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# Extended analysis of the Ångström band system ( $B^1\Sigma^+ - A^1\Pi$ ) in the rare $^{12}\text{C}^{17}\text{O}$ isotopologue

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## Abstract

The Ångström band system ( $B^1\Sigma^+ - A^1\Pi$ ), so far unobserved in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue, was obtained under high resolution as an emission spectrum using high accuracy dispersive optical spectroscopy. In total, 200 transition wave numbers belonging to the 0–1 and 0–2 bands were precisely measured and rotationally analysed. The obtained result was the merged rotational constants  $B_0 = 1.898\,8823(41)\text{ cm}^{-1}$  and  $D_0 = 6.4283(26) \times 10^{-6}\text{ cm}^{-1}$  for the  $B^1\Sigma^+$  Rydberg state as well as the individual rotational constants  $B_1 = 1.540\,88(12)\text{ cm}^{-1}$ ,  $D_1 = 6.950(87) \times 10^{-6}\text{ cm}^{-1}$ ,  $B_2 = 1.519\,292(69)\text{ cm}^{-1}$ ,  $D_2 = 8.22(16) \times 10^{-6}\text{ cm}^{-1}$  for the  $A^1\Pi$  state in the  $^{12}\text{C}^{17}\text{O}$  isotopologue. The  $\sigma_{0-v''}$  band origins were also calculated. Numerous rotational perturbations observed in the  $A^1\Pi$  state in this molecule have been identified. The observed perturbations were confronted with those predicted from theoretical calculations.

## 1. Introduction

There is considerable experimental and theoretical interest in the spectra of the CO molecule, because carbon monoxide is, after  $\text{H}_2$ , the most abundant molecule in the universe. Owing to this fact, it gives a detectable signal from interstellar space for even rarer natural isotopomers. For instance, its occurrence has been documented [1–18] in the atmospheres of planets and stars, in comet tails, interstellar space, etc. Detection and quantification of the different stable isotopomers of CO in the interstellar medium are of particular interest for modelling interstellar clouds and stellar evolution [19]. The solar-spectrum, obtained under high resolution with the ATMOS infrared Fourier transform interferometer, has shown the presence of all natural isotopes of CO [20]. For this reason, it appears to be a very urgent and justified task to carry out a comprehensive high-resolution spectroscopic study paying particular attention to the set of accurate rotational molecular constants and band origins for all electronic excited states of all isotopes of carbon monoxide. Apart from this, the

CO molecule has continued to be of interest to several areas of science, including environmental investigations, chemical physics, the technology of new materials based on connecting metals with carbon monoxide (e.g. metal carbonyls), medicine etc.

The comprehensive experimental study of the  $B^1\Sigma^+$  state in the  $^{12}\text{C}^{16}\text{O}$  molecule has already been provided in various transitions using diverse spectroscopic (both laser as well as conventional) methods [21–45]. Much less information about this state is available for other isotopologues [25, 43, 46–49, 51, 52].

The  $B^1\Sigma^+ - A^1\Pi$  system of carbon monoxide has been the subject of numerous studies since its discovery by Ångström [53] in the  $^{12}\text{C}^{16}\text{O}$  ordinary molecule [54–57] as well as in other isotopologues:  $^{12}\text{C}^{18}\text{O}$  [59, 48];  $^{13}\text{C}^{16}\text{O}$  [58–61];  $^{13}\text{C}^{18}\text{O}$  [46, 62, 63];  $^{14}\text{C}^{16}\text{O}$  [47, 64] and  $^{14}\text{C}^{18}\text{O}$  [49]. Recently Hakalla *et al* [65] have obtained, under high resolution, the Ångström band system in the rarest of the stable CO isotopomers, namely in  $^{13}\text{C}^{17}\text{O}$ . However, the  $B^1\Sigma^+ - A^1\Pi$  system has never been observed in the very rare  $^{12}\text{C}^{17}\text{O}$  isotopologue. Moreover, in this isotopic molecule, the  $B^1\Sigma^+$  Rydberg state has never been observed nor analysed within any transitions.

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**Table 1.** Summary of the observations and analyses of the Ångström ( $B^1\Sigma^+ - A^1\Pi$ ) system in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue.

Band	Number of lines	Number of lines used in the fits	Band head ( $\text{cm}^{-1}$ )	$J_{\max}$	$\sigma^a \times 10^3$ ( $\text{cm}^{-1}$ )
0–1	102	89	20 692.816	34	1.16
0–2	98	90	19 265.069	33	1.08

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

Besides, the investigations of the isotopomers of carbon monoxide make it possible to obtain additional information about one of the most abundant natural molecules and to verify its data. At the same time, they enlarge the spectroscopic information about the spectrum and energetic structure of the CO molecule as a whole.

In this paper we present details of the experimental investigations and rotational analysis of the  $B^1\Sigma^+ - A^1\Pi$  band system obtained for the first time in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue.

## 2. Experimental details

The experimental details are almost the same as described in our previous paper [65], so some parts of this work have been included with the consent of Elsevier Limited (License agreement number 2920140428884).

So far unobserved in the very rare  $^{12}\text{C}^{17}\text{O}$  isotopologue, the  $0 - v''$  progression of the Ångström band system has been registered as a high resolution emission spectra using a high accuracy dispersive optical spectroscopy. The 0–1 and 0–2 bands belonging to the  $B^1\Sigma^+ - A^1\Pi$  transition of  $^{12}\text{C}^{17}\text{O}$  molecule were observed in the 19 250–21 300  $\text{cm}^{-1}$  spectral region.

The typical standard deviation of the least-squares fit for the 30–40 thorium atomic calibration lines [66] derived from a water-cooled, hollow-cathode tube was approximately 0.0011–0.0015  $\text{cm}^{-1}$ .

The water-cooled, hollow-cathode lamp with two anodes [67] was used to obtain the molecular spectra of the  $^{12}\text{C}^{17}\text{O}$ . It was initially filled with a mixture of helium and acetylene  $\text{C}_2\text{D}_2$ . The electric current was passed through the mixture for about 80 hours. After a small quantity of  $^{12}\text{C}$  carbon became deposited on the electrodes, the lamp was evacuated and oxygen containing 60% of the isotope  $^{17}\text{O}_2$  was admitted. The CO lines appeared with a maximum signal-to-noise ratio of about 130 : 1 and approximately 150 : 1 for the 0–1 and 0–2 band, respectively. Consequently, the wavenumbers for the strong and isolated lines were determined with an accuracy better than  $\pm 0.0013 \text{ cm}^{-1}$ , excluding lines marked by an asterisk (in tables 2 and 3).

The statistical information for the analysed bands is shown in table 1 and their wavenumbers are provided in tables 2 and 3. The parts of their high quality spectrum in the range of their band heads are shown in figures 1 and 2.

The clear diagram of the experimental setup and its detailed description is featured in the work of Hakalla *et al* [65]. This measurement system has been assembled and calibrated in our laboratory for the last couple of years. Apart

**Table 2.** Observed wavenumbers and rotational assignments of the 0–1 band lines of the Ångström system in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue (in  $\text{cm}^{-1}$ ). Values in parentheses denote observed minus calculated values in units of the last quoted digit. Asterisks denote the less accurate lines and not used in the evaluation of molecular constants.

$J$	$P_{11ee}(J)$	$Q_{11ef}(J)$	$R_{11ee}(J)$
1	20 697.6053 *	20 701.6649 (0)	20 708.9984 *
2	20 695.2896 (–3)	20 702.9613 (0)	20 714.2781 (3)
3	20 693.6913 (6)	20 705.1211 (0)	20 720.2722 (–5)
4	20 692.8162 (–7)	20 708.0274 (0)	20 726.9926 (8)
5	20 692.6559 (–3)	20 711.6399 (0)	20 734.4229 (2)
6	20 693.2307 (–2)	20 716.0135 (0)	20 742.5875 (1)
7	20 694.5088 (–8)	20 721.0857 (0)	20 751.4547 (8)
8	20 696.5025 (0)	20 726.8894 (0)	20 761.0386 *
9	20 699.2158 (0)	20 733.3813 (0)	20 771.3339 *
10	20 702.6428 *	20 740.6006 (0)	20 782.3403 (0)
11	20 706.7934 (0)	20 748.5336 (0)	20 794.0671 *
12	20 711.6399 *	20 757.1827 (0)	20 806.4973 (0)
13	20 717.2272 (0)	20 766.5472 (0)	20 819.6432 *
14	20 723.5184 (0)	20 776.5989 (0)	20 833.5009 *
15	20 730.5279 (–3)	20 787.4239 (0)	20 848.0669 (4)
16	20 738.2567 (1)	20 798.9321 (0)	20 863.3508 (–1)
17	20 746.7119 *	20 811.2426 (0)	20 879.3680 (0)
18	20 755.9022 *	20 824.6940 (0)	20 896.1068 (0)
19	20 765.8613 (0)	20 837.2964 (0)	20 913.6004 *
20	20 776.7432 (14)	20 851.8561 (0)	20 932.0047 (–13)
21	20 785.8095 (–3)	20 866.9982 (0)	20 948.6016 (2)
22	20 799.1280 (16)	20 882.8527 (0)	20 969.4373 (–16)
23	20 812.0475 *	20 899.5075 (0)	20 989.8873 (0)
24	20 825.6183 (–9)	20 914.8602 (0)	21 010.9531 (10)
25	20 839.8962 (–10)	20 934.3100 (0)	21 032.7302 (10)
26	20 853.6951 (–2)	20 953.5328 (0)	21 054.0187 (2)
27	20 870.0221 (4)	20 972.0576 (0)	21 077.8276 (–4)
28	20 886.5358 (–13)	20 992.3447 (0)	21 101.8192 (13)
29	20 903.6564 (7)	21 013.2355 (0)	21 126.4014 (–8)
30	20 921.5063 (10)	21 034.8087 (0)	21 151.7074 (–11)
31	20 940.0364 (–9)	21 057.1204 (0)	21 177.6885 (8)
32	20 959.2941 (4)	21 080.1836 (0)	21 204.3811 (–5)
33	20 979.3134 (6)	21 104.0129 (0)	21 231.8276 (–6)
34	21 000.0321 (–8)	21 128.8367 (0)	21 259.9662 (7)

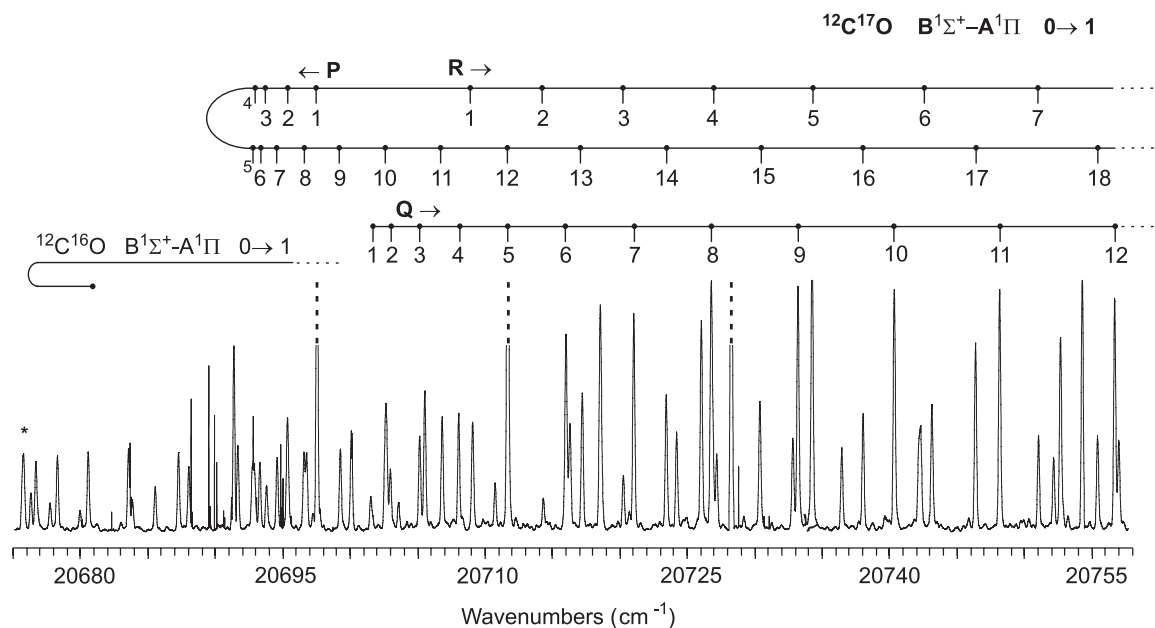
from examining the carbon monoxide molecule [61, 65], it has also been used to analyse a very little known  $\text{AlH}$  [68–70] and  $\text{AlH}^+$  ionic [71] as well as CD radical [72] molecules.

## 3. Analysis and results

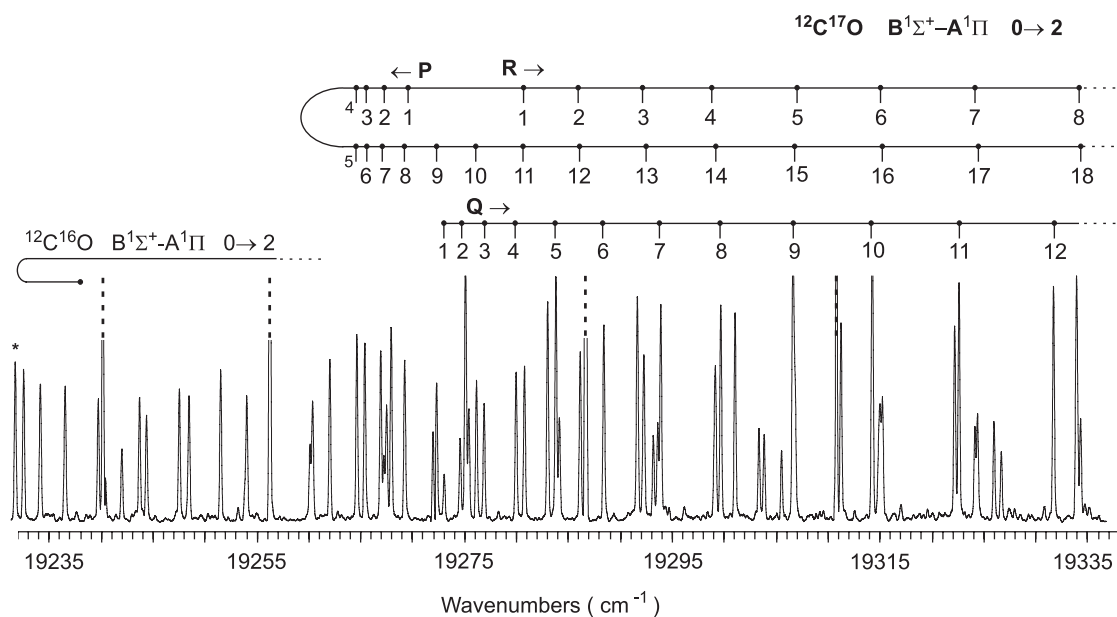
The obtained molecular constants for the  $B^1\Sigma^+(v' = 0)$  and  $A^1\Pi(v'' = 1, 2)$  levels in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue will be presented and discussed in this section.

### 3.1. Identification of the spectra

The vibrational–rotational identification of the recorded  $B^1\Sigma^+ - A^1\Pi$  transition in the  $^{12}\text{C}^{17}\text{O}$  molecule was initiated by determining the upper and lower vibrational levels, a preliminary quantum of  $J$ -numbering of the lines belonging to the 0–1 and 0–2 bands of the system under consideration, as well as by assembling all the lines into  $P$ ,  $Q$ , and  $R$  branches. It was executed on the basis of the results obtained by Keřpa *et al* [57] for the ordinary molecule and by means of recalculations for the  $^{12}\text{C}^{17}\text{O}$  molecule by means of a standard Dunham's



**Figure 1.** Band-head region of the  $B^1\Sigma^+ - A^1\Pi$  emission spectrum of the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue for the 0-1 band. Part of the less intense 0-1 band of the Ångström system in the  $^{12}\text{C}^{16}\text{O}$  molecule is shown on the left (its band head is marked with an asterisk). The dotted lines indicate the tips of the relatively very strong calibration lines as well as the strongest overlapped molecular line at  $20711\text{ cm}^{-1}$  (which consists of the lines  $P(12)$  and  $Q(5)$  from  $^{12}\text{C}^{17}\text{O}$  as well as  $Q(8)$  from  $^{12}\text{C}^{16}\text{O}$ ).



**Figure 2.** Band-head region of the  $B^1\Sigma^+ - A^1\Pi$  emission spectrum of the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue for the 0-2 band. Part of the less intense 0-2 band of the Ångström system in the  $^{12}\text{C}^{16}\text{O}$  molecule is shown on the left (its band head is marked with an asterisk). The dotted lines indicate the tips of the relatively very strong calibration lines.

isotopic relationship. The appropriate formulas were given by Dunham [73] and Brown *et al* [74].

The gas used in the hollow-cathode lamp included about 40% of the  $^{16}\text{O}_2$  isotope apart from the  $^{17}\text{O}_2$  isotope of molecular oxygen. Hence, the recorded spectrum of the molecule under consideration also included the weaker spectrum of the  $B^1\Sigma^+ - A^1\Pi$  system of the  $^{12}\text{C}^{16}\text{O}$  molecule in the studied region. The identification of these undesirable spectroscopic lines, aiming to marginalize them in the further identification process of the spectrum under consideration,

has been carried out on the basis of the data obtained by LeFloch and Amiot [56]. The regions of the band heads coming from the  $^{12}\text{C}^{16}\text{O}$  molecule have been appropriately marked and described in figures 1 and 2.

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

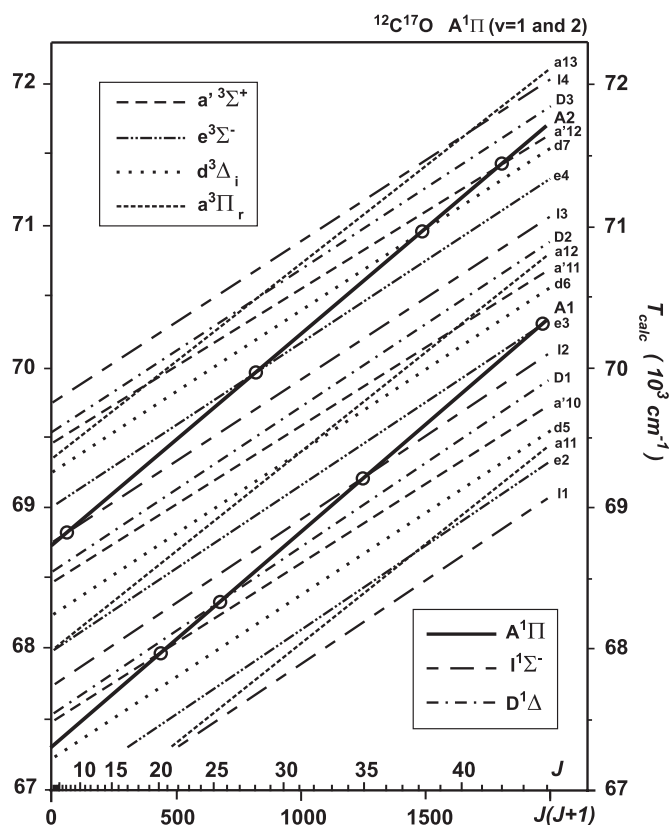
The  $A^1\Pi$  state in the  $^{12}\text{C}^{16}\text{O}$  molecule has been analysed several times [21, 30, 39, 41, 54-57, 75-97]. In the region of  $66000\text{ cm}^{-1}$ , in addition to the  $A^1\Pi$  state, six other electronic

**Table 3.** Observed wavenumbers and rotational assignments of the 0–2 band lines of the Ångström system in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue (in  $\text{cm}^{-1}$ ). Values in parentheses denote observed minus calculated values in units of the last quoted digit. Asterisks denote the less accurate lines and not used in the evaluation of molecular constants.

$J$	$P_{11ee}(J)$	$Q_{11ef}(J)$	$R_{11ee}(J)$
1	19 269.6331 *	19 273.4155 (0)	19 281.0261 (0)
2	19 267.3634 *	19 274.9369 (0)	19 286.3512 (0)
3	19 265.8212 *	19 277.2192 (0)	19 292.4037 (0)
4	19 265.0686 *	19 280.2664 (0)	19 299.2424 (0)
5	19 265.0686 *	19 284.0692 (0)	19 306.8346 (0)
6	19 265.8212 *	19 288.6542 (0)	19 315.1771 (0)
7	19 267.3634 *	19 294.1079 (0)	19 324.3094 (0)
8	19 269.6331 *	19 299.8689 (0)	19 334.1628 (0)
9	19 272.6915 (5)	19 306.7799 (0)	19 344.8035 (–6)
10	19 276.4953 (4)	19 314.4066 (0)	19 356.1878 (–3)
11	19 281.0702 (1)	19 322.7674 (0)	19 368.3400 (–1)
12	19 286.4052 (0)	19 331.8919 (0)	19 381.2486 (1)
13	19 292.5120 (–7)	19 341.7796 (0)	19 394.9261 (7)
14	19 299.3731 (0)	19 352.4275 (0)	19 409.3510 (0)
15	19 306.9975 (0)	19 363.8382 (0)	19 424.5363 (1)
16	19 315.4023 (1)	19 376.0083 (0)	19 440.4968 (–1)
17	19 324.5472 (–2)	19 388.9564 (0)	19 457.19 33 (3)
18	19 334.4939 (–3)	19 402.6632 (0)	19 474.6856 (3)
19	19 345.2148 (2)	19 417.1371 (0)	19 492.9452 (–3)
20	19 356.7067 (9)	19 432.3824 (0)	19 511.9697 (–8)
21	19 369.0011 (7)	19 448.4002 (0)	19 531.7917 (–8)
22	19 382.0996 (–21)	19 465.1692 (0)	19 552.4167 (21)
23	19 396.0894 (–6)	19 482.7850 (0)	19 573.9173 (5)
24	19 411.3115 (–4)	19 501.1822 (0)	19 596.6457 (4)
25	19 428.7392 (14)	19 520.4231 (0)	19 621.5689 (–14)
26	19 440.0386 (–2)	19 540.6328 (0)	19 640.3627 (2)
27	19 457.4971 (6)	19 562.2160 (0)	19 665.3024 (–7)
28	19 475.3789 (–4)	19 586.4838 (0)	19 690.6608 (3)
29	19 494.0035 (5)	19 600.0131 (0)	19 716.7495 (–5)
30	19 513.4854 (–4)	19 624.0077 (0)	19 743.6898 (4)
31	19 533.5327 (11)	19 647.8855 (0)	19 771.1812 (–12)
32	19 547.8958 (–11)	19 672.2991 (0)	19 792.9863 (11)
33	19 573.0659 (0)	19 697.5183 (0)	

states are located, namely:  $I^1\Sigma^-$ ,  $D^1\Delta$ ,  $e^3\Sigma^-$ ,  $a^3\Sigma^+$ ,  $a^3\Pi_r$ , and  $d^3\Delta_i$ . Therefore there are perturbations of the rotational structure observed in each vibrational level of the A state. The systematic classification of these perturbations in the  $^{12}\text{C}^{16}\text{O}$  was carried out by Krupenie [75] and completed by Simmons *et al* [76]. The deperturbation calculation on the basis of the data obtained up to 1971 was performed by Field [78] and Field *et al* [79]. Le Floch *et al* [82] conducted an extensive study of the  $A^1\Pi$  ( $v = 0$ ) state perturbation. Le Floch [85] performed perturbation calculations for the  $A^1\Pi$  ( $v = 0-4$ ) state. Finally, Le Floch [87] collected the exact term values for  $A^1\Pi$  ( $v = 0-8$ ) state of  $^{12}\text{C}^{16}\text{O}$ . Much less information about the  $A^1\Pi$  state is available for other isotopologues [46–52, 58–65, 77, 96, 98–108].

The  $A^1\Pi$  electronic state in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue is hardly known. The only laboratory research was conducted by Steinmann *et al* [105] and Plessis *et al* [107], where 34 lines of the  $A^1\Pi(v' = 0-5)-X^1\Sigma^+(v'' = 0)$  system were recorded altogether in the vacuum ultraviolet region. In the work of Plessis *et al* [107], only the values of the few first rotational terms ( $J' = 1-4$ ) of a few lowest vibrational levels ( $v' = 0-5$ ) of the  $A^1\Pi$  state were calculated with weaker



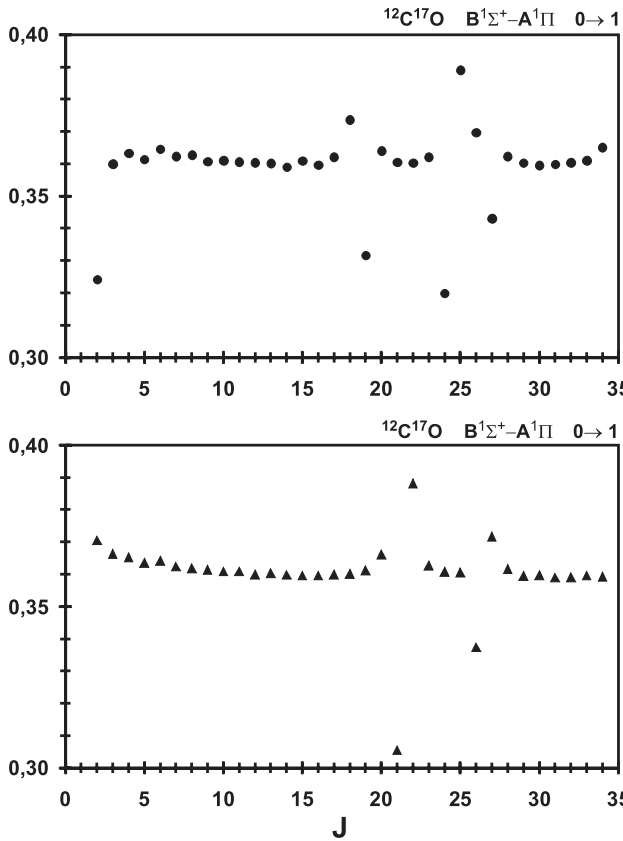
**Figure 3.** The values of rovibronic terms of the perturbed  $A^1\Pi$  ( $v = 1$  and  $2$ ) levels together with perturbing  $I^1\Sigma^-(v = 1-4)$ ,  $D^1\Delta(v = 1-3)$ ,  $e^3\Sigma^-(v = 2-4)$ ,  $a^3\Sigma^+(v = 10-12)$ ,  $d^3\Delta_i(v = 5-7)$ , and  $a^3\Pi_r(v = 11-13)$  levels in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue versus  $J(J+1)$ . Circles show the regions for which the strongest perturbations are expected.

perturbations, impossible to detect due to too big experimental errors amounting to  $\pm 0.79 \text{ cm}^{-1}$ . Hence, there is currently no experimental information concerning the perturbations for the A state in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue.

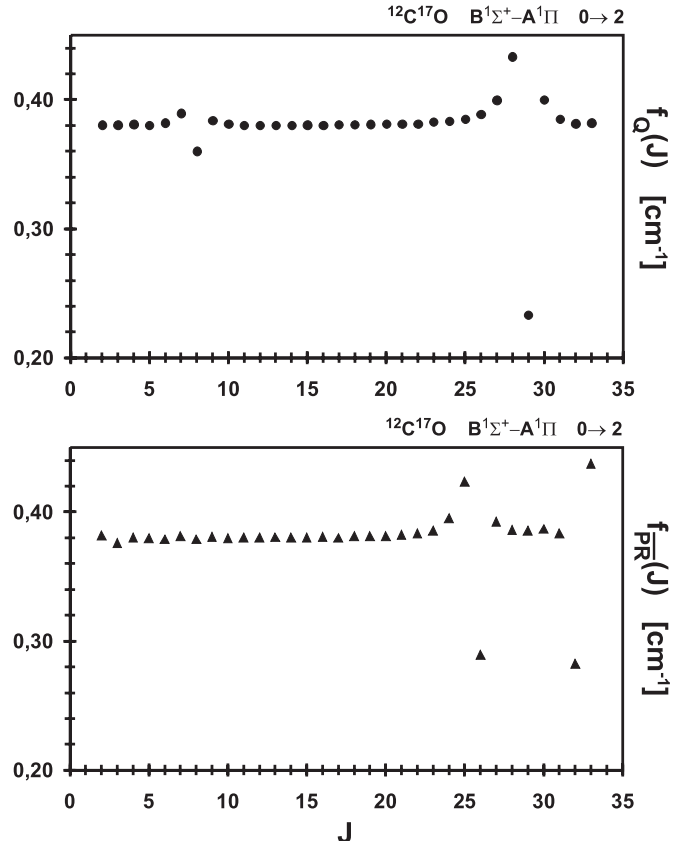
This work presents the results of the first observations and the identifications of perturbations in the  $A^1\Pi$  ( $v = 1$  and  $2$ ) levels of the natural and rare  $^{12}\text{C}^{17}\text{O}$  isotopologue.

To begin with, the positions of the predicted perturbations were estimated on the basis of the predicted rovibronic term crossing the diagram of the perturbing  $I^1\Sigma^-(v = 1-4)$ ,  $D^1\Delta(v = 1-3)$ ,  $e^3\Sigma^-(v = 2-4)$ ,  $a^3\Sigma^+(v = 10-12)$ ,  $a^3\Pi_r(v = 11-13)$ , and  $d^3\Delta_i(v = 5-7)$  states, together with the perturbed  $A^1\Pi(v = 1-2)$  state. The results are highlighted in figure 3. The points of intersection of these plots correspond to the regions for which the strongest perturbations are expected. The respective calculations were performed by making use of the rovibronic structure constants for the  $A^1\Pi$  in the range of  $v = 1-2$  and  $J = 1-40$  levels for the A, I, e, a', a and d states calculated by Field [78], and by means of the constants for the D state, calculated by Kittrell and Garetz [109] for the  $^{12}\text{C}^{16}\text{O}$  molecule and recalculated for the  $^{12}\text{C}^{17}\text{O}$  molecule by means of standard isotope relations.

Next, the places of occurrence of the observed perturbations were determined following the course of functions  $f_x(J)$  and  $g_x(J)$  (where  $x = Q$  and  $\overline{PR}$ ), as



**Figure 4.** The  $f_x(J)$  functions of Kovács [111], where  $x = Q$  or  $\overline{P}\overline{R}$ , for the 0–1 band of the  $B^1\Sigma^+ - A^1\Pi$  system in the  $^{12}\text{C}^{17}\text{O}$  isotopologue.



**Figure 5.** The  $f_x(J)$  functions of Kovács [111], where  $x = Q$  or  $\overline{P}\overline{R}$ , for the 0–2 band of the  $B^1\Sigma^+ - A^1\Pi$  system in the  $^{12}\text{C}^{17}\text{O}$  isotopologue.

introduced by Gerö [110] and Kovács [111]. In the case of this experiment, there is a negligible difference between the centrifugal distortion constants  $D'$  and  $D''$ , so  $f_x(J)$  and  $g_x(J)$  can be displayed simply as functions of  $J$ . The selected charts for the Ångström system in the  $^{12}\text{C}^{17}\text{O}$  isotopologue are shown in figures 4 and 6 as well as in figures 5 and 7 for the 0–1 and 0–2 bands, respectively. The deviations from the regularity of these functions indicated the appearance of some specific perturbation interactions and enabled the localization of the observed perturbation. The identifications of the perturbing states were made by the analyses of correlations between these residuals in the mentioned functions and the results of the calculations for the rovibronic term crossing diagram, presented in figure 3.

The perturbation occurrence in the rotational structure of the observed bands for both  $e$ - and  $f$ -parity levels can also be directly exhibited by a plot of the deviations of the observed (perturbed)  $T(v, J)_{\text{obs}}$  term values from those of the calculated (un-perturbed)  $T(v, J)_{\text{calc}}$  ones, versus the rotational quantum number  $J$ . Such plots for the  $A^1\Pi$  ( $v = 1$  and 2) levels of the rare  $^{12}\text{C}^{17}\text{O}$  molecule are highlighted in figure 8. The methods used to obtain both of these kinds of rotational term values were given in subsection 3.3. As one can see, strong discontinuities occur at different  $J$  values for each vibrational  $A^1\Pi$  level, more or less. These are characteristics of the observed irregularities. The comparison of the observed perturbations with the predicted ones for both  $\Lambda$ -doubling

components of the  $A^1\Pi$  state in the  $^{12}\text{C}^{17}\text{O}$  molecule can be found in table 4. There is a noticeable correspondence between figure 8 and table 4.

When analysing the 0–1 and 0–2 bands of the Ångström system ( $B^1\Sigma^+ - A^1\Pi$ ) in the  $^{12}\text{C}^{17}\text{O}$  isotopologue with respect to perturbations, we stated that the  $v' = 0$  vibrational level of the  $B^1\Sigma^+$  state in the molecule under consideration is quite regular up to the observed  $J_{\text{max}}$  rotational level.

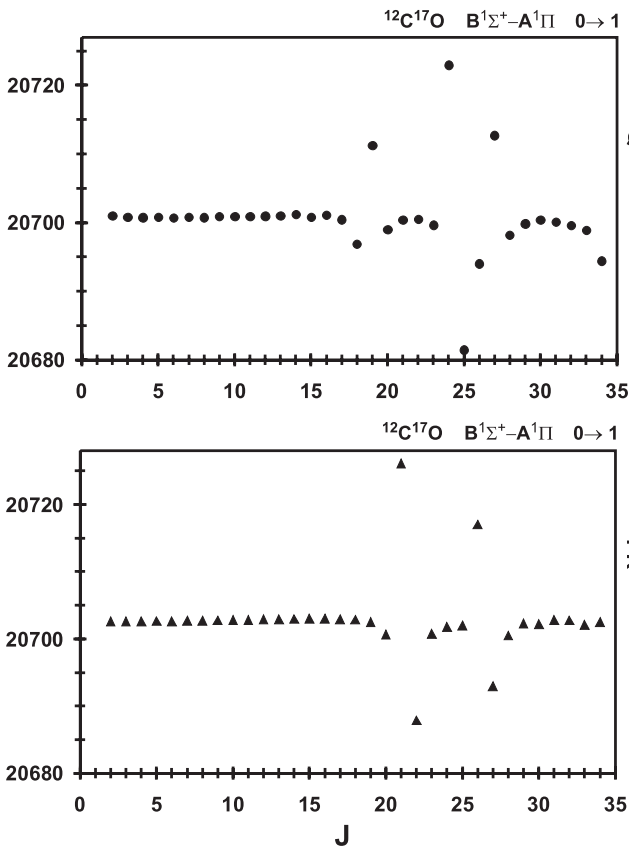
### 3.3. Molecular parameters

Due to the fact that the  $A^1\Pi$  ( $v'' = 1$  and 2) levels are widely and intensively perturbed, whereas the  $v' = 0$  level of the  $B^1\Sigma^+$  state is regular, further calculations were performed in stages and by means of several methods.

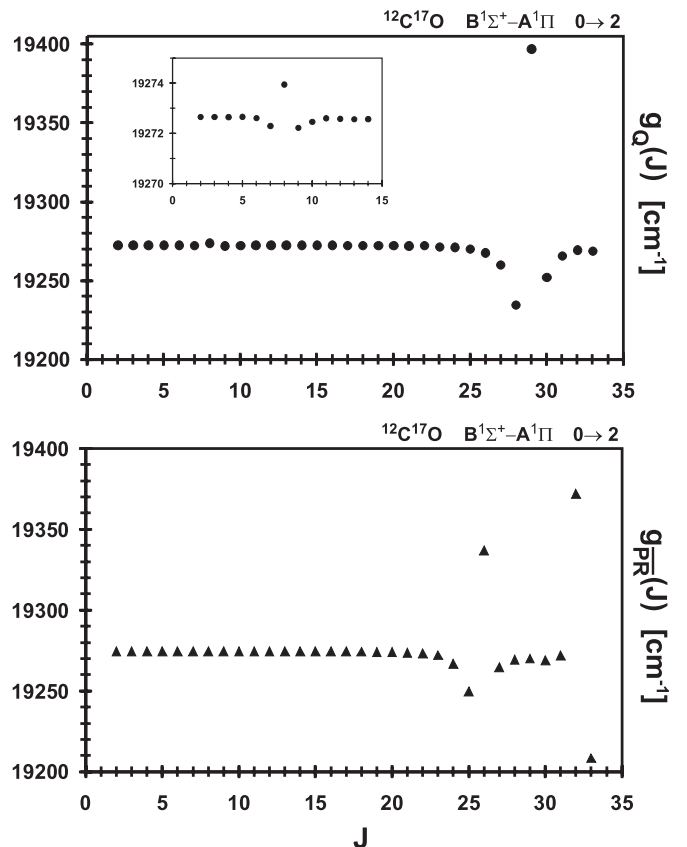
In the first stage the reduction of all calculated wavenumbers to rovibronic parameters was conducted within the framework of an individual band-by-band analysis, using the linear least-squares method proposed by Curl and Dane [112] and Watson [113]. This procedure makes it possible to separate molecular information about the  $B^1\Sigma^+$  ( $v' = 0$ ) upper state from that concerning the  $A^1\Pi$  ( $v'' = 1, 2$ ) lower state of the Ångström system. In the method under consideration, the  $B^1\Sigma^+$  state is represented by the effective Hamiltonian of Brown *et al* [114] (the widely known theoretical model, shown and described in our latest work [65]). The application of the method described above enabled us to obtain individual

**Table 4.** Observed and calculated perturbations of the  $A^1\Pi$  state of the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue. Asterisks indicate the regions unverified by the experiment.

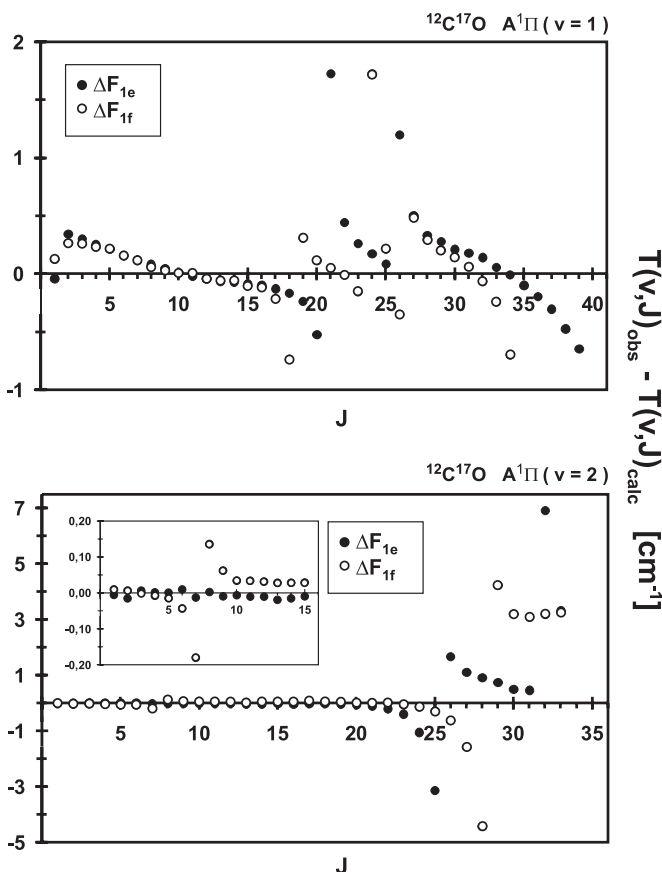
$A^1\Pi(v)$	Level crossing ( $J$ )				Perturbing state	
	$f$ -parity		$e$ -parity		Triplet component	Vibrational level
	Observed	Calculated	Observed	Calculated		
1	< 1	< 1	< 1	< 1	$F(3)$	$d^3\Delta_i(v=5)$
	< 1	< 1	< 1	< 1	$F(2)$	
	< 1	< 1	< 1	< 1	$F(1)$	
	18–19	18			$F(1)$	$a^3\Sigma^+(v=10)$
			20–21	21	$F(2)$	
	23–24	24			$F(3)$	
	26–27	26	26	26		$D^1\Delta(v=1)$
	*	35				$I^1\Sigma^-(v=2)$
			*	40–41	$F(1)$	$e^3\Sigma^-(v=3)$
	*	43–44			$F(2)$	
		*	46–47	$F(3)$		
2	7–8	7				$I^1\Sigma^-(v=3)$
			25–26	25	$F(1)$	$e^3\Sigma^-(v=4)$
	28–29	28			$F(2)$	
			30–31	31	$F(3)$	
	33–*	33–34	32–33	33–34	$F(3)$	$d^3\Delta_i(v=7)$
	*	37–38	*	37–38	$F(2)$	
	*	41–42	*	41–42	$F(1)$	
	*	38–39	*		$F(1)$	$a^3\Sigma^+(v=12)$
			*	41–42	$F(2)$	
	*	44–45			$F(3)$	



**Figure 6.** The  $g_x(J)$  functions of Kovács [111], where  $x = Q$  or  $\overline{PR}$ , for the 0–1 band of the  $B^1\Sigma^+ - A^1\Pi$  system in the  $^{12}\text{C}^{17}\text{O}$  isotopologue.



**Figure 7.** The  $g_x(J)$  functions of Kovács [111], where  $x = Q$  or  $\overline{PR}$ , for the 0–2 band of the  $B^1\Sigma^+ - A^1\Pi$  system in the  $^{12}\text{C}^{17}\text{O}$  isotopologue. The small graph presents the region where there is a relatively weaker perturbation.



**Figure 8.** The plot of deviations  $[T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}]$  of the  $A^1\Pi$  ( $v = 1$  and  $2$ ) rovibrational levels versus  $J$  in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue. The small graph presents the region where there is a relatively weaker perturbation.

**Table 5.** Individual and merged rotational constants of the  $B^1\Sigma^+$  Rydberg state in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue (in  $\text{cm}^{-1}$ ). Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

	Individual constant		Merged constant
	for 0–1 band	for 0–2 band	
$B_0$	1.898 877(12)	1.898 8840(93)	1.898 8823(41)
$D_0 \times 10^6$	6.4262(70)	6.4283(65)	6.4283(26)

molecular constants for the  $B^1\Sigma^+$  ( $v' = 0$ ) level as well as the real (perturbed)  $T(v, J)_{\text{obs}}$  term values for the  $v'' = 1, 2$  levels of the  $A^1\Pi$  state in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue.

The calculations of the final molecular parameters for the studied ( $v = 0$ ) level of the  $B^1\Sigma^+$  state in  $^{12}\text{C}^{17}\text{O}$  isotopologue were conducted at the second stage by the least-squares merge fit, proposed by Albritton *et al* [115] and Coxon [116]. All individual molecular constants of the  $B^1\Sigma^+$  obtained in this work have been applied. The estimated variances of the merging and the number of degrees of freedom were  $\sigma_M^2 = 0.32$  and  $f_M = 2$ , respectively; the results are shown in table 5.

At the third stage of the molecular parameter calculations the individual effective rotational constants for the lower  $A^1\Pi$  ( $v'' = 1$  and  $2$ ) state, as well as the band origins for the 0–1 and

**Table 6.** Rotational constants of the  $A^1\Pi$  state in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue (in  $\text{cm}^{-1}$ ). Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

Individual effective constant	$v = 1$ level	$v = 2$ level
$B_v$	1.540 88(12)	1.519 292(69)
$D_v \times 10^6$	6.950(87)	8.22(16)

**Table 7.** Band origins of the Ångström system in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue (in  $\text{cm}^{-1}$ ). Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

Band	0–1	0–2
Band origin	20 699.839(29)	19 271.1469(64)

0–2 bands of the  $B^1\Sigma^+ - A^1\Pi$  transition in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue, were obtained. In this case, both states under consideration were represented by the effective Hamiltonian of Brown *et al* [114]. As for the  $A^1\Pi$  state, this model was simplified to the version in which additional perturbing matrix elements were disregarded. Only the unperturbed lines as well as the well-determined values of the final molecular constants of the  $B^1\Sigma^+$  ( $v' = 0$ ) upper state were considered in the least-squares fit. The results are highlighted in tables 6 and 7. In the frame of the body of this fit, the calculated (un-perturbed)  $T(v, J)_{\text{calc}}$  rotational term values for the  $v'' = 1$  and  $v'' = 2$  levels of the  $A^1\Pi$  state were derived and used to plot the differences between the observed and calculated rovibrational term values (figure 8).

#### 4. Discussion and conclusions

This paper presents the first observation and analysis of the Ångström ( $B^1\Sigma^+ - A^1\Pi$ ) system in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue by means of high resolution spectroscopic methods. The molecular information regarding the high lying  $B^1\Sigma^+$  Rydberg state was obtained for the first time in the  $^{12}\text{C}^{17}\text{O}$ , which considerably extends our knowledge about Rydberg states in the carbon monoxide molecule.

The above analyses have indicated that the  $v' = 0$  vibrational level of the  $B^1\Sigma^+$  state in the molecule under consideration is quite regular up to the observed  $J_{\text{max}}$  rotational level. By contrast, the  $v'' = 1$  and  $2$  vibrational levels of the  $A^1\Pi$  state are extensively multi-state perturbed in the  $^{12}\text{C}^{17}\text{O}$ , as in other isotopomers of the CO molecule, which has been indicated in subsection 3.2. A careful investigation of the Kovács functions (figures 4–7) and the plot of the deviations of the  $T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}$  term values (figure 8) allowed us to confirm the occurrence of the greater part of the predicted rotational perturbations in the  $A^1\Pi$  ( $v = 1$  and  $2$ ) state. The respective  $J$  values in table 4 show (with one exception detailed below) the greater consistency of the observed perturbations and the expected ones.

By means of the experiment (reflected in figures 4, 6 and 8) and according to our theoretical calculations presented in figure 3, it was found that the  $A^1\Pi(v = 1)$  level is strongly



and multi-state affected by the  $d^3\Delta_i(v=5)$ ,  $a^3\Sigma^+(v=10)$ ,  $D^1\Delta(v=1)$ ,  $I^1\Sigma^-(v=2)$ , and  $e^3\Sigma^-(v=3)$  vibrational levels. The interaction originating from the  $d^3\Delta_i(v=5)$  state, with level crossings occurring at  $J < 1$  (for both  $e^-$  and  $f^-$ -parity levels), causes the term shifts at about  $0.5\text{ cm}^{-1}$ , which with certainty, substantially influenced both the value and the relatively lower precision of the calculation of the  $\sigma_{0-1}^{BA} = 20699.839(29)$  band origin in the  $^{12}\text{C}^{17}\text{O}$  isotopologue. Moreover, the  $a^3\Sigma^+(v=10)$  together with  $D^1\Delta(v=1)$  states caused the simultaneous interaction at  $J = 24\text{--}26$  of the  $f^-$ -parity levels, which causes the anomalous deviations of the term shifts, shown in figure 8. The largest magnitude of the term shifts occurs at  $J = 21$  for the  $e^-$ -parity levels, as well as at  $J = 24$  for the  $f^-$ -parity levels; it equals on average approximately  $1.5\text{--}2\text{ cm}^{-1}$  as a result of the interaction of the  $a^3\Sigma^+(v=10)$  as well as the  $D^1\Delta(v=1)$  along with the  $a^3\Sigma^+(v=10)$  perturbing levels, respectively. All of the observed perturbations in the  $A^1\Pi(v=1)$  state in the  $^{12}\text{C}^{17}\text{O}$  are in accordance with the theoretical predictions. The results are collected in table 4.

We have also shown experimentally (reflected in figures 5, 7 and 8) and theoretically (see figure 3) that the  $A^1\Pi(v=2)$  level in the  $^{12}\text{C}^{17}\text{O}$  isotopologue also has a strong interaction with the  $I^1\Sigma^-(v=3)$ ,  $e^3\Sigma^-(v=4)$ ,  $d^3\Delta_i(v=7)$ , and  $a^3\Sigma^+(v=12)$  vibrational levels. The  $e^3\Sigma^-(v=4)$  state, together with the  $d^3\Delta_i(v=7)$  state, caused the simultaneous perturbations at  $J = 32\text{--}33$  for the  $f^-$ -parity levels, which causes a non-characteristic rovibrational term shift, shown in figure 8. This multi-state interaction caused the largest magnitude (about  $7\text{ cm}^{-1}$ ) of the term shifts observed, exactly at  $J = 32$  for the  $e^-$ -parity levels. All of the observed perturbations in the  $A^1\Pi(v=2)$  state in the  $^{12}\text{C}^{17}\text{O}$  molecule are in accordance with the theoretical predictions in the frame of this work, except the multi-state crossing level at  $J = 32\text{--}33$  for the  $e^-$ -parity level. All results are collected in table 4.

In conclusion, we believe that the first observations and rotational analysis of the Ångström ( $B^1\Sigma^+ - A^1\Pi$ ) band system in the rare  $^{12}\text{C}^{17}\text{O}$  isotopologue significantly extend and improve the spectroscopic and quantum-mechanical information about the energetic structure of the CO molecule as a whole.

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## References

- [1] Hall D N B 1973 *Astrophys. J.* **182** 977
- [2] Encrenaz P J, Wannier P G, Jefferts K B, Penzias A A and Wilson R W 1973 *Astrophys. J.* **186** L77
- [3] Wannier P G, Lucas R, Linke R A, Encrenaz P J, Penzias A A and Wilson R W 1975 *Astrophys. J.* **205** L169
- [4] Frerking M A and Langer W D 1981 *J. Chem. Phys.* **74** 6990
- [5] Frerking M A, Langer W D and Wilson R W 1982 *Astrophys. J.* **262** 590
- [6] Dame T M, Hartmann D and Thaddeus P 2001 *Astrophys. J.* **547** 792
- [7] Bensch F, Park I, Wouterloot J G A, Klapper G and Winnewisser G 2001 *Astrophys. J.* **562** L185
- [8] Ladd E F 2004 *Astrophys. J.* **610** 320
- [9] Lellouch E, Moreno R and Paubert G 2005 *Astron. Astrophys.* **430** L37
- [10] Lupu R E, Feldman P D, Weaver H A and Tozzi G P 2007 *Astrophys. J.* **670** 1473
- [11] Jewitt D, Garland C A and Aussel H 2008 *Astron. J.* **135** 400
- [12] Rho J, Jarrett T H, Reach W T, Gomez H and Andersen M 2009 *Astrophys. J.* **693** L693
- [13] Martín S, George M R, Wilner D J and Espada D 2010 *Astron. J.* **139** 2241
- [14] Weaver H A, Feldman P D, A'Hearn M F, Dello Russo N and Stern S A 2011 *Astrophys. J.* **734** L5
- [15] Visscher C and Moses J I 2011 *Astrophys. J.* **738** 72
- [16] Schindhelm E, France K, Burgh E B, Herczeg G J, Green J C, Brown A, Brown J M and Valenti J A 2012 *Astrophys. J.* **746** 97
- [17] Rho J, Onaka T, Cami J and Reach W T 2012 *Astrophys. J.* **747** L6
- [18] Rodler F, Lopez-Morales M and Ribas I 2012 *Astrophys. J.* **753** L25
- [19] Balser D S, McMullin J P and Wilson T L 2002 *Astrophys. J.* **572** 326
- [20] Farrenq R, Guelachvili G, Sauval A J, Grevesse N and Farmer C B 1991 *J. Mol. Spectrosc.* **149** 375
- [21] Klopotek P and Vidal C R 1985 *J. Opt. Soc. Am. B* **2** 869
- [22] Rottke H and Zacharias H 1985 *Opt. Commun.* **55** 87
- [23] Keça R 1986 *Chem. Phys.* **110** 123
- [24] Amiot C, Roncin J-Y and Verges J 1986 *J. Phys. B: At. Mol. Phys.* **19** 19
- [25] Eidelsberg M, Roncin J-Y, Le Floch A, Launay F, Letzelter C and Rostas J 1987 *J. Mol. Spectrosc.* **121** 309
- [26] Masaki T, Adachi Y and Hirose C 1987 *Chem. Phys. Lett.* **139** 62
- [27] Sekine S, Adachi Y and Hirose C 1989 *J. Chem. Phys.* **90** 5346
- [28] Hart D J and Bourne O L 1989 *Chem. Phys.* **133** 103
- [29] Tjossem P J H and Smyth K C 1989 *J. Chem. Phys.* **91** 2041
- [30] Choe J-I, Lee D-K, Le Floch A C and Kukolich S G 1989 *J. Mol. Spectrosc.* **136** 173
- [31] Sekine S, Iwata S and Hirose C 1991 *Chem. Phys. Lett.* **180** 173
- [32] Kanik I, Ratliff M and Trajmar S 1993 *Chem. Phys. Lett.* **208** 341
- [33] Sekine S and Hirose C 1993 *Chem. Phys. Lett.* **212** 129
- [34] Roncin J-Y, Ross A and Boursey E 1993 *J. Mol. Spectrosc.* **162** 353
- [35] Baker J 1994 *J. Mol. Spectrosc.* **167** 323
- [36] Baker J 1995 *J. Chem. Phys.* **102** 3956
- [37] Komatsu M, Ebata T, Maeyama T and Mikami N 1995 *J. Chem. Phys.* **103** 2420
- [38] Hasegawa H and Tsukiyama K 1996 *Appl. Phys. B: Laser Opt.* **63** 311
- [39] Drabbels M, ter Meulen J J and Meerts W L 1997 *Chem. Phys. Lett.* **267** 127
- [40] Di Teodoro F, Rehm J E, Farrow R L and Paul P H 2000 *J. Chem. Phys.* **113** 3046
- [41] Sakoda A, Mutoh H and Tsukiyama K 2001 *Appl. Phys. B* **72** 411
- [42] Katayanagi H, Matsumoto Y, de Lange C A, Tsubouchi M and Suzuki T 2003 *J. Chem. Phys.* **119** 3737
- [43] Eidelsberg M, Sheffer Y, Federman S R, Lemaire J L, Fillion J H, Rostas F and Ruiz J 2006 *Astrophys. J.* **647** 1543
- [44] Eidelsberg M, Launay F, Ito K, Matsui T, Hinnen P C, Reinhold E, Ubachs W and Huber K P 2004 *J. Chem. Phys.* **121** 292
- [45] Eidelsberg M et al 2012 *Astron. Astrophys.* **543** A69

- [46] Malak Z, Rytel M, Janjić J and Pešić D S 1984 *Acta Phys. Hung.* **55** 85
- [47] Domin J, Domin U, Malak Z and Rytel M 1984 *Acta Phys. Hung.* **55** 165
- [48] Kępa R 1986 *Acta Phys. Hung.* **60** 227
- [49] Danielak J, Domin J, Domin U and Rytel M 1987 *J. Mol. Spectrosc.* **125** 251
- [50] Kępa R, Para A, Rytel M and Janjić J 1990 *Acta Phys. Hung.* **68** 205
- [51] Prasad C V V and Reddy S P 1988 *J. Mol. Spectrosc.* **130** 62
- [52] Haridass C, Reddy S P and LeFloch A C 1994 *J. Mol. Spectrosc.* **168** 429
- [53] Ångström A J and Thalén T R 1875 *Nova Acta R. Soc. Sci. Ups.* **3** 9
- [54] Danielak J, Kępa R, Ojczyk K and Rytel M 1971 *Acta Phys. Pol. A* **39** 29
- [55] Kępa R and Rytel M 1970 *Acta Phys. Pol. A* **37** 585
- [56] Le Floch A C and Amiot C 1985 *Chem. Phys.* **97** 379
- [57] Kępa R and Rytel M 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 3355
- [58] Rytel M 1970 *Acta Phys. Pol. A* **37** 559
- [59] Janjić J, Danielak J, Kępa R and Rytel M 1972 *Acta Phys. Pol. A* **41** 757
- [60] Kępa R, Domin U and Porada K 2003 *Acta Phys. Pol. A* **103** 441
- [61] Hakalla R, Szajna W, Zachwieja M and Kępa R 2012 *Acta Phys. Pol. A* at press
- [62] Kępa R, Rytel M, Janjić J D and Pešić D S 1972 *Acta Phys. Pol. A* **41** 377
- [63] Prasad C V V, Bhale G L and Reddy S P 1984 *J. Mol. Spectrosc.* **104** 165
- [64] Kępa R 1994 *Acta Phys. Hung.* **74** 319
- [65] Hakalla R and Zachwieja M 2012 *J. Mol. Spectrosc.* **272** 11
- [66] Palmer B A and Engleman R 1983 *Atlas of the Thorium Spectrum Los Alamos National Laboratory* (Los Alamos, NM: unpublished)
- [67] Bacis R 1976 *J. Phys. E: Sci. Instrum.* **9** 1081
- [68] Szajna W and Zachwieja M 2009 *Eur. Phys. J. D* **55** 549
- [69] Szajna W and Zachwieja M 2010 *J. Mol. Spectrosc.* **260** 130
- [70] Szajna W, Zachwieja M, Hakalla R and Kępa R 2011 *Acta Phys. Pol. A* **120** 417
- [71] Szajna W and Zachwieja M 2011 *J. Mol. Spectrosc.* **269** 56
- [72] Zachwieja M, Szajna W and Hakalla R 2012 *J. Mol. Spectrosc.* **275** 53
- [73] Dunham J L 1932 *Phys. Rev.* **41** 721
- [74] Brown J M, Colbourn E A, Watson J K G and Wayne F D 1979 *J. Mol. Spectrosc.* **74** 294
- [75] Krupenie P H 1966 *The Band Spectrum of Carbon Monoxide* (Washington, DC: National Bureau of Standards)
- [76] Simmons J D, Bass A M and Tilford S G 1969 *Astrophys. J.* **155** 345
- [77] Kępa R 1969 *Acta Phys. Pol. A* **36** 1109
- [78] Field R W 1971 *PhD Thesis* Harvard University, Cambridge, MA
- [79] Field R W, Wicke B G, Simmons J D and Tilford S G 1972 *J. Mol. Spectrosc.* **44** 383
- [80] Burnham R L, Isler R C and Wells W C 1972 *Phys. Rev. A* **6** 1327
- [81] Klopotek P and Vidal C R 1984 *Can. J. Phys.* **62** 1426
- [82] Le Floch A C, Launay F, Rostas J, Field R W, Brown C M and Yoshino K 1987 *J. Mol. Spectrosc.* **121** 337 and references therein
- [83] Le Floch A C, Rostas J and Schamps J 1988 *Mol. Phys.* **63** 677
- [84] Kępa R 1989 *J. Mol. Spectrosc.* **135** 119
- [85] Le Floch A C 1989 *PhD Thesis* University Paris-Sud, Orsay, France
- [86] Hallstadius H and Lundberg H 1989 *Phys. Scr.* **40** 652
- [87] Le Floch A C 1992 *J. Mol. Spectrosc.* **155** 177
- [88] Stark G, Lewis B R, Gibson S T and England J P 1998 *Astrophys. J.* **505** 452
- [89] Zetner P W, Kanik I and Trajmar S 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2395
- [90] Jolly A, Lemaire J L, Belle-Oudry D, Edwards S, Malmasson D, Vient A and Rostas F 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 4315
- [91] Sykora T and Vidal C R 1998 *J. Chem. Phys.* **108** 6320
- [92] Borges I, Caridade P J S B and Varandas A J C 2001 *J. Mol. Spectrosc.* **209** 24
- [93] Sun M, Liu J, Sun W, Chen X, Jiang B and Sha G 2002 *Chem. Phys. Lett.* **365** 244
- [94] Cyrul B, Darlak K and Domin J 2003 *Proc. SPIE* **5125** 345
- [95] Liu J, Sun M, Jiang B and Sha G 2004 *Chem. Phys. Lett.* **388** 306
- [96] Du Plessis A, Rohwer E G and Steenkamp C M 2007 *J. Mol. Spectrosc.* **243** 124
- [97] Bartels N, Schfer T, Hhnert J, Field R W and Wodtke A M 2012 *J. Chem. Phys.* **136** 214201
- [98] Kępa R 1978 *Acta Phys. Hung.* **45** 133
- [99] Kępa R, Rzeszut Z and Rytel M 1978 *Acta Phys. Pol. A* **54** 355
- [100] Kępa R 1982 *Acta Phys. Pol. A* **62** 467
- [101] Prasad C V V, Reddy S P and Sandys-Wunsch M 1985 *J. Mol. Spectrosc.* **114** 436
- [102] Kępa R 1988 *J. Mol. Spectrosc.* **132** 545
- [103] Haridass C, Reddy S P and LeFloch A C 1994 *J. Mol. Spectrosc.* **167** 334
- [104] Kępa R, Jarosz M, Kocan A, Piotrowska-Domagala I and Porada K 1998 *Acta Phys. Hung.* **8** 207
- [105] Steinmann C M, Rohwer E G and Stafast H 2003 *Astrophys. J.* **590** L123
- [106] Domin J, Fran M and Ploskon B 2004 *Proc. SPIE* **5484** 346
- [107] Plessis A, Rohwer E G and Steenkamp C M 2006 *Astrophys. J. Suppl.* **165** 432
- [108] Kępa R, Ostrowska-Kopeć M and Piotrowska I 2011 *J. Mol. Spectrosc.* **266** 104
- [109] Kittrell C and Garetz B A 1989 *Spectrochim. Acta A* **45** 31
- [110] Gerö L 1935 *Z. Phys.* **93** 669
- [111] Kovács I 1969 *Rotational Structure in the Spectra of Diatomic Molecules* (London: Hilger)
- [112] Curl R F and Dane C B 1988 *J. Mol. Spectrosc.* **128** 406
- [113] Watson J K G 1989 *J. Mol. Spectrosc.* **138** 302
- [114] Brown J M, Colbourn E A, Watson J K G and Wayne F D 1979 *J. Mol. Spectrosc.* **74** 294
- [115] Albritton D L, Schmeltekopf A L and Zare R N 1977 *J. Mol. Spectrosc.* **67** 132
- [116] Coxon J A 1978 *J. Mol. Spectrosc.* **72** 252