1\Pi$ state of $^{12}C^{17}O$.

We have also plotted a graph of deviations of the observed (perturbed) $T(\upsilon, J)_{obs}$ term values from those of the calculated (un-perturbed) $T(\upsilon, J)_{calc}$ ones, versus the rotational quantum number J. These term values were calculated by means of the methods described in Section 3. The results are presented in Fig. 6.

4.2. Predissociation of the $B^1\Sigma^+$ Rydberg state

The predissociation of $B^1\Sigma^+$ occurring for the $\upsilon > 1$ vibrational levels [11,40–43] is also observed in the framework of this research in the $^{12}C^{17}O$ molecule as a dramatic weakening of intensities of the 1–5 band molecular lines of the Ångström system. This weakening occurs clearly in the $J > 18$ region of this band. We were able to observe this phenomenon very clearly for lines $Q(19)$ and $Q(20)$ of the 1–5 band, which are far weaker than the lines preceding them in the energy scale. Their maximum signal-to-noise ratio amounted to about 33:1, 35:1, 40:1 and 22:1, 26:1 for the $Q(16)$, $Q(17)$, $Q(18)$ and $Q(19)$, $Q(20)$, respectively. Also, the broadening of lines $Q(19)$ as well as $Q(20)$ in relation to the lines that precede them energetically may prove that the predissociation appears in this region. The spectral widths of these lines equals about 0.15 cm^{-1}, 0.16 cm^{-1}, 0.15 cm^{-1} for the $Q(16)$, $Q(17)$, $Q(18)$ lines and 0.23 cm^{-1}, 0.18 cm^{-1} for the $Q(19)$, $Q(20)$ lines. A detailed description of this problem will be soon presented in the work [30].

5. Isotopic dependences of the $B^1\Sigma^+$ state of natural CO isotopologues

Carbon and oxygen have three natural, most abundant isotopes: ^{12}C, ^{13}C, ^{14}C, and ^{16}O, ^{17}O, ^{18}O, respectively. They constitute nine different isotopologues of the CO molecule. Up to 2012, in which the study on the $^{13}C^{17}O$ isotopologue was published by Hakalla et al. [18], information on the first Rydberg state of the CO molecule, that is $B^1\Sigma^+$, was known for six isotopic species: $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{14}C^{16}O$, $^{13}C^{18}O$, and $^{14}C^{18}O$. The research conducted by Hakalla et al. in 2013 into the $^{13}C^{17}O$ [19] and $^{12}C^{17}O$ molecules (this work, Table 6) allowed for the first determination of equilibrium constants of the $B^1\Sigma^+$ state in those two successive isotopologues of CO. Using considerably extended data, the reduced mass relationship of the B_e and ω_e constants for the $B^1\Sigma^+$ state of the CO molecule has been examined. These constants show a relatively high isotopic dependence, and they have major significance in the attempt to determine possible deviations from the Born–Oppenheimer approximation.

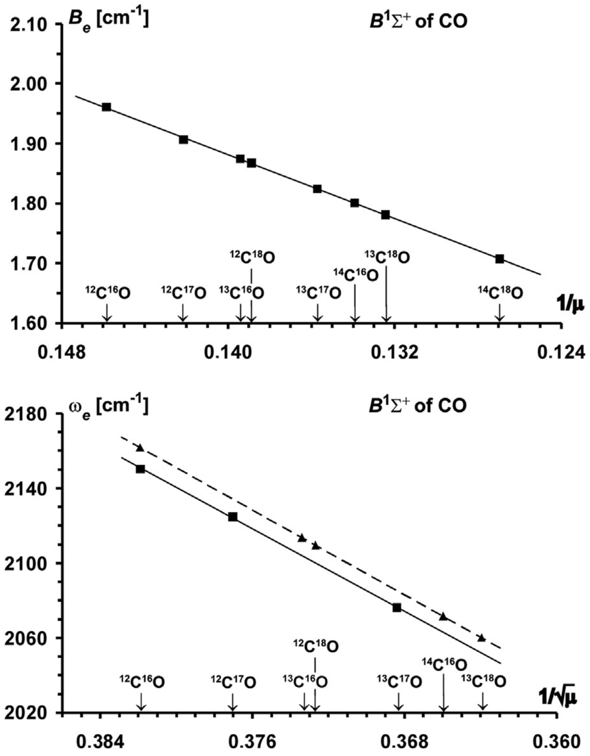

Fig. 7. Experimental values of the reduced mass dependence of B_e and ω_e equilibrium constants of the $B^1\Sigma^+$ state, in function of a μ^{-1} and $\mu^{-1/2}$ argument, respectively. To plot the dependence, the values taken from eight and seven isotopologues of CO were used, respectively (for details see Table 10). On the lower graph, the values indicated in square were calculated within the scope of this work (for $^{12}C^{17}O$) and the publication by Kępa et al. [28] (for $^{12}C^{16}O$) and Hakalla et al. [19] (for $^{13}C^{17}O$); however, the values indicated by triangles were plotted on the basis of the data of Eidelsberg et al. [11]. Standard deviation is impossible to show because of the relatively large scale of the plot.

Table 10
Equilibrium molecular constants (cm^{-1}) used to calculate the isotopically invariant parameters of the $B^1\Sigma^+$ state of the CO molecule[a].

Constant	Isotopologue							
	$^{12}C^{16}O$	$^{12}C^{17}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{14}C^{16}O$	$^{13}C^{18}O$	$^{14}C^{18}O$
ω_e	After Kępa et al. [28]	This work	after Eidelsberg et al. [11]	After Eidelsberg et al. [11]	After Hakalla et al. [19]	After Eidelsberg et al. [11]	After Eidelsberg et al. [11]	
	2150.41 (58) 2161.75 [b]	2124.92 (43)	2113.56	2109.53	2076.04 (57)	2071.52	2060.12	
B_e	After Kępa et al. [28]	This work	After Hakalla et al. [33]	After Eidelsberg et al. [11]	After Hakalla et al. [19]	After Eidelsberg et al. [11]	After Eidelsberg et al. [11]	After Danielak et al. [32]
	1.96103 (16)	1.911250 (13)	1.874641 (27)	1.8677	1.824678 (15)	1.8010	1.7812	1.7076 (7)

[a] 1σ in parentheses.
[b] After Eidelsberg et al. [11].

Table 11
Isotopically invariant parameters (cm^{-1}) of the $B^1\Sigma^+$ Rydberg state in the CO molecule[a].

Molecule	State	Isotopically invariant parameter [b]	
CO	$B^1\Sigma^+$	U_{10}	5635.812 (31)
			5660.4 (14) [c]
		U_{01}	13.44420 (35)
			13.44738 (28)[c]

[a] 1σ in parentheses.

[b] The symbols were taken from the Eq. (1) used and described in this publication (after Dunham [37]). The values were calculated for the strictly fulfilled the Born–Oppenheimer approximation.

[c] After Eidelsberg et al. [11].

The reduced mass dependence of the rotational B_e constants (presented in Table 10) in function of a μ^{-1} argument is graphically presented in Fig. 7. Linear graph $B_e = f(\mu^{-1})$ suggests that for the model of isotopic dependence of the Y_{kl} Dunham parameter [37], the following equation can be used

$$Y_{kl} = \mu^{-(k+2l)/2}\, U_{kl}, \tag{1}$$

where U_{kl} is an isotopically invariant parameter (so-called *Dunham coefficient*), and μ is the reduced mass of the CO molecule. This formula is applicable when the Born–Oppenheimer approximation is strictly fulfilled, which takes place in a satisfactory way in the molecules that have relatively large reduced mass, such as the tested molecule of carbon monoxide. Using Eq. (1) in the form of $Y_{01} = \mu^{-1} U_{01}$ and values of B_e equilibrium constants for the CO isotopologues, provided in Table 10, for the $B^1\Sigma^+$ state we calculated the experimental value of the U_{01} isotopically invariant parameter. The calculations were performed by means of the weighted linear least-square method. The results are presented in Table 11.

In a similar way, we checked isotopic dependence of the ω_e vibrational molecular constant of the $B^1\Sigma^+$ state (provided in Table 10) in function of a $\mu^{-1/2}$ argument (Fig. 7). Linear graph $\omega_e = f(\mu^{-1/2})$ for the value ω_e allows for the use of the Eq. (1) again, but this time in the form of $Y_{10} = \mu^{-1/2} U_{10}$. The U_{10} isotopically invariant parameter was calculated by means of the weighted linear least-square method. The value obtained in this way is presented in Table 11.

When there is a breakdown of the Born–Oppenheimer approximation, another equation [43] should be added to Eq. (1). In this case the Dunham coefficients should be written as

$$Y_{kl} = \mu^{-(k+2l)/2}\, U_{kl}\left(1 + \frac{m_e}{M_A}\Delta_{kl}^{A} + \frac{m_e}{M_B}\Delta_{kl}^{B}\right), \tag{2}$$

where M_A, M_B are the atomic masses, m_e is the electron mass, and Δ_{kl}^{A}, Δ_{kl}^{B} are dimensionless isotopically invariant coefficients. The attempt to determine the Δ_{01} and Δ_{10} coefficients from Eq. (2) for the $B^1\Sigma^+$ state of the CO molecule, on the basis of all the available experimental data, did not provide satisfactory results. The precision and isotopic variation of values B_e and especially ω_e (see Table 10), studied by us, unfortunately, are still insufficient to determine possible, small deviations from the Born–Oppenheimer approximation.

However, we believe that this work and the studies described in it will substantially contribute to future precise determination of the Born–Oppenheimer approximation breakdown in both the $B^1\Sigma^+$ as well as the $A^1\Pi$ states of the CO molecule.

6. Discussion and conclusion

The comparison of Fig. 6 concerning, among others, perturbations of the reanalyzed $\upsilon = 1$ vibrational level of the $A^1\Pi$ state in the $^{12}C^{17}O$ molecule with the analogous ones provided in our earlier study by Hakalla et al. [17] shows inconsistency for the early *J*'s. The reason for this, discovered by us after the publication of the work [17], is the misassignment of the $Q(1)$ and $P(1)$ lines of the 0–1 band of the *B*–*A* transition in the $^{12}C^{17}O$ molecule. This error has been corrected in the present study. The characteristics of the remaining spectrum regions in Fig. 6 show high compatibility with the analogous data in the work [17]. This compatibility confirms the correctness of the interpretation and analyses carried out in the $A^1\Pi$ $(\upsilon = 1)$ state in the range $J \le 19$ in $^{12}C^{17}O$.

Both vibrational and rotational equilibrium constants calculated in this work for the $A^1\Pi$ state are compatible with analogous constants obtained by means of deperturbation analyses of this state performed by Beaty et al. [44] and Field [34] and recalculated using Dunham's isotopic relationships to the studied $^{12}C^{17}O$ isotopologue. However, the vibrational constant ω_e obtained by Field [34] is an exception. These constants are gathered in Table 6.

The reduced mass dependence of the vibrational ω_e molecular constant of the $B^1\Sigma^+$ state, on the basis of the values given in Table 10 for seven isotopologues of the CO molecule, were presented graphically in Fig. 7 in function of a $\mu^{-1/2}$ argument. One should pay attention to the fact that there are two series of the data, which are not collinear. The continuous line has been plotted on the basis of the linear least-square method for the experimental data obtained by Kępa et al. [28] for $^{12}C^{16}O$, and within this work for $^{12}C^{17}O$, and also by Hakalla et al. [19] for $^{13}C^{17}O$. In the studies concerning the $^{12}C^{17}O$ and $^{13}C^{17}O$ molecules, the ω_e and $\omega_e x_e$ vibrational constants of the $B^1\Sigma^+$ state were determined on the basis of the derived $\Delta G_{1/2}$ vibrational quantum from already known, all values for the CO isotopologues. A broken line was used to indicate the straight line plotted on the basis of the values of the vibrational constants provided by Eidelsberg et al. [11] for the $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{18}O$ molecules and $^{14}C^{16}O$, the constants of which were determined from the Dunham coefficient obtained from a simultaneous fit of all available isotopic data for the $B^1\Sigma^+$ state in 1987. The problem of the apparent incompatibility of the results (two not collinear series of values in Fig. 7), which also translates into the discrepancy of the value of the isotopically invariant parameter U_{10} (see Table 11), has been fully described in the work by Eidelsberg et al. [11]. The authors explain that even with very good compatibility of the $\Delta G_{1/2}$ values, significantly different set of values ω_e and $\omega_e x_e$ arises from the data reduction, due to a large correlation ($\approx 99\%$) between the T_e, ω_e and $\omega_e x_e$. This hypothesis has been precisely documented in a quantitative way in Table VII of the work [11] (page 321) on the example of the $^{12}C^{16}O$ molecule. We want to add that this problem also seems to result from both partial fit models and the use of slightly different parameter definitions.

While determining the $\Delta G_{1/2}$ vibrational quantum for the $^{12}C^{17}O$ isotopologue, the rotational $\Delta B = B_1 - B_0$ quantum was also obtained, which amounted to $\Delta B = -2.4644(36) \times 10^{-2}\ \mathrm{cm}^{-1}$. Good compatibility of this value with the difference of values of the merged rotational constant B_1 (this work) and B_0 (from [17]), which amounts to $\Delta B = -2.4736630(26) \times 10^{-2}$, confirms the high quality of the results obtained. This difference should, in principle, be equal to the α_e rovibrational equilibrium constant and as can be seen in Table 6, this is actually happening.

All precise results presented in this study concerning the $1-\upsilon''$ progression of the Ångström ($B^1\Sigma^+ - A^1\Pi$) band system, not studied so far in the lesser-abundant $^{12}C^{17}O$ molecule, also with regard to other CO isotopologues, broaden and improve the spectroscopic and quantum-mechanical information on the first, lowest lying Rydberg $B^1\Sigma^+$ state, and on the strongly perturbed $A^1\Pi$ state, thereby they contribute to a much better understanding of the whole carbon monoxide molecule, which plays a crucial and important role both in environmental research and in innovative, industrial technologies, as well as, above all, in basic astrophysical research.

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