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First analysis of the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system in the less-abundant $^{13}C^{17}O$ isotopologue

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This work presents high-resolution emission spectra measurements of the Herzberg band system, which has not been observed and analysed in the $^{13}C^{17}O$ isotopologue so far. Bands C → A (0,1), (0,2) and (0,3) were recorded in a region at 22 950–26 050 cm^{-1} using high-accuracy dispersive optical spectroscopy. The $^{13}C^{17}O$ molecules were formed and excited in a stainless steel hollow-cathode lamp with two anodes. All 224 rovibrational spectra lines, up to $J_{max} = 30$, were precisely measured with an accuracy of about 0.0030 cm^{-1} and rotationally analysed. In this work the following have been determined in $^{13}C^{17}O$ for the first time: the merged rotational constants of the $C^1\Sigma^+(v = 0)$ Rydberg state and the individual rotational constants of the $A^1\Pi(v = 3)$ state, as well as the rotational and vibrational equilibrium constants for the $C^1\Sigma^+$ state, the band origins of the C → A system, the isotope shifts, and the $\Delta G^C_{1/2}$ vibrational quantum. The combined analysis of the Herzberg bands obtained now and the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) system analysed earlier (R. Hakalla *et al.*, *J. Phys. Chem. A*, 2013, **117**, 12299 and R. Hakalla *et al.*, *J. Mol. Spectrosc.*, 2012, **272**, 11) yielded a precisely relative characteristic of the $C^1\Sigma^+(v = 0)$ and $B^1\Sigma^+(v = 0$ and 1) Rydberg states in the $^{13}C^{17}O$ molecule, among others ν^{CB}_{00}, ν^{CB}_{01} vibrational quanta. Also, many molecular constant values of the $C^1\Sigma^+$ state in the $^{12}C^{16}O$, $^{12}C^{17}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ isotopologues were determined, which have not been published so far, as well as the RKR turning points, Franck–Condon factors, relative intensities, r-centroids for the Herzberg band system and the main, isotopically invariant parameters of the $C^1\Sigma^+$ state in the CO molecule within the Born–Oppenheimer approximation. In the $A^1\Pi(v = 3)$ state of the $^{13}C^{17}O$ molecule, extensive, multi-state rotational perturbations were found, which were analysed and substantiated in detail. The vibrational level $v = 0$ of the $C^1\Sigma^+$ state was analysed, paying special attention to possible irregularities, and no noticeable perturbations were found in it up to the observed J_{max}.

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1. Introduction

Carbon monoxide is one of the most important molecules in astronomy, because it is readily detectable and chemically stable as well as being the second, after H_2, most abundant molecular constituent in star-forming clouds and the main gas-phase reservoir of interstellar carbon. 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. A large CO abundance gives a detectable signal for even rarer isotopologues. Spectroscopic research into CO and its lesser-abundant isotopologues is fully justified because of its special significance as the main tracer of gas properties, structure and kinematics in a wide variety of astrophysical environments.[1–11] They control much of the chemistry in the gas phase and are the precursors to more complex molecules.[12–15] The CO molecule is also highly relevant in research into Earth's atmosphere. Its concentrations in different layers of the troposphere, stratosphere, and mesosphere vary strongly. Because of short atmospheric lifetime (about 2 months), changes in sources and sinks in the environment are reflected in atmospheric concentrations faster than other molecules.[16,17]

Research on lesser-abundant isotopologues of CO, such as $^{13}C^{17}O$, are more and more appreciated and extensively discussed because of their unique application possibilities, such as partial elimination of a serious optical problem called 'depth effects' in the ISM method[18] or more precise determination of the $[^{12}C]/[^{13}C]$ ratio in outer space than on the basis of the ordinary $^{12}C^{16}O$ or even $^{12}C^{18}O$ isotopologues, which in turn leads to determination of the primary/secondary nuclear processing ratio of the stars.[18] The first observation of interstellar $^{13}C^{17}O$ was made by Bensch *et al.*[18] towards the ρ-Ophiuchi molecular cloud. In laboratory conditions its recording and analysis were made several times,[9,17,19–26] recently by Hakalla *et al.*[27,28]

Highly excited electronic states of CO now belong to one of the main trends in the research into this molecule.[19,27–45] A

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special area of interest are the states lying in the region of dissociation energy, among others – the $(np\sigma)$ $C^1\Sigma^+$ Rydberg state. This state, since its discovery by Hopfield and Birge,[46] has been observed and analysed in the following transitions: the Hopfield–Birge ($C^1\Sigma^+ \rightarrow X^1\Sigma^+$),[30,31,47–56] as well as recently discovered $C^1\Sigma^+ \rightarrow d^3\Delta_i$[57] and $C^1\Sigma^+ \rightarrow B^1\Sigma^+$.[52,58,59] However, the most comprehensive and complete information about the $C^1\Sigma^+$ state comes from the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system,[40,54–56,60–70] whose spectrum is situated in the VIS range. This system was precisely analysed for most isotopologues of CO, that is: $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{14}C^{16}O$, $^{13}C^{18}O$, and $^{14}C^{18}O$, but it remained unknown in the $^{13}C^{17}O$ molecule up to now. The only information concerning the upper state of this system in $^{13}C^{17}O$ is a preliminary analysis of the $C^1\Sigma^+(v = 1)$ vibrational level on the basis the C $\rightarrow$ X transition.[31] Therefore, I have decided to make the first recording of the Herzberg band system in $^{13}C^{17}O$. A complete analysis of the experimental material enabled me to receive the first piece of information about the energetic structure parameters of the $C^1\Sigma^+ \rightarrow A^1\Pi$ transition, as well as about the $C^1\Sigma^+(v = 0)$ and $A^1\Pi(v = 3)$ states in the isotopologue under consideration.

2. Experiment

The experimental methods have been described in ref. 28, therefore, only details that are relevant for the current results are presented in this section.

The source of spectra of the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system in $^{13}C^{17}O$ was a water-cooled, hollow-cathode lamp with two anodes.[71] At first it was filled with a mixture of acetylene $^{13}C_2D_2$ (99.98% purity of ^{13}C) and helium under pressure of about 6 and 1 Torr, respectively. Next, I passed an electric current through the mixture in order to obtain a sufficient amount of deposit of ^{13}C on the electrodes. This process lasted for about 100 h. In the next stage, the 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. Finally, the electrodes were powered by direct current of the following parameters: 2 $\times$ 670 V and 2 $\times$ 36 mA. These experimental conditions had been previously tested several times and chosen as optimal to fulfil the aim of this work. In this way, the Herzberg system in the $^{13}C^{17}O$ isotopologue was recorded for the first time, in particular (0,1), (0,2), and (0,3) bands of the C $\rightarrow$ A transition.

Measurement equipment that is used to record the Herzberg band system in the $^{13}C^{17}O$ molecule has been recently constructed in our laboratory. It uses a high accuracy dispersive optical spectroscopy[72–76] (see also Fig. 1 of ref. 28). The molecular spectra were observed in the 6th order for (0,1) and (0,2) bands, as well as in the 5th order for (0,3) band of the $C^1\Sigma^+ \rightarrow A^1\Pi$ transition. The reciprocal dispersion was in a range of 0.07–0.11 nm mm^{-1}, and theoretical resolving power was approximately 273 600 for (0,1) and (0,2) bands, as well as 228 000 for the (0,3) band. As a calibration spectrum, an atomic spectrum of thorium was used,[77] which was produced in the water-cooled, hollow-cathode tube with the cathode lined with thin Th foil, from a few overlapping orders.

The peak positions of spectral lines were calculated by means of a least-squares procedure assuming a Gaussian lineshape for each spectral contour (30 points per line), 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, the 7th-, 4th-, and 5th-order interpolation polynomials were used and the typical standard deviation of the least-squares fit for the 25–35 calibration lines was approximately 1.7 $\times$ 10^{-3} cm^{-1}, 1.6 $\times$ 10^{-3} cm^{-1}, and 1.7 $\times$ 10^{-3} cm^{-1} for the (0,1), (0,2), and (0,3) bands, respectively.

Intense and single lines of the CO molecule had a spectral width of about 0.15 cm^{-1}. Their maximum signal-to-noise ratio was about 60 : 1, 65 : 1, and 55 : 1 for the (0,1), (0,2), and (0,3) bands, respectively. The most intense lines produce the count rates of about 7000 photons per s, 8000 photons per s, and 6000 photons per s for the (0,1), (0,2), and (0,3) bands, respectively.

Accuracy of the measurements of the $^{13}C^{17}O$ strong and single lines amounted to about 0.0030 cm^{-1}. Some of the weaker and blended lines were measured with lower accuracy, which amounted to about 0.0060 cm^{-1}. Summary of the observation and analyses of the $C^1\Sigma^+ \rightarrow A^1\Pi$ system in the $^{13}C^{17}O$ isotopologue is given in Table 1.

In this experiment altogether 224 spectral emission lines were recorded that belong to the Herzberg band system in $^{13}C^{17}O$. Their wavenumbers are presented in Table 2. A high quality, expanded view of these bands together with their rotational assignments are provided in Fig. 1–3.

3. Description of the spectra

The three most intense (0,1), (0,2) and (0,3) bands belonging to the $C^1\Sigma^+ \rightarrow A^1\Pi$ system in $^{13}C^{17}O$ were recorded in the region 22 950–26 050 cm^{-1}. It is the first observation of this system in the $^{13}C^{17}O$ isotopologue as there was a misprint in the work by Hakalla *et al.*[27] (Fig. 2 and 3), where the band heads C $\rightarrow$ A(0,2) and C $\rightarrow$ A(0,3), which appeared there as belonging to the $^{13}C^{17}O$, in fact belong the $^{13}C^{16}O$ molecule.

Preliminary interpretation of the bands, that is, identification of branches and *J*-numbering of the lines were carried out with the use of the previous information concerning the lower state of the Herzberg system, that is, the $A^1\Pi(v'' = 1, 2)$ state[27,28] as well as by means of well – known spectroscopic methods.

Table 1 Summary of observation and analyses of the $C^1\Sigma^+ \rightarrow A^1\Pi$ system in the $^{13}C^{17}O$ isotopologue

Band	Remarks	Band head[a]	n^b	J_{max}	f^c	$(\sigma \times 10^3)^d$
(0,1)	First analysis	25 721.2184 (8)	77	26	22	1.25
(0,2)	First analysis	24 324.5528 (15)	78	30	19	1.64
(0,3)	First analysis	22 958.6704 (1)	69	25	18	1.08

[a] In cm^{-1}, 1σ in parentheses. [b] Total number of observed lines. [c] 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[78] and Watson.[79] [d] Standard deviation of the fit (in cm^{-1}) for the individual band-by-band analysis using the linear least-squares method proposed by Curl and Dane[78] and Watson.[79]

Table 2 Observed wavenumbers (in cm^{-1}) and their rotational assignments of the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system in the $^{13}C^{17}O$ isotopologue[a]

J	$P_{11ee}(J)$		$Q_{11ef}(J)$		$R_{11ee}(J)$	
(0,1) band						
1	25 725.8655	*	25 729.4075	(0)	25 736.7235	(0)
2	25 723.6738	(−3)	25 730.7075	(0)	25 741.7706	(2)
3	25 722.1800	(−5)	25 732.7651	(0)	25 747.5149	(5)
4	25 721.3674	(−1)	25 735.5791	(0)	25 753.9381	(1)
5	25 721.2184	(−8)	25 739.0904	(0)	25 761.0261	(8)
6	25 721.7609	(7)	25 743.2781	(0)	25 768.7996	(−7)
7	25 722.9069	(3)	25 748.1045	(0)	25 777.1785	(−4)
8	25 724.7457	(1)	25 753.6045	(0)	25 786.2481	(−1)
9	25 727.2543	(3)	25 759.7540	(0)	25 795.9843	(−3)
10	25 730.4327	(−11)	25 766.5608	(0)	25 806.3911	(12)
11	25 734.2899	(−7)	25 774.0345	(0)	25 817.4703	(8)
12	25 738.8083	(6)	25 782.1732	(0)	25 829.2058	(−5)
13	25 744.0098	(3)	25 790.9934	(0)	25 841.6242	(−3)
14	25 749.8744	(−1)	25 800.4757	(0)	25 854.7023	(1)
15	25 756.4304	(3)	25 810.6398	(0)	25 868.4664	(−3)
16	25 763.6543	(11)	25 821.4665	(0)	25 882.8936	(−11)
17	25 771.5625	(5)	25 832.9707	(0)	25 898.0035	(−4)
18	25 780.1409	(2)	25 845.1476	(0)	25 913.7783	(−1)
19	25 789.4081	(−7)	25 858.0132	(0)	25 930.2382	(8)
20	25 799.3539	(−7)	25 871.5368	(0)	25 947.3698	(8)
21	25 809.9405	(−4)	25 885.7593	(0)	25 965.1359	(4)
22	25 821.2283	(14)	25 900.6472	(0)	25 983.5947	(−14)
23	25 833.2159	(−2)	25 916.2223	(0)	26 002.7541	(2)
24	25 845.9040	(−24)	25 932.4561	(0)	26 022.6088	(23)
25	25 859.2706	(17)	25 949.4114	(0)	26 043.1232	(−17)
26	25 873.3247	(0)	25 967.0644	(0)		
(0,2) band						
1	24 329.0005	*	24 332.6019	(0)	24 339.8588	(0)
2	24 326.8040	(−2)	24 334.0366	(0)	24 344.9010	(2)
3	24 325.3431	(1)	24 336.1890	(0)	24 350.6772	(−1)
4	24 324.5803	(4)	24 339.0526	(0)	24 357.1506	(−4)
5	24 324.5528	(−15)	24 342.6406	(0)	24 364.3597	(15)
6	24 325.2242	(1)	24 346.9687	(0)	24 372.2646	(−2)
7	24 326.6361	(−10)	24 352.0892	(0)	24 380.9111	(9)
8	24 328.7408	(−10)	24 357.5260	(0)	24 390.2462	(10)
9	24 331.5832	(−5)	24 364.0934	(0)	24 400.3157	(5)
10	24 335.1340	(7)	24 371.2617	(0)	24 411.0897	(−7)
11	24 339.4130	(6)	24 379.1658	(0)	24 422.5917	(−6)
12	24 344.4085	(−4)	24 387.7637	(0)	24 434.8089	(5)
13	24 350.1225	(−19)	24 397.0884	(0)	24 447.7421	(19)
14	24 356.5664	(15)	24 407.1397	(0)	24 461.3921	(−14)
15	24 363.7283	(23)	24 417.9027	(0)	24 475.7611	(−23)
16	24 371.6039	(−3)	24 429.3919	(0)	24 490.8466	(3)
17	24 380.2221	(−10)	24 441.6017	(0)	24 506.6664	(9)
18	24 389.5645	(−2)	24 454.5307	(0)	24 523.2030	(3)
19	24 399.6452	(18)	24 468.1977	(0)	24 540.4704	(−17)
20	24 410.4760	(15)	24 482.5763	(0)	24 558.4872	(−15)
21	24 422.0568	(−12)	24 497.7064	(0)	24 577.2534	(12)
22	24 434.4693	(−12)	24 513.5773	(0)	24 596.8401	(12)
23	24 447.8874	(0)	24 530.2069	(0)		
24	24 463.6597	(0)	24 547.6119	(0)		
25	24 472.9260	(0)	24 565.8989	(0)		
26	24 489.1007	(0)	24 585.3910	(0)		
27	24 505.0891	(0)				
28	24 522.8370	(0)				
29	24 540.6194	(0)				
30	24 559.1643	(0)				

Table 2 (*Contd.*)

J	$P_{11ee}(J)$		$Q_{11ef}(J)$		$R_{11ee}(J)$	
(0,3) band						
1	22 962.7250	*	22 966.2885	(0)	22 973.5829	(0)
2	22 960.6167	(1)	22 967.8074	(0)	22 978.7127	(−2)
3	22 959.2675	(1)	22 970.0817	(0)	22 984.6012	(−1)
4	22 958.6704	(−1)	22 973.1184	(0)	22 991.2411	(2)
5	22 958.8342	(−7)	22 976.9160	(0)	22 998.6414	(6)
6	22 959.7551	(0)	22 981.4756	(0)	23 006.7951	(0)
7	22 961.4636	(0)	22 986.7994	(0)	23 015.7291	*
8	22 963.9146	(7)	22 992.8806	(0)	23 025.4156	(−8)
9	22 967.1513	(7)	22 999.7251	(0)	23 035.8804	(−8)
10	22 971.1433	(−7)	23 007.3378	(0)	23047.1008	(8)
11	22 975.8988	(8)	23 015.7291	(0)	23 059.0760	(−8)
12	22 981.4405	(−1)	23 024.9156	(0)	23 071.8392	(1)
13	22 987.7428	(0)	23 034.9604	(0)	23 085.3575	(−1)
14	22 994.8781	(8)	23 046.3929	(0)	23 099.7042	(−8)
15	23 002.9034	(−14)	23 055.4444	(0)	23 114.9428	(13)
16	23 012.1705	(−14)	23 068.2595	(0)	23 131.4147	(13)
17	23 016.9919	(7)	23 081.3794	(0)	23 143.4324	(−7)
18	23 029.0170	(4)	23 096.4837	(0)	23 162.6539	(−5)
19	23 040.2729	(−9)	23 109.9910	(0)	23 181.1036	(10)
20	23 052.0410	(12)	23 122.2876	(0)	23 200.0531	(−12)
21	23 064.4702	(−4)	23 139.9343	(0)	23 219.6659	(4)
22	23 077.6547	(2)	23 156.8946	(0)	23 240.0240	(−1)
23	23 091.5662	(0)				
24	23 106.2391	(0)				
25	23 121.6477	(0)				

[a] 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 the $C^1\Sigma^+$ and $A^1\Pi$ states.

A rotational interpretation of the molecular spectra of the $^{13}C^{17}O$ molecule is very complicated because of the fact that they are accompanied by analogous spectra of the $^{13}C^{16}O$ molecule of intensity 30 : 70 in comparison to the spectra that are being studied, which can be well seen, for example, in Fig. 1. It resulted from the application of a gas in the spectral lamp, including 70% of the $^{17}O_2$ isotope. Additionally, despite the application of carbon of high spectral purity, that is 99.98% of ^{13}C in the experiment, impurities appeared in the spectrum caused by the lines belonging to the $^{12}C^{16}O$ and $^{12}C^{17}O$ molecules, which had an impact on the weaker lines of the spectrum studied. The impact of those impurities was taken into account in the interpretation process on the basis of the previous data concerning the C → A system in the $^{12}C^{16}O$[68] and $^{13}C^{16}O$[63] molecules. Detailed data concerning the B → A(1,0) band in $^{13}C^{17}O$ obtained from ref. 27 allowed us to eliminate its influence on the interpretation and spectrum analysis belonging to the C → A(0,2) transition.

4. Analyses and calculations

A reduction of the $^{13}C^{17}O$ Herzberg spectral lines to the rovibronic molecular parameters was carried out in a few stages using the well-known theoretical model, in which both states

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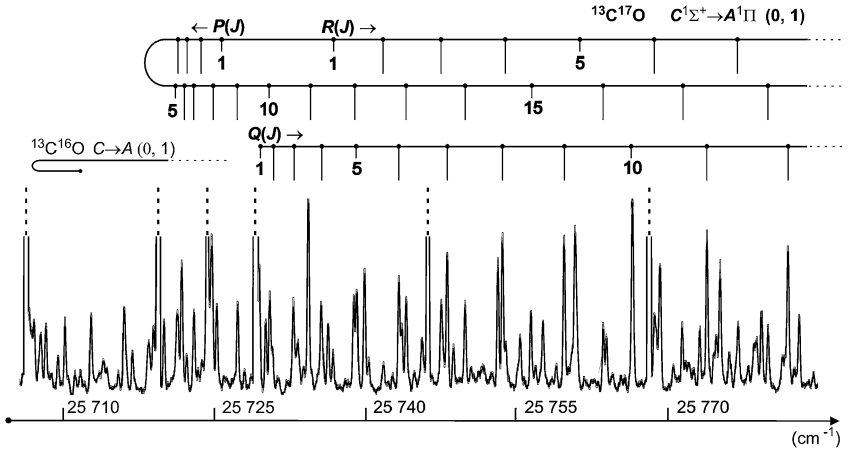

Fig. 1 The emission spectrum of carbon monoxide showing the first observation and rotational interpretation of the $C^1\Sigma^+ \rightarrow A^1\Pi$ (0,1) transition in the $^{13}C^{17}O$ isotopologue, on an expanded scale. Due to relatively high intensity of the Th calibration lines, their peaks are marked with broken lines. The positions of the band-head region of the less intense $C^1\Sigma^+ \rightarrow A^1\Pi$(0,1) transition of $^{13}C^{16}O$ was indicated at 25 706 cm^{-1}. See Section 3 for further information.

participating in the studied transition are represented by the proper Hamiltonians; for the upper $C^1\Sigma^+$ state:

$$\langle H\rangle = T'_v + B'_vJ(J+1) - D'_vJ^2(J+1)^2 + \ldots, \quad (1)$$

and for both Λ-components of the $A^1\Pi$ lower state:

$$\langle H\rangle = T''_v + B''_v[J(J+1) - 1] - D''_v[J(J+1) - 1]^2 + \ldots, \quad (2)$$

where expressions T'_v and T''_v denote the rotation-less energies for the $C^1\Sigma^+$ and $A^1\Pi$ states, respectively, calculated with regard to the lowest rovibrational level of the $X^1\Sigma^+$ ground state. Considering the precision of obtained wavenumbers of the lines and the observed J_{max} value of the rotational quantum number in the spectra, only B_v and D_v for the $C^1\Sigma^+$ and $A^1\Pi$ states, as well as the $\nu_0(\nu', \nu'') = T'_v - T''_v$ band origins were statistically significant in reproducing the experimental wavenumbers.

In order to calculate individual rotational constants B_v and D_v of the $C^1\Sigma^+(v = 0)$ state, the linear least-squares method was used in the version proposed by Curl and Dane[78] and Watson[79] by an individual band-by-band analysis. This method is an efficient means to separate molecular information concerning the upper $C^1\Sigma^+(v' = 0)$ state, which is considered to be regular in all analysed isotopologues,[30] from that which concerns the strongly perturbed state of $A^1\Pi(v'' = 1, 2)$[27,28] and $A^1\Pi(v'' = 3)$ (this work). These constants are gathered in Table 4. With the use of the constants, the following have been calculated: ν_0(0,1), ν_0(0,2), and ν_0(0,3) band origins of the C → A transition and effective rotational constants of the $A^1\Pi(v'' = 3)$ state in the $^{13}C^{17}O$ molecule, using the least-squares method. The results are presented in Tables 3 and 4, respectively.

Finally, the molecular constants obtained from the individual fit of the C → A(0,1), (0,2), and (0,3) bands, were used as the input data for the merge fit procedure proposed by Albritton

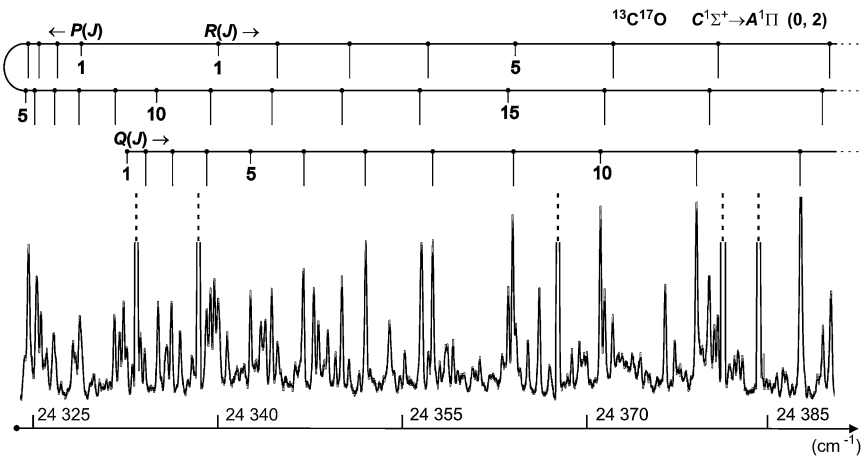

Fig. 2 The emission spectrum of carbon monoxide showing the first observation and rotational interpretation of the $C^1\Sigma^+ \rightarrow A^1\Pi$ (0,2) transition in the $^{13}C^{17}O$ isotopologue, on an expanded scale. Due to relatively high intensity of the Th calibration lines, their peaks are marked with broken lines. See Section 3 for further information.

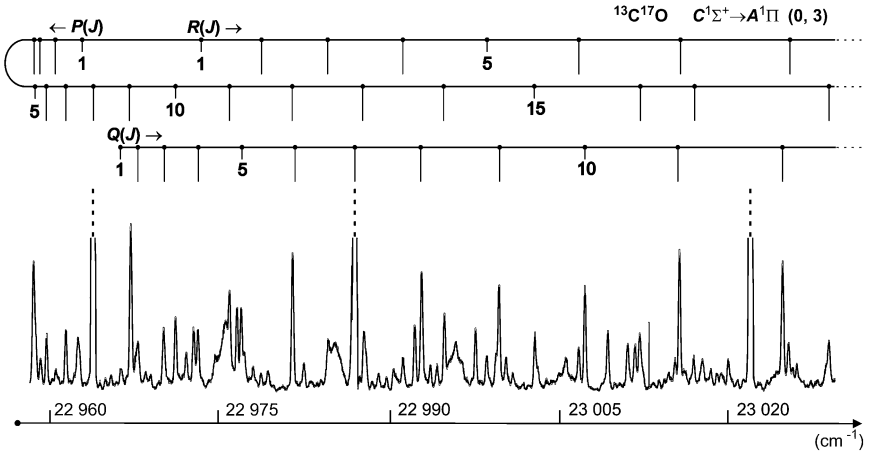

Fig. 3 The emission spectrum of carbon monoxide showing the first observation and rotational interpretation of the $C^1\Sigma^+ \rightarrow A^1\Pi$ (0,3) transition in the $^{13}C^{17}O$ isotopologue, on an expanded scale. Due to relatively high intensity of the Th calibration lines, their peaks are marked with broken lines. See Section 3 for further information.

Table 3 Band origins and isotope shifts of the $C^1\Sigma^+ \rightarrow A^1\Pi$ transition in $^{13}C^{17}O^{a,b}$

Band	Band origin	Isotope shift[c]
(0,1)	25 727.9077 (62)	−40.621 (25)
(0,2)	24 330.4469 (46)	−88.738 (22)
(0,3)	22 964.1402 (68)	−135.194 (17)

[a] In cm^{-1}. [b] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. [c] Calculated as $\nu_0(^{12}C^{16}O) - \nu_0(^{13}C^{17}O)$ experimental values. The $\nu_0(^{12}C^{16}O)$ were taken from ref. 68.

Table 4 Individual and merged molecular constants (in cm^{-1}) for the $C^1\Sigma^+$ and $A^1\Pi$ states of $^{13}C^{17}O^a$

State	v	B_v	$D_v \times 10^6$	Description
$C^1\Sigma^+$	0	1.809707 (15)	5.528 (17)	From C → A (0,1)
		1.809738 (23)	5.566 (33)	From C → A (0,2)
		1.809703 (16)	5.520 (23)	From C → A (0,3)
		1.8097113 (93)	5.532 (12)	Merged value[b]
$A^1\Pi$	3	1.43134 (30)	6.17 (47)	From C → A (0,3)

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. [b] The estimated variance and the number of degrees of freedom of the merging were $\sigma_M{}^2 = 0.43$ and $f_M = 4$, respectively.

et al.[80] and Coxon,[81] giving the final rotational constants for the observed $C^1\Sigma^+(v = 0)$ Rydberg state in the $^{13}C^{17}O$ isotopologue. The estimated variance and the number of degrees of freedom of the merging were $\sigma_M{}^2 = 0.43$ and $f_M = 4$, respectively. The results are highlighted in Table 4.

In the next step, combination differences between corresponding lines of two bands belonging to the Herzberg (this work) and Ångström[27,28] systems were calculated: CA(0,1)–BA(0,1), CA(0,2)–BA(0,2), and CA(0,1)–BA(1,1) with a common lower vibronic level, in accordance with the formula introduced by Jenkins and McKellar:[82]

$$\begin{aligned} R_{v_2'v''}(J-1) - R_{v_1'v''}(J-1) &= Q_{v_2'v''}(J) - Q_{v_1'v''}(J) \\ &= P_{v_2'v''}(J+1) - P_{v_1'v''}(J+1) \\ &= G'(v_2') - G'(v_1') \\ &\quad - (B_{v_1'} - B_{v_2'})J(J+1), \end{aligned} \tag{3}$$

where symbols used in the equation are commonly known. By plotting these combination differences against $J(J+1)$ a straight line is expected for a negligibly small difference $(D_{v_1'} - D_{v_2'})$, and this condition is fulfilled quite good in the studied C–A system.

Thanks to this procedure, it was possible to precisely determine ν_{00}^{CB} and ν_{01}^{CB} parameters of the rovibronic structure differences of the $C^1\Sigma^+(v = 0)$ and $B^1\Sigma^+(v = 0$ and 1) states in $^{13}C^{17}O$. Within this calculation, the ΔB_{00}^{CB} and ΔB_{01}^{CB} rotational parameters differences were also obtained. The final values of ν_{00}^{CB} and ΔB_{00}^{CB} parameters were calculated by means of a weighted arithmetic mean. All the results are collected in Table 5. A relative analysis of the Herzberg and Ångström band systems carried out in this way allowed for both elimination of the perturbation effect of the $A^1\Pi(v = 1$ and 2) state, as well as verification of the regularity of the $C^1\Sigma^+(v = 0)$ and $B^1\Sigma^+(v = 0$ and 1) states. The Jenkins and McKellar functions of the Herzberg $C^1\Sigma^+(v = 0) \rightarrow A^1\Pi(v = 1, 2)$ band system relative to the Ångström $B^1\Sigma^+(v = 0, 1) \rightarrow A^1\Pi(v = 1, 2)$ transition in the $^{13}C^{17}O$ isotopologue are illustrated in Fig. 4.

At the next stage of molecular parameters' calculations, the rotational equilibrium constants for the $C^1\Sigma^+$ state were determined in the $^{13}C^{17}O$ molecule for the first time. It was carried out by means of the weighted least-squares method using the merged rotational constants obtained in this work for the $C^1\Sigma^+(v = 0)$ state and the individual rotational constants published by Cacciani *et al.*[31] for the $C^1\Sigma^+(v = 1)$

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Table 5 Molecular constants (in cm^{-1}) of the $C^1\Sigma^+(v = 0)$ relative to the $B^1\Sigma^+(v = 0$ and 1) vibrational levels in the CO molecule[a]

	$^{13}C^{17}O$		$^{12}C^{16}O$	$^{13}C^{16}O$
Quantum	Experimental[b]	Calculated	Calculated	Calculated
ν_{00}^{CB}	5001.80086 (12)	5001.792 (6)[c]		
ν_{01}^{CB}	2990.8355 (30)	2990.877 (24)[d]		
ν_{10}^{CB}			7149.438 (78)[f]	7101.64[g]
			7149.38[e]	5064.33[g]
ν_{11}^{CB}			5067.276 (78)[f]	
			5067.12[e]	
$\Delta B_{00}^{CB} \times 10^3$	−3.4805 (41)	−3.483 (15)[e]		
$\Delta B_{01}^{CB} \times 10^2$	1.989 (26)	1.9484 (32)[e]		

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. [b] Calculated by means of the rovibronic combination differences of the recorded lines of the Herzberg bands system obtained in this work and the respective lines of the Ångström system from ref. 27 and 28, on the basis of the formulae introduced by Jenkins and McKellar,[82] in accordance with the description given in Section 4. [c] Calculated on the basis of values of band origins obtained in this work and given by Hakalla *et al.*,[28] as a weighted arithmetic mean of the differences $(\nu_0)_{01}^{CA}-(\nu_0)_{01}^{BA}$ and $(\nu_0)_{02}^{CA}-(\nu_0)_{02}^{BA}$. [d] Calculated on the basis of values of band origins obtained in this work and given by Hakalla *et al.*,[27] as the difference $(\nu_0)_{01}^{CA}-(\nu_0)_{11}^{BA}$. [e] Calculated on the basis of the difference of values of the merged molecular constants obtained in this work and by Hakalla *et al.*[27,28] for the $C^1\Sigma^+(v = 0)$ and $B^1\Sigma^+(v = 0$ and 1) levels, respectively. [f] The ν_{10}^{CB} quantum was calculated on the basis of the difference of values $(\sigma_{10}^{C-X}-\sigma_{00}^{B-X})$ given by Amiot *et al.*[52] [g] The ν_{10}^{CB} quantum was calculated on the basis of the difference of values $(\sigma_{10}^{C-X}-\sigma_{00}^{B-X})$ given by Tilford *et al.*[51]

state. The results are given in Table 6. Because only two vibrational levels of the $C^1\Sigma^+$ state are known for $^{13}C^{17}O$, the constants were determined from a fit of the data in which the amount of data equals the number of determined parameters. In that case standard deviations of equilibrium parameters were calculated by means of the Gauss error propagation method.

In order to determine the vibrational equilibrium constants for the $C^1\Sigma^+$ Rydberg state in the $^{13}C^{17}O$ isotopologue, the values $\Delta G_{1/2}^C$ vibrational quanta of the $C^1\Sigma^+$ state were determined using T_1^C and T_0^C values for $^{12}C^{16}O$,[52] $^{12}C^{17}O$,[50] $^{13}C^{16}O$,[50] $^{12}C^{18}O$,[50] and $^{13}C^{18}O$[40] as well as using the weighted least-squares method. The vibrational equilibrium constants of the $C^1\Sigma^+$ state for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ were also

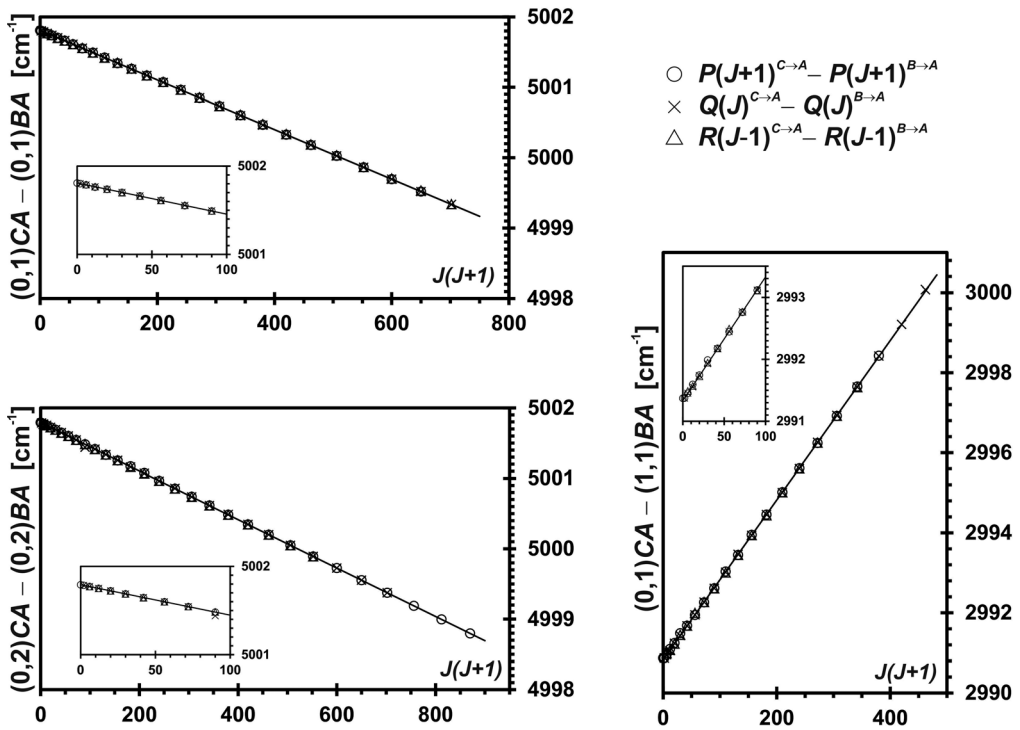

Fig. 4 The Jenkins and McKellar functions[82] of the Herzberg $C^1\Sigma^+(v = 0) \rightarrow A^1\Pi(v = 1, 2)$ band system relative to the Ångström $B^1\Sigma^+(v = 0, 1) \rightarrow A^1\Pi$ ($v = 1, 2$) transition in the $^{13}C^{17}O$ isotopologue. The small graphs have been included to precisely present the regions of J's origins.

Table 6 Vibrational quanta and equilibrium molecular constants for the $C^1\Sigma^+$ state in the CO molecule[a]

Constant	Isotopologue					
	$^{12}C^{16}O$	$^{12}C^{17}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$
$\Delta G^C_{1/2}$	**2146.529 (80)**[b]	**2120.20 (48)**[c]	**2099.40 (3)**[c]	**2095.43 (16)**[c]		**2046.95 (3)**[d]
ω_e	**2173.6 (15)**[e]		**2125.1 (15)**[e]	**2121.0 (10)**[e]	**2096.8 (14)**[e]	**2071.4 (14)**[e]
	2175.92[f]					
	2119.23 (16)[g]					
$\omega_e x_e$	**13.45 (76)**[e]		**12.85 (72)**[e]	**12.80 (51)**[e]	**12.51 (70)**[e]	**12.21 (69)**[e]
	14.76[f]					
	36.353 (79)[g]					
B_e	**1.95321 (53)**[k]		**1.86760 (11)**[k]	**1.86080 (32)**[k]	**1.81848 (39)**	**1.77504 (11)**[p]
	1.953276 (76)[j]		1.86716[m]	1.86004[m]	**1.81770**[m]	1.773932[m]
	1.95436 (38)[g]				1.81820[l]	
	1.95381 (36)[l]				1.81773[i]	
	1.9533[f]				1.81871[h]	
$\alpha_e \times 10^2$	**1.954 (10)**[k]		**1.820 (20)**[k]	**1.860 (29)**[k]	**1.754 (55)**	**1.7052 (86)**[p]
	1.979 (15)[j]		1.850[m]	1.839[m]	1.856[h]	1.7128[m]
	2.067 (41)[g]				1.760[i]	
	2.005 (39)[l]				**1.776**[n]	
	1.96[f]					
$D_e \times 10^6$	**6.1501 (51)**[k]		**5.6346 (62)**[k]	**6.64 (26)**[o]	**5.471 (49)**	**5.2431 (44)**[p]
	6.75 (35)[j]		5.6198[n]	5.58[n]	5.326[n]	5.0726[n]
					5.85[m]	
$\beta_e \times 10^7$	**1.47 (10)**[k]		{1.31}[n]	{1.30}[n]	{1.23}[n]	{1.1554}[n]

[a] In cm^{-1}. Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. Values given in braces were constrained during the calculation. Values calculated within this work are given in bold. [b] Calculated on the basis of T_1^C and T_0^C values given by Amiot *et al.*[52] [c] Calculated on the basis of T_1^C and T_0^C values given by Ubachs *et al.*[50] [d] Calculated on the basis of T_1^C and T_0^C values given by Haridass *et al.*[40] [e] Obtained on the basis of all values of the $\Delta G^C_{1/2}$ vibrational quanta for the CO isotopologues, given in this table. [f] After Tilford and Simmons.[51] [g] After Kępa.[68] [h] Evaluated from the $^{12}C^{16}O$ parameters given by Kępa[68] using Dunham's isotopic relationships. [i] Evaluated from the $^{12}C^{16}O$ parameters given by Tilford and Simmons[51] using Dunham's isotopic relationships. [j] Calculated on the basis of the values of individual rotational constants given by Amiot *et al.*[52] for the $C^1\Sigma^+$ state. [k] Calculated on the basis of the values of individual rotational constants given by Ubachs *et al.*[50] for the $C^1\Sigma^+$ state. [l] After Kępa.[63] [m] Evaluated from the $^{12}C^{16}O$ parameters calculated in this work on the basis of the data provided by Amiot *et al.*,[52] using Dunham's isotopic relationships. [n] Evaluated from the $^{12}C^{16}O$ parameters calculated in this work on the basis of the data provided by Ubachs *et al.*,[50] using Dunham's isotopic relationships. [o] Calculated on the basis of the values of individual rotational constants given by Roncin *et al.*[58] and Cacciani *et al.*[31] for the $C^1\Sigma^+$, $v = 0$, and 1 vibrational level, respectively. [p] Calculated on the basis of the values of individual rotational constants given by Kępa[67] and Cacciani *et al.*[31] for the $C^1\Sigma^+$, $v = 0$ and 1 vibrational level, respectively.

calculated. The determination in this work of the vibrational equilibrium constants for the ordinary $^{12}C^{16}O$ molecule deserves special attention, because they aspire to solve the problem of incompatibility between the values given by Tilford *et al.*[47,51] and by Kępa.[62,68] Table 6 presents finally results.

The rotational and vibrational equilibrium constants allowed for determining parameters of the potential curve of the $C^1\Sigma^+$ Rydberg state in the $^{13}C^{17}O$ molecule: the RKR turning points, Y_{00} Dunham's factor, zero point energy and the r_e equilibrium inter-nuclear distance. These results are gathered in Table 7. Also, the Franck–Condon factors, relative intensities, and r-centroids for the Herzberg band system in the lesser-abundant $^{13}C^{17}O$ isotopologue were calculated, additionally using the rotational and vibrational equilibrium constants of the $A^1\Pi$ state calculated by Hakalla *et al.*[27] The results are presented in Table 8.

Table 7 Vibrational levels and RKR turning points for the $C^1\Sigma^+$ Rydberg state of $^{13}C^{17}O$[a]

	Y_{00}	0.5745
	r_e	1.121 71 (12)
$v = 0$	$G(v) + Y_{00}$	1045.2725[b]
	r_{min}	1.07765
	r_{max}	1.17134
$v = 1$	$G(v) + Y_{00}$	3117.0525
	r_{min}	1.04858
	r_{max}	1.21164
$v = 2$[c]	$G(v) + Y_{00}$	5163.8125
	r_{min}	1.02999
	r_{max}	1.24158

[a] $G(v)$ and Y_{00} are in cm^{-1}; r_e, r_{min}, and r_{max} values are in Å. [b] The value of the $C^1\Sigma^+$ zero-point energy in the $^{13}C^{17}O$ isotopologue. [c] Extrapolated for the experimentally unobserved $C^1\Sigma^+(v = 2)$ vibrational level of the $^{13}C^{17}O$ isotopologue on the basis of rovibrational equilibrium constants listed in Table 6.

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

Carbon and oxygen have two: ^{12}C, ^{13}C and three: ^{16}O, ^{17}O, ^{18}O natural and stable isotopes, respectively. Thus, these two elements make up six stable isotopologues of the CO molecule,

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Table 8 Franck–Condon factors, relative intensities, and r-centroids for the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system in the $^{13}C^{17}O$ isotopologue[a]

$C^1\Sigma^+$ (v), $A^1\Pi$ (v)	0	1	2[b]
0	8.1321×10^{-2}	0.2217	0.2852
	3.4477	10.0000	10.0000
	1.1833	1.2104	1.2377
1	0.1803	0.1810	2.2038×10^{-2}
	7.8652	7.7679	0.7376
	1.1643	1.1906	1.2136
2	0.2183	3.6493×10^{-2}	5.0347×10^{-2}
	10.0000	1.5369	1.6064
	1.1461	1.1709	1.2015
3	0.1926	3.6515×10^{-3}	0.1156
	9.2294	0.1615	3.5132
	1.1285	1.1590	1.1814
4[c]	0.1384	5.7538×10^{-2}	5.8338×10^{-2}
	6.9187	2.6620	1.8281
	1.1115	1.1380	1.1632

[a] The values given one below the other denote – in the following order: Franck–Condon factors, relative intensities (in $\frac{\text{energy}}{\text{s}}$ scaled to 10), and r-centroids (in Å) for each band. [b] Extrapolated for the experimentally unobserved $C^1\Sigma^+(v = 2)$ vibrational level in the $^{13}C^{17}O$ isotopologue on the basis of rovibrational equilibrium constants listed in Table 6. [c] Extrapolated for the experimentally unobserved $A^1\Pi(v = 4)$ vibrational level in the $^{13}C^{17}O$ isotopologue on the basis of rovibrational equilibrium constants given by Hakalla *et al.*[27]

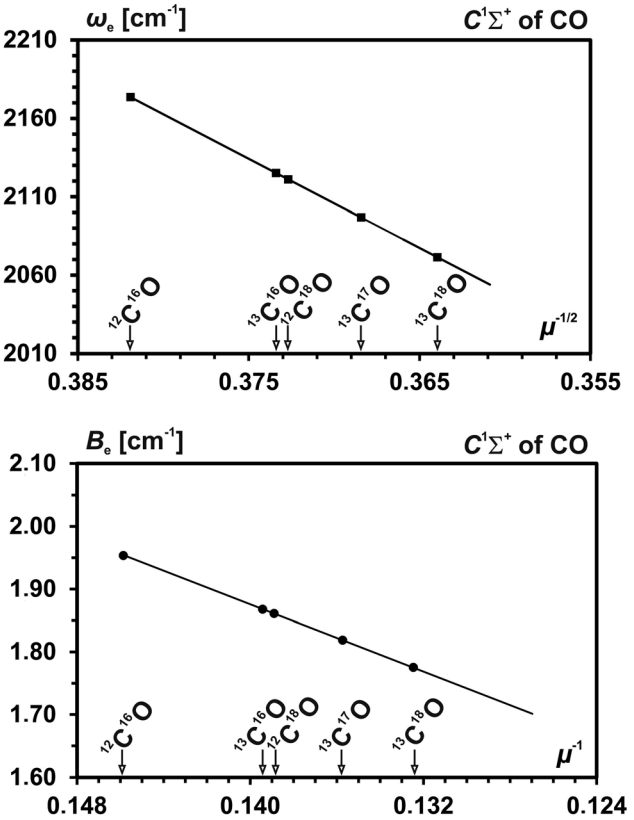

Fig. 5 Experimental values of the reduced mass dependence of $\omega_e = f(\mu^{-1/2})$ and $B_e = f(\mu^{-1})$ equilibrium constants of the $C^1\Sigma^+$ Rydberg state in the carbon monoxide molecule. Corresponding values (see Table 9) were calculated for the $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{17}O$ and $^{13}C^{18}O$ isotopologues. The regression lines in both graphs were plotted by means of the weighted linear least-square method. Standard deviation is impossible to show because of a relatively large scale of the plot.

from which the least-abundant is the $^{13}C^{17}O$ isotopologue. For example, all isotopologues, important for research into the Earth's atmosphere, have the following natural abundance: 98.7% ($^{12}C^{16}O$), 1.1% ($^{13}C^{16}O$), 0.2% ($^{12}C^{18}O$), 0.04% ($^{12}C^{17}O$), 0.0023% ($^{13}C^{18}O$), and 0.0004% ($^{13}C^{17}O$).[17]

Although the $C^1\Sigma^+(v = 0)$ state was observed in almost all natural isotopologues of CO, $^{13}C^{17}O$ and $^{14}C^{17}O$ still remained an exception. The experimental values of the rotational and vibrational equilibrium constants of the $C^1\Sigma^+$ Rydberg state have been so far known only for the ordinary $^{12}C^{16}O$ molecule.[51,63,68]

In order to study the reduced mass relationship of the ω_e vibrational equilibrium constant for the $C^1\Sigma^+$ state of CO, values ω_e were used that were calculated in this work for both the $^{13}C^{17}O$, as well as for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ isotopologues, using methods described in Section 4. The results of the calculations are provided in Table 9.

Using considerably extended data, we checked isotopic dependence of the ω_e constant of the $C^1\Sigma^+$ state through plotting a graph of all known values of this quantity in a function of a $\mu^{-1/2}$ argument, which is graphically illustrated in Fig. 5. The linear graph suggests that for the model of isotopic dependence of the Y_{kl} Dunham parameter,[83] the following equation can be used:

$$Y_{kl} = \mu^{-\frac{k+2l}{2}} U_{kl}, \quad (4)$$

Table 9 Rotational and vibrational equilibrium constants (in cm^{-1}) used to calculate the isotopically invariant parameters of the $C^1\Sigma^+$ Rydberg state in the CO molecule[a,b]

	Isotopologue				
Constant	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$
ω_e	2173.6 (15)	2125.1 (15)	2121.0 (10)	2096.8 (14)	2071.4 (14)
B_e	1.953276 (76)	1.86760 (11)	1.86080 (32)	1.81848 (39)	1.77504 (11)

[a] 1σ in parentheses. [b] For more details see Table 6 and text.

Table 10 Isotopically invariant parameters (in cm^{-1}) for the $C^1\Sigma^+$ Rydberg state in the CO molecule[a]

Molecule	State	Isotopically invariant parameter[b]	
CO	$C^1\Sigma^+$	U_{10}	5691.35 (45)
		U_{01}	13.39749 (59)

[a] 1σ in parentheses. [b] The values were calculated for the strictly fulfilled the Born–Oppenheimer approximation (see description in Section 5).

where U_{kl} is an isotopically invariant parameter (Dunham coefficient), and μ is the reduced mass of the CO molecule. Conditions of using this formula have been discussed in detail in ref. 38.

Using eqn (4) in the form of $Y_{10} = \mu^{-\frac{1}{2}} U_{10}$ and values of the ω_e equilibrium constants for the $C^1\Sigma^+$ state, provided in Table 9, the experimental value of the U_{10} isotopically invariant parameter was calculated. The calculations were performed by means of the weighted linear least-square method. The result is highlighted in Table 10.

Next, in order to study the reduced mass relationship of the B_e rotational equilibrium constant for the $C^1\Sigma^+$ state of CO, B_e values were used that were determined in this work for both $^{13}C^{17}O$ by means of the method described in Section 4, as well as for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ with the same method but on the basis of individual rotational constants B_0 and B_1 given for $^{12}C^{16}O$,[52] $^{13}C^{16}O$,[50] $^{12}C^{18}O$,[50] and $^{13}C^{18}O$.[31,40] The results of these calculations are given in Tables 6 and 9.

Using eqn (4), the isotopic dependence of the B_e rotational molecular constant of the $C^1\Sigma^+$ state in a function of μ^{-1} argument was checked (see Fig. 5). A linear graph $B_e = f(\mu^{-1})$ allows for the use of the eqn (4) in the form of $Y_{01} = \mu^{-1}U_{01}$. The U_{01} isotopically invariant parameter was calculated by means of the weighted linear least-square method. The value obtained in this way is presented in Table 10.

If there is a breakdown of the Born–Oppenheimer approximation then instead of eqn (4), we should use the formula describing the Dunham coefficients in the following form:[84]

$$Y_{kl} = \mu^{-\frac{k+2l}{2}} U_{kl}\left(1 + \frac{m_e}{M_A}\Delta_{kl}^{A} + \frac{m_e}{M_B}\Delta_{kl}^{B}\right), \quad (5)$$

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. Unfortunately, an attempt to determine the Δ_{01} and Δ_{10} coefficients from eqn (5) on the basis of the U_{10} and U_{01} isotopically invariant parameters for the $C^1\Sigma^+$ state of CO did not give satisfactory results. Precision and isotopic variation of the calculated values ω_e and B_e are still not enough to determine possible, small deviations from the Born–Oppenheimer approximation. I believe that higher precision of determining the wavenumbers, maybe in the range of the fifth decimal place, will allow for a calculation of the Born–Oppenheimer approximation breakdown in the CO molecule in future analyses.

6. Irregularities inside the Herzberg band system in the $^{13}C^{17}O$ isotopologue

6.1. Perturbations of the $A^1\Pi(v = 3)$ state in $^{13}C^{17}O$

The most comprehensive observations and analyses of extensive and multi-state perturbations of the $A^1\Pi$ state in CO have been so far carried out in the ordinary $^{12}C^{16}O$ molecule,[10,85–93] as it has been described in ref. 27. An improved analysis of the $v = 0$ and 1 levels of this state in the $^{12}C^{16}O$ molecule has been recently presented by Niu *et al.*[94] There is far less information on perturbations appearing in this state in the natural CO isotopologues,[41,60,95–98] especially in the least-abundant $^{13}C^{17}O$.[27,28] The $A^1\Pi(v = 3)$ vibrational level in $^{13}C^{17}O$ has not been studied so far.

The analysis of perturbations which appear in the $A^1\Pi(v = 3)$ state of the $^{13}C^{17}O$ molecule, done in this work, was carried out in the aspect of confrontation of the perturbations observed and predicted from analyses of possibilities of interactions between the $A^1\Pi(v = 3)$ state and nearby lying states in the region 70 000–74 000 cm^{-1}.

To locate perturbations of the $A^1\Pi(v = 3)$ state in the $^{13}C^{17}O$ isotopologue, the graph of functions $f_Q(J)$ with $f_{\overline{PR}}(J)$ and $g_Q(J)$ with $g_{\overline{PR}}(J)$ was used, which were introduced by Gerö[99] and Kovács.[100] They were plotted for respective lines of the branches of the C → A(0,3) band. The results are presented in Fig. 6 and 7. The non-linear function graph clearly indicates the location of the sought irregularities. Detailed description of the properties and applications of the f_x and g_x functions, where $x = Q$ and $\overline{PR}$, was presented in my previous work.[28]

The predicted perturbations for both Λ-components of the $A^1\Pi(v = 3; J = 0–45)$ state in $^{13}C^{17}O$ were determined by means of the rovibronic term-crossing diagram for this state and the nearby lying $I^1\Sigma^-(v = 4, 5)$, $D^1\Delta(v = 3, 4)$, $e^3\Sigma^-(v = 5, 6)$, $a'^3\Sigma^+(v = 13)$, $a^3\Pi_r(v = 14)$ and $d^3\Delta_i(v = 8, 9)$ states, and also by means of the parity selection rules.[101] The above calculations were performed by means of molecular constants for the $A^1\Pi$ state determined in this work and those given by Field[87] and Kittrell *et al.*[102] for the $^{12}C^{16}O$ molecule and recalculated to the $^{13}C^{17}O$ molecule by means of standard isotopic relations[83] for $I^1\Sigma^-$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $a^3\Pi_r$, and $d^3\Delta_i$, as well as for $D^1\Delta$, respectively. The results are given in Fig. 8.

The identification of the perturbing state was made through analyses of correlations between the irregularities of experimental functions $f_Q(J)$ with $f_{\overline{PR}}(J)$ and $g_Q(J)$ with $g_{\overline{PR}}(J)$ (Fig. 6 and 7) and the predicted maxima of perturbations resulting from the rovibronic term-crossing diagram (Fig. 8) as well as the selection rules for perturbations.[101] In Table 11 complete information was gathered on the places of perturbations and states responsible for them, which appear in the $A^1\Pi(v = 3)$ level of the $^{13}C^{17}O$ molecule.

The perturbations occurrence in the rotational structure of the observed bands can also be directly exhibited by a plot of the differences between the observed and calculated term values $[T(v, J)_{obs} - T(v, J)_{calc}]$ *versus* the rotational quantum number J. Such a graph for the $A^1\Pi(v = 3)$ state of the $^{13}C^{17}O$ molecule is

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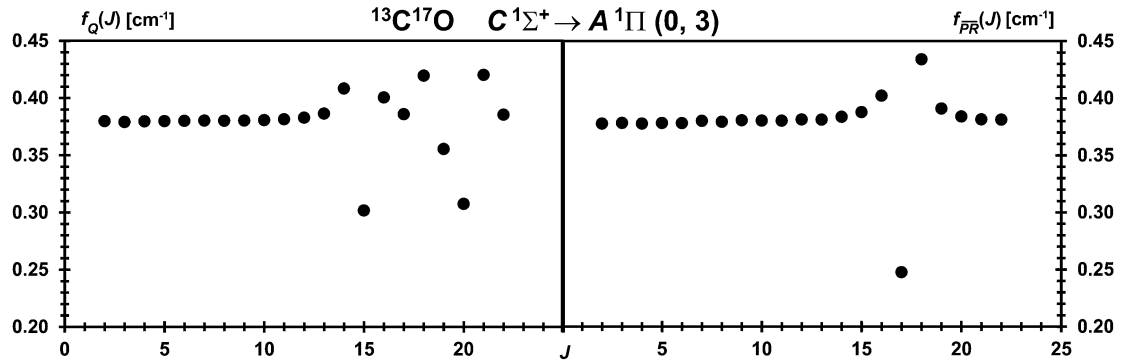

Fig. 6 Rotational perturbations of the $A^1\Pi(v = 3)$ state in the $^{13}C^{17}O$ isotopologue illustrated by the $f_x(J)$ functions of Kovács,[100] where $x = Q$ and $\overline{PR}$. The graphs were plotted for the $C^1\Sigma^+ \rightarrow A^1\Pi$ (0,3) transition. Uncertainties of single measurements are negligibly small in the scales used in these graphs.

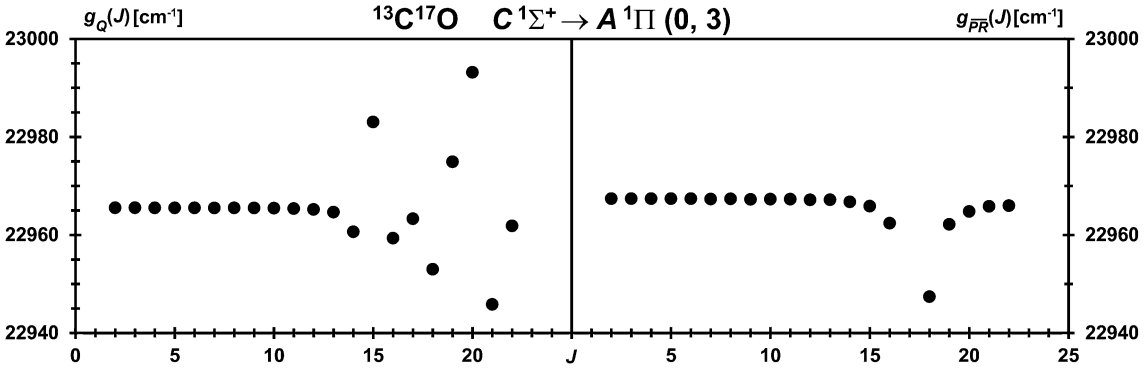

Fig. 7 Rotational perturbations of the of the $A^1\Pi(v = 3)$ state in the $^{13}C^{17}O$ isotopologue illustrated by the $g_x(J)$ functions of Kovács,[100] where $x = Q$ and $\overline{PR}$. The graphs were plotted for the $C^1\Sigma^+ \rightarrow A^1\Pi$ (0,3) transition. Uncertainties of single measurements are negligibly small in the scales used in these graphs.

presented in Fig. 9. As one can see, more or less discontinuities occur at different J values for $A^1\Pi(v = 3)$ state. It is a characteristic phenomenon in the regions where perturbations occur.

6.2. Regularity of the $C^1\Sigma^+(v = 0)$ Rydberg state in the $^{13}C^{17}O$ isotopologue

Studies on highly excited electron states of the CO molecule, carried out in the last two decades, and based on detailed analysis of the observed transitions $C^1\Sigma^+(v = 0) \rightarrow X^1\Sigma^+$,[30,48,50] $c^3\Pi(v = 0) \rightarrow X^1\Sigma^+$,[30] and $k^3\Pi \rightarrow X^1\Sigma^+$ [30,103] in $^{12}C^{16}O$ molecule showed that the $C^1\Sigma^+(v = 0)$ Rydberg state lies closely both to the $k^3\Pi(v = 1,2)$ as well as the $c^3\Pi(v = 0)$ states and it should cross these states at low and higher J, respectively.[30,50] Therefore, the $C^1\Sigma^+(v = 0)$ state should be irregular.

The Jenkins and McKellar functions of the Herzberg $C^1\Sigma^+(v = 0) \rightarrow A^1\Pi(v = 1, 2)$ band system relative to the Ångström $B^1\Sigma^+(v = 0, 1) \rightarrow A^1\Pi(v = 1, 2)$ transitions in the $^{13}C^{17}O$ isotopologue, presented in Fig. 4, completely eliminate the impact of the common $A^1\Pi$ $(v = 1, 2)$ lower rovibronic state. Therefore, a detailed analysis of the regular and linear course of these functions allows us to state precisely and unambiguously that in the observed spectrum regions and within experimental error limits, the observed $C^1\Sigma^+(v = 0)$ i $B^1\Sigma^+(v = 0$ and 1) levels in the $^{13}C^{17}O$ isotopologue are completely regular and without rotational perturbations up to the observed J_{max}, just as it is in the ordinary $^{12}C^{16}O$ molecule.[30,50] Thus, an interaction between the $C^1\Sigma^+(v = 0)$ state and the $k^3\Pi$ and $c^3\Pi$ states in the $^{13}C^{17}O$ isotopologue, if it exists at all, is so weak that one cannot observe it within measuring error limits. At the same time, as Ubachs *et al.*[19,50] conclude, the $C^1\Sigma^+(v = 0)$ state is not affected by accidental predissociation.

7. Discussion and conclusions

The first observations and analyses of the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system in the natural and stable least-abundant $^{13}C^{17}O$ isotopologue enabled us to calculate the set of molecular constants both for the upper and lower state of this system as well as to present an outline of the first comprehensive characteristics of the $C^1\Sigma^+$ Rydberg state.

A careful investigation of the Kovács functions' course (see Fig. 6 and 7) and the $[T(v, J)_{obs} - T(v, J)_{calc}]$ differences (see Fig. 9) for the $A^1\Pi(v = 3)$ state in $^{13}C^{17}O$, allowed for precise identification of all places of perturbations and states responsible for them. The results of these observations and analyses are given in Table 11. In Fig. 9 in the region $J = 9$–20 clearly

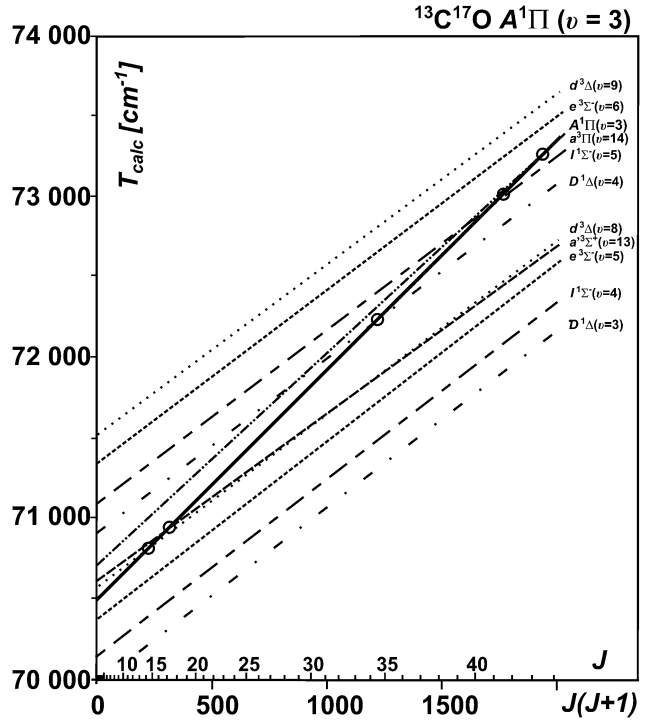

Fig. 8 Rovibronic term crossing diagram for the perturbed $A^1\Pi(v = 3)$ state in $^{13}C^{17}O$ isotopologue together with $I^1\Sigma^-(v = 4, 5)$, $D^1\Delta(v = 3, 4)$, $e^3\Sigma^-(v = 5, 6)$, $a'^3\Sigma^+(v = 13)$, $a^3\Pi_r(v = 14)$ and $d^3\Delta_i(v = 8, 9)$ perturbing states. Places marked with circles indicate regions for which the strongest perturbations are expected.

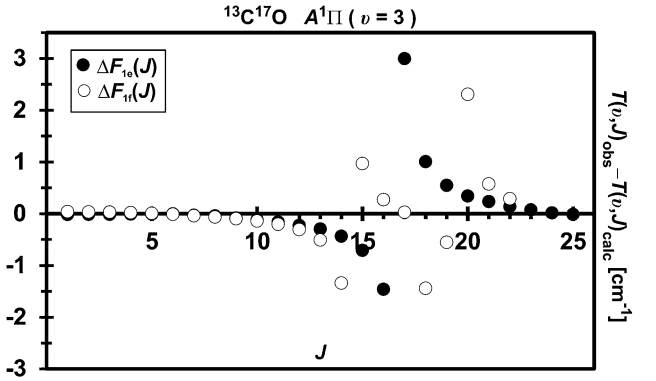

Fig. 9 Differences between the observed $[T(v, J)_{obs}]$ and calculated $[T(v, J)_{calc}]$ term values of the $A^1\Pi(v = 3)$ vibrational level in the $^{13}C^{17}O$ isotopologue. See Table 11 and Section 6 for more details relevant to identification of the states responsible for the observed perturbations.

multistate perturbations overlap deriving from the $d^3\Delta_i(v = 8)$ and $a'^3\Sigma^+(v = 13)$ states giving maximum deviations of the terms by almost 3 cm^{-1} for $J = 17$ (e-component) and causing an uncharacteristic course of rotational perturbation for $J = 18$–20 (f-component). Far weaker perturbations for $J = 9$ (e- and f-components) and $J = 13$ (e-component) are denoted in Table 11 as "experimentally unverified" because they are not distinguished from the impact of successive perturbations, closely lying to them. Therefore, we cannot state explicitly that they exist.

The difference of values between the ν_{00}^{CB} and ν_{01}^{CB} vibrational quanta should result in the value of vibrational distance between the $v = 0$ and $v = 1$ levels of the $B^1\Sigma^+$ electronic state, that is, the $\Delta G_{1/2}^B$ vibrational quantum. The value calculated in this way for $^{13}C^{17}O$ on the basis of the data from Table 5 for the C → A system equals 2010.9654 (31) cm^{-1} and it remains consistent with the value of 2010.9622 (69) cm^{-1} calculated by Hakalla *et al.*[27] on the basis of the analysis of 1 → v'' (ref. 27) and 0 → v''(ref. 28) progressions of the B → A band system.

During the process of determining experimental values of the ν_{00}^{CB} and ν_{01}^{CB} vibrational quanta for the $^{13}C^{17}O$ isotopologue, also the values of the $\Delta B_{00}^{CB} = B_0^C - B_0^B$ and $\Delta B_{01}^{CB} = B_0^C - B_1^B$ rotational quanta were calculated. They are presented in Table 5. These values equal $-3.4805(41) \times 10^{-3}$cm^{-1} and $1.989(26) \times 10^{-2}$ cm^{-1}, respectively. The results are consistent with the values calculated on the basis of direct difference of the merged rotational constants B_0^C (this work) and B_0^B [28] as well as B_0^C (this

Table 11 Observed and predicted perturbations of the $A^1\Pi(v = 3)$ vibrational level in $^{13}C^{17}O$[a]

Maximum of perturbation (J) of the Λ-doubling component				Perturbing state	
f		e			
Observed	Calculated	Observed	Calculated	Triplet component	Vibrational level
*	9	*	9	$F(3)$	$d^3\Delta_i$ ($v = 8$)
14–15	13	*	13	$F(2)$	
18–20	17	16–17	17	$F(1)$	
14–15	14			$F(1)$	$a'^3\Sigma^+$ ($v = 13$)
		16–17	17	$F(2)$	
18–20	20			$F(3)$	
*	34–35	*	34–35		$D^1\Delta$ ($v = 4$)
*	41–42				$I^1\Sigma^-$ ($v = 5$)
*	40	*	40		$a^3\Pi_r$ ($v = 14$)
*	44	*	44		
*	48	*	48		

[a] Asterisks indicates regions experimentally unverified.

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work) and B_1^B,[27] which equal $-3.483(15) \times 10^{-3}$ cm^{-1} and $1.9484(32) \times 10^{-2}$ cm^{-1}, respectively. This consistency confirms high quality of the calculations performed in this work.

As a result of the analyses carried out in this work, both vibrational and rotational equilibrium constants of the $C^1\Sigma^+$ state for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{17}O$ and $^{13}C^{18}O$ isotopologues were determined, which are given in Table 6. For many years an important problem has not been solved in the ordinary $^{12}C^{16}O$ molecule, that is, a considerable inconsistency between the values of the vibrational equilibrium constants ω_e and $\omega_e x_e$, given by Tilford *et al.*,[47,51] and those given by Kępa.[62,68] The results presented in this work, that is $\omega_e = 2173.6(15)$ cm^{-1} and $\omega_e x_e = 13.45(76)$ cm^{-1} allow for the final solution of this problem in favour of the values given by Tilford *et al.*,[47,51] which are consistent with the presented one within two standard deviations.

At the current stage of the research, it is still not possible to determine the $\Delta G_{1/2}^C$ vibrational quantum for the $C^1\Sigma^+$ state in $^{13}C^{17}O$ by means of rovibrational combination differences[104] because of the lack of observed transitions in this molecule from the $C^1\Sigma^+(v = 1)$ state to the $A^1\Pi$ state or from the $C^1\Sigma^+(v = 0)$ state to the $X^1\Sigma^+$ ground state. That is why I decided to assess this value on the basis of the determined vibrational equilibrium constants given in Table 6 and using the formula $\Delta G_{1/2}^C = \omega_e - 2\omega_e x_e$.[104] The result is $\Delta G_{1/2}^C = 2071.8\ (28)$ cm^{-1} for the $^{13}C^{17}O$ isotopologue.

Conclusions

Presented high-quality measurements and analyses, as well as the precise results for the Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band system, which has not been so far studied in $^{13}C^{17}O$, allowed us to considerably extend the spectroscopic and quantum-mechanical information on the $C^1\Sigma^+$ Rydberg state and on the strongly perturbed $A^1\Pi$ state in the CO molecule.

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