

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/258057501>

First Analysis of the $1 - v''$ Progression of the Ångström (B(1) Σ^+ –A(1) Π) Band System in the Rare (13)C(17)O Isotopologue.

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · OCTOBER 2013

Impact Factor: 2.69 · DOI: 10.1021/jp4077239 · Source: PubMed

CITATIONS

4

READS

27

3 AUTHORS, INCLUDING:



Rafal Hakalla

Rzeszów University

20 PUBLICATIONS 68 CITATIONS

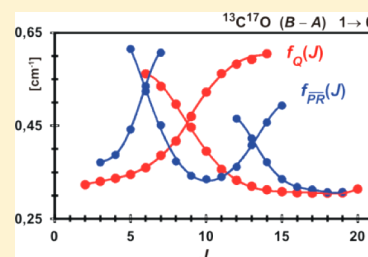
SEE PROFILE

First Analysis of the $1-v''$ Progression of the Ångström ($B^1\Sigma^+-A^1\Pi$) Band System in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue

Rafał Hakalla,* Mirosław Zachwieja, and Wojciech Szajna

Materials Spectroscopy Laboratory, Center for Innovation and Transfer of Engineering and Natural Science Knowledge, University of Rzeszów, 35-959 Rzeszów, Poland

ABSTRACT: The $1-v''$ progression of the Ångström band system, so far unobserved in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue, was obtained under high resolution as an emission spectrum using a high accuracy dispersive optical spectroscopy. In the studied region 22 700–24 500 cm^{-1} , 146 spectral lines were observed, among which 118 were interpreted as belonging to the $1-0$ and $1-1$ bands of $B-A$ system, and the next 28 were interpreted as extra lines belonging to the $1-1$ band of $B^1\Sigma^+-e^3\Sigma^-$ intercombination system, also unobserved in the $^{13}\text{C}^{17}\text{O}$ molecule so far. All those lines were precisely measured with an estimated accuracy better than 0.0025 cm^{-1} , and rotationally analyzed. As a result the following in the $^{13}\text{C}^{17}\text{O}$ molecule were calculated for the first time: the merged rotational constants $B_1 = 1.790\,227(23)\text{ cm}^{-1}$, $D_1 = 6.233(47) \times 10^{-6}\text{ cm}^{-1}$, and $\Delta G_{1/2} = 2010.9622(69)\text{ cm}^{-1}$ and the equilibrium constants, $\omega_e = 2076.04(57)\text{ cm}^{-1}$, $\omega_e x_e = 32.54(28)\text{ cm}^{-1}$, $B_e = 1.824\,678(15)\text{ cm}^{-1}$, $\alpha_e = 2.2967(24) \times 10^{-2}\text{ cm}^{-1}$, $D_e = 5.226(25) \times 10^{-6}\text{ cm}^{-1}$, and $\beta_e = 6.71(48) \times 10^{-7}\text{ cm}^{-1}$ for the $B^1\Sigma^+$ Rydberg state, as well as the individual rotational constant $B_0 = 1.504\,85(78)\text{ cm}^{-1}$, and the equilibrium constants $\omega_e = 1463.340(21)\text{ cm}^{-1}$, $B_e = 1.499\,02(12)\text{ cm}^{-1}$, $\alpha_e = 1.778\,2(49) \times 10^{-2}\text{ cm}^{-1}$, $D_e = 7.36(56) \times 10^{-6}\text{ cm}^{-1}$ for the $A^1\Pi$ state, and $\sigma_e = 21\,854.015(51)\text{ cm}^{-1}$, RKR turning points, Franck–Condon factors (FCF), relative intensities, and r centroids for the Ångström band system. With the help of the strong and vast $A^1\Pi(v=0) \sim e^3\Sigma^-(v=1)$ interaction, the experimental parameters of the $e^3\Sigma^-(v=1)$ perturbing state were established in the $^{13}\text{C}^{17}\text{O}$ molecule for the first time.



1. INTRODUCTION

It is true that the carbon monoxide molecule plays an important role in astrophysical research on outer space because of its widespread occurrence in cosmic space. From this respect only molecular hydrogen outweighs it. Carbon monoxide has been discovered in comet tails, interstellar space, planets, solar and stellar atmospheres, the solar spectrum and in the spectra of different cosmic objects.^{1–18} Isotopologues of the CO are very often used as tracers to determine the hydrogen-containing molecular clouds, to map the distribution of matter.^{19–22} Special significance is attached to the discovery and quantification of different natural isotopologues of the CO molecule to model the evolution of stars and interstellar clouds.²³ The spectrum of the Sun recorded at high resolution with the ATMOS infrared Fourier transform interferometer, indicates the presence of all natural isotopes of the CO molecule, including a most rare one, that is, $^{13}\text{C}^{17}\text{O}$.²⁴

The CO molecule is also important in other branches of science, including research on chemical physics, microbiology, molecular biology, environment of Earth, technology of new materials, metallurgy, engineering processes, etc.^{25–40} Due to this fact, it is an important and open issue to thoroughly and comprehensively study all natural isotopologues of the CO molecule to derive precise values of quantum-mechanical parameters and molecular constants of all excited states of the molecule under consideration. In this respect, high resolution spectroscopy based on a high accuracy dispersive

optical method is very useful. This method was applied to obtain results described in the frame of the present work.

The $B^1\Sigma^+$ Rydberg state, taking part in different rovibronic transitions within the energetic structure of carbon monoxide, has been the subject of preliminary and more advanced experimental analyses in the ordinary $^{12}\text{C}^{16}\text{O}$ molecule, using conventional as well as laser methods.^{41–65} Far fewer experimental studies have been carried out taking into account this state in other CO isotopologues.^{45,63,66–72} The above-mentioned publications also indicate that only the $v=0, 1$ vibrational levels are involved in emission from the $B^1\Sigma^+$ state, whereas, the remaining existing vibrational levels take part only in absorption transitions: $B^1\Sigma^+(v=2)$,⁴⁵ $B^1\Sigma^+(v=3)$,⁵⁵ together with the recently analyzed $B^1\Sigma^+(v=6)$ state, recorded in the $6-0$ band of the transition from the $X^1\Sigma^+$ ground state of the following isotopologues: $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{13}\text{C}^{18}\text{O}$ by Eidelsberg et al.⁶³ As regards the analysis of $B^1\Sigma^+$ state in the very rare $^{12}\text{C}^{17}\text{O}$ and $^{13}\text{C}^{17}\text{O}$ isotopologues, pioneering and experimental works have been recently published by Hakalla et al.⁷³ for the $^{13}\text{C}^{17}\text{O}$ molecule and by Hakalla et al.⁷⁴ for the $^{12}\text{C}^{17}\text{O}$ molecule.

The $B^1\Sigma^+-A^1\Pi$ band system was the subject of many studies for the $^{12}\text{C}^{16}\text{O}$ molecule beginning with its discovery by Ångström,⁷⁵ as well as in other works.^{76–79} Far fewer

Received: August 2, 2013

Revised: October 18, 2013

Published: October 21, 2013



discoveries accompanied this system in other isotopologues of the CO molecule, such as: $^{12}\text{C}^{18}\text{O}$,^{68,80} $^{13}\text{C}^{16}\text{O}$,^{81–83} $^{13}\text{C}^{18}\text{O}$,^{66,84,85} $^{14}\text{C}^{16}\text{O}$,^{67,86} and $^{14}\text{C}^{18}\text{O}$.⁶⁸ However, when it comes to the studies that concern this system in the rarest, natural isotopologues of carbon monoxide, there are only those conducted by Hakalla et al.⁷⁴ and by Hakalla et al.⁷³ for the $^{12}\text{C}^{17}\text{O}$ and $^{13}\text{C}^{17}\text{O}$ molecules, respectively. Both works have been based on the analysis of the 0– ν'' progression of B–A system. However, the 1– ν'' progression of the Ångström ($\text{B}^1\Sigma^+ - \text{A}^1\Pi$) band system has not been so far observed in any of those rare isotopologues of the CO molecule.

In this work we present a comprehensive description of the experiment and quantum-mechanical analyses on the 1– ν'' progression of the Ångström ($\text{B}^1\Sigma^+ - \text{A}^1\Pi$) system in the rarest molecule among all natural and stable isotopologues of the CO molecule, that is, in $^{13}\text{C}^{17}\text{O}$.

II. EXPERIMENT

The experimental details are almost the same as described in our previous paper,⁷³ so some parts of this work have been included with the consent of Elsevier License (number 3198791136656).

As the emission spectra sources of the B–A band system in the $^{13}\text{C}^{17}\text{O}$ molecule, like in the earlier work on this system in our laboratory,⁷³ the water-cooled, hollow-cathode lamp with two anodes was used.⁸⁷ It was initially filled with a mixture of helium and acetylene $^{13}\text{C}_2\text{D}_2$ (99.98% purity of ^{13}C) under pressure of about 6 Torr plus 1 Torr of the helium. Next an electric current was run through the mixture for about 100 h. After formation of satisfactory amount of carbon ^{13}C on the electrodes, the lamp was pumped out and into this space molecular oxygen was placed in, including 70% of the $^{17}\text{O}_2$ isotope, as nonflowing gas under pressure of about 2 Torr. At this time the electrodes worked live with 2×650 V, and the direct current flowing through the mixture was 2×35 mA. Such conditions were tested and recognized as optimal for obtaining the most intense 1–0 and 1–1 bands of the 1– ν'' progression of the Ångström system in the rare $^{13}\text{C}^{17}\text{O}$ molecule.

The measurement system that enables us to obtain and record emission spectra using methods of high accuracy dispersive optical spectroscopy has been built in our laboratory in recent years^{73,74,83,88–92} (Figure 1). In those publications the conditions of its calibration were precisely described. The molecular spectra were observed in $m = 6$ and 5 order, respectively, for 1–0 and 1–1 bands of the Ångström system in the $^{13}\text{C}^{17}\text{O}$ molecule by means of a 2 m Ebert plane grating PGS-2 spectrograph equipped with 651 grooves/mm grating with a total of 45 600 grooves, blazed at $1.0 \mu\text{m}$. The reciprocal dispersion was in the range of 0.07–0.11 nm/mm, and the theoretical resolving power was approximately 273 000 and 228 000 for the 1–0 and 1–1 bands, respectively.

The spectrum of the CO molecule was recorded by means of a photomultiplier tube (HAMAMATSU R943-02) on a linear stage (HIWIN KK5002) along the focal curve of the spectrograph. The input and exit slit were $35 \mu\text{m}$ in width. The intensity of lines was measured by means of photon counting (HAMAMATSU C3866 photon counting unit and M8784 photon counting board) with a counter gate time of 500 ms (no dead time between the gates). The position of the exit slit was measured by means of a He–Ne laser interferometer (LASERTEX) synchronized with the photon

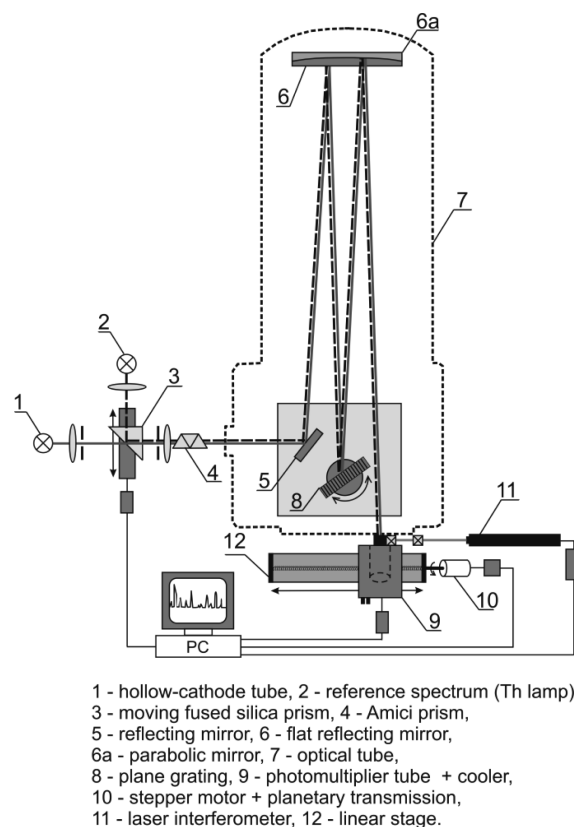


Figure 1. Experimental setup (Elsevier license no. 3198790976666).

counting board. During one exposure of the counter gate, the position was measured 64 times and mean value with the number of counts were transmitted to a PC as a measurement point.

The optical alignment of the CO and Th reference lamps were corrected to obtain the same light distribution along the exit slit. The repeatability of the line position measurements was measured to be 0.2–0.5 μm , according to variations in atmospheric pressure. The atomic spectrum of thorium was used as a calibration spectrum⁹³ obtained from a few overlapping orders received in the water cooled hollow-cathode tube with the cathode lined with thin Th foil.

The positions of peaks of spectral lines were calculated by means of a least-squares procedure assuming a Gaussian line-shape for each spectral contour (30 points per line), with an uncertainty of the peak position for a single line of approximately 0.1–0.2 μm . To calculate the wavenumbers of the CO molecule, fifth- and sixth-order interpolation polynomials were used for the 1–0 and 1–1 bands, respectively. The typical standard deviation of the least-squares fit for the 20–30 calibration lines was approximately 0.0015–0.0017 cm^{-1} . The calibration procedure was tested (with two Th lamps simultaneously: one as an examination light source and the second one to provide the reference spectrum) to be $\pm 0.0015 \text{ cm}^{-1}$. The spectral widths of strong and isolated lines of the CO was 0.15 cm^{-1} and their maximum signal-to-noise ratio amounted to about 60:1 and 70:1 for the 1–0 and 1–1 bands of the B–A system for the $^{13}\text{C}^{17}\text{O}$ isotopologue, respectively. The most intense lines produce count rates of the order of 8 000 photons/s for 1–0 band and 10 000 photons/s for 1–1 band.

Table 3. Observed Wavenumbers and Their Rotational Assignments for the 1–1 Band of the Ångström ($B^1\Sigma^+-A^1\Pi$) Band System in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

J	$P_{11ec}(J)$		$Q_{11ef}(J)$		$R_{11ec}(J)$	
1	22734.9945	<i>c</i>	22738.5346	(0)	22745.7343	(0)
2	22732.8002	(6)	22739.7552	(0)	22750.7005	(−5)
3	22731.2289	(5)	22741.7116	(0)	22756.2889	(−4)
4	22730.2725	(−3)	22744.3408	(0)	22762.4925	(3)
5	22729.9734	(−4)	22747.6461	(0)	22769.3507	(4)
6	22730.2725	(3)	22751.6279	(0)	22776.8039	(−3)
7	22731.2289	<i>c</i>	22756.1842	(0)	22784.9101	(0)
8	22732.8002	(−9)	22761.3376	(0)	22793.6387	(9)
9	22734.9945	(5)	22767.1413	(0)	22802.9790	(−6)
10	22737.8182	(0)	22773.5475	(0)	22812.9444	<i>c</i>
11	22741.2568	(6)	22780.5719	(0)	22823.5297	(−6)
12	22745.3620	<i>c</i>	22788.2375	(0)	22834.7690	(0)
13	22750.0588	(0)	22796.5364	(0)	22846.6130	<i>c</i>
14	22755.4190	(−11)	22805.4712	(0)	22859.1017	(10)
15	22761.4135	(6)	22815.0387	(0)	22872.2201	(−6)
16	22768.0439	(−7)	22825.2076	(0)	22885.9756	(7)
17	22775.3228	(15)	22836.0402	(0)	22900.3678	(−15)
18	22783.2229	(0)	22847.5075	(0)		
19	22791.7560	(0)	22859.5994	(0)		
20	22800.9285	(0)	22872.3288	(0)		
21			22885.6859	(0)		

^aIn cm^{-1} , values in parentheses denote observed minus calculated values in units of 10^{-4} cm^{-1} . ^cThe less accurate lines not used in the evaluation of individual rotational constants of the states under consideration.

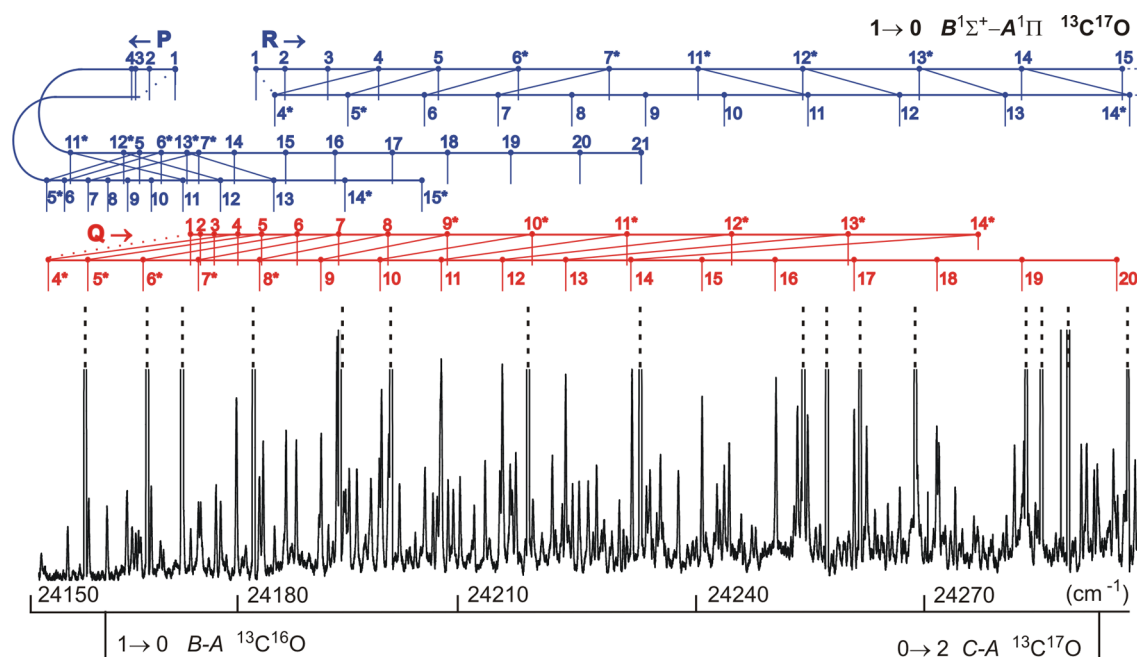


Figure 2. Expanded view of the 1–0 band of the Ångström ($B^1\Sigma^+-A^1\Pi$) system in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue together with the rotational assignments. The dotted lines indicate the tips of the relatively very strong Th calibration lines. The band-head regions of the less intense 1–0 band of the Ångström ($B^1\Sigma^+-A^1\Pi$) system in the $^{13}\text{C}^{16}\text{O}$ molecule and for the first time recorded in molecule $^{13}\text{C}^{17}\text{O}$ the part of the (0–2) band of the Herzberg ($C^1\Sigma^+-A^1\Pi$) system are indicated at the bottom of the figure. An asterisk indicates extra lines belonging to the 1–1 band of the ($B^1\Sigma^+-e^3\Sigma^-$) intercombination system, which is the result of the strong interaction $A^1\Pi (\nu = 0) \sim e^3\Sigma^- (\nu = 1)$.

on further interpretation process. For the same purpose, we also carried out the preliminary and partial rotational interpretation of the region of the 0–2 band head of the Herzberg (C–A) system in the $^{13}\text{C}^{17}\text{O}$ molecule. We also evaluated rotational molecular constants for the upper and lower states of the Ångström system in the $^{13}\text{C}^{17}\text{O}$ molecule on the basis of the data provided by Kępa⁷⁹ for the $^{12}\text{C}^{16}\text{O}$

molecule by means of the Dunham's isotopic relationship. The appropriate formulas were given by Dunham⁹⁵ and Brown et al.⁹⁶ On this basis, theoretical values of wavenumbers of the bands lines, which interest us, were calculated. Then, we carried out the preliminary assignment of rotational quantum numbers of the lines belonging to the 1–0 and 1–1 bands of the examined system in the $^{13}\text{C}^{17}\text{O}$ molecule, and assigned them to

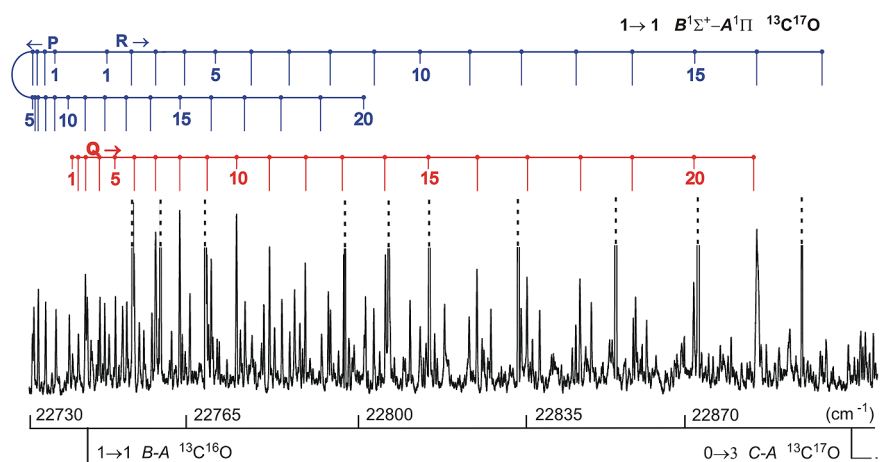


Figure 3. Expanded view of the 1–1 band of the Ångström ($B^1\Sigma^+ - A^1\Pi$) system in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue together with the rotational interpretation. The dotted lines indicate the tips of the relatively very strong Th calibration lines. The band-head regions of the less intense 1–1 band of the Ångström ($B^1\Sigma^+ - A^1\Pi$) system in the $^{13}\text{C}^{16}\text{O}$ molecule and for the first time recorded in molecule $^{13}\text{C}^{17}\text{O}$ the part of the (0–3) band of the Herzberg ($C^1\Sigma^+ - A^1\Pi$) system are indicated at the bottom of the figure.

the correct branch: P, Q, or R. Some of the lines were interpreted as extra lines belonging to the $B^1\Sigma^+(\nu = 1) - e^3\Sigma^-(\nu = 1)$ transition. The extra lines brought relevant information on the $e^3\Sigma^-$ state, so far unobserved for the rare $^{13}\text{C}^{17}\text{O}$ molecule.

The method of a final verification of the correctness of the examined bands interpretation was described in the next section. A high quality, expanded view of the 1–0 and 1–1 bands of the Ångström (B–A) system in $^{13}\text{C}^{17}\text{O}$ molecule together with the rotational interpretation is presented in Figures 2 and 3, respectively.

IV. ANALYSIS AND RESULTS

Due to the strong and vast perturbation (described in detail in section V) appearing in the $A^1\Pi$ state (especially in the $\nu = 0$ vibrational level) reduction of the wavenumbers of the examined molecular lines of the 1–0 and 1–1 bands of the B–A system in the $^{13}\text{C}^{17}\text{O}$ molecule to rovibronic parameters was carried out by means of an individual band-by-band analysis, using the linear least-squares method proposed by Curl and Dane⁹⁷ and Watson.⁹⁸ This method allowed us to separate molecular information about the regular $B^1\Sigma^+(\nu = 1)$ upper state from the one that concerned the strongly perturbed $A^1\Pi(\nu = 0, 1)$ lower state of the Ångström system. In this method the $B^1\Sigma^+$ state was represented by the effective Hamiltonian proposed by Brown et al.⁹⁶ (a widely known theoretical model, shown and described in our previous work⁷³). This procedure allowed us to obtain two series of individual rotational molecular constants for the $B^1\Sigma^+(\nu = 1)$ state, received from separate fits of the 1–0 and 1–1 bands of the Ångström system in the $^{13}\text{C}^{17}\text{O}$ molecule. During this procedure we also obtained real (perturbed) $T(\nu; j)_{\text{obs}}$ term values for the ($\nu = 0, 1$) vibrational levels of the $A^1\Pi$ state in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue.

The calculation of the final rotational molecular constants of the $B^1\Sigma^+$ state in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue was carried out by means of the least-squares merge fit method proposed by Albritton et al.⁹⁹ and Coxon¹⁰⁰ with the use of the 1–0 and 1–1 bands, analyzed in this work. The estimated variance of the merging and the numbers of degrees of freedom were $\sigma_M^2 = 0.94$ and $f_M = 2$, respectively. Constants of the $B^1\Sigma^+$ state for the $^{13}\text{C}^{17}\text{O}$ molecule were obtained for the first time. The results are shown in Table 4.

Table 4. Molecular Constants of the $B^1\Sigma^+$ Rydberg State in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

$B^1\Sigma^+$	individual constant		merged constant
	from 1 to 0 band	from 1 to 1 band	
B_1	1.790 216 (42)	1.790 238 (27)	1.790 227 (23)
$10^6 D_1$	6.181 (79)	6.271 (58)	6.233 (47)

^aIn cm^{-1} , 1σ in parentheses.

Next, the individual rotational constants of the strongly perturbed $A^1\Pi(\nu = 0, 1)$ lower state and the 1–0 and 1–1 band origins of the Ångström system in the rare $^{13}\text{C}^{17}\text{O}$ molecule were calculated by means of the linear least-squares method, in which both states taking part in transitions were represented by the effective Hamiltonian of Brown et al.⁹⁶ However, for the perturbed $A^1\Pi$ state, this model was simplified to the version in which additional perturbing matrix elements were disregarded and only the wavenumbers of regular spectral lines were used in this fit by means of the computer program described by Bembenek et al.¹⁰¹ Therefore, molecular constants obtained in this way for the $A^1\Pi$ state are effective ones. Those constants for the ($\nu = 0$) vibrational level of $A^1\Pi$ state in the rare $^{13}\text{C}^{17}\text{O}$ molecule are presented for the first time. During this fit, constants of the regular $B^1\Sigma^+(\nu = 1)$ upper state were constrained to the very precise and well described, merged molecular constants, calculated in the previous stage. The results are presented in Table 5. The band origins of the 1–0 and 1–1 bands of the B–A system, unknown so far in the $^{13}\text{C}^{17}\text{O}$ molecule, are presented in Table 6. During this

Table 5. Molecular Constants of the $A^1\Pi(\nu = 0)$ State in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

$A^1\Pi$	individual effective constant
B_0	1.504 85 (78)
$D_0 \times 10^6$	7.52 ^b

^aIn cm^{-1} , 1σ in parentheses. ^bObtained from the deperturbed molecular constants of the $^{12}\text{C}^{16}\text{O}$ molecule given by Field¹⁰² by using standard isotope relations and constrained during the evaluation of the individual effective molecular constants to determine the rotational constants B_0 with greater precision.

procedure the unperturbed $T(v;J)_{\text{calc}}$ term values of the $A^1\Pi$ ($v = 0$, and 1) state were also calculated.

Table 6. Band Origins of the Ångström ($B^1\Sigma^+ - A^1\Pi$) System in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

band	band origin
1–0	24 172.57 (15)
1–1	22 737.0306 (79)

^aIn cm^{-1} , 1 σ in parentheses.

The rotational equilibrium constants in the rare $^{13}\text{C}^{17}\text{O}$ molecule were determined for both the $B^1\Sigma^+$ and $A^1\Pi$ states in this work for the first time. Those calculations were made by means of the weighted least-squares method on the basis of the merged rovibronic constant values, determined in this work and in the work of Hakalla et al.,⁷³ assuming their traditionally recognized polynomial dependence on the vibrational quantum number.

Calculating the rotational equilibrium constants for the $A^1\Pi$ state, highly precise, deperturbed rotational constants of this state were used, given by Field et al.¹⁰² for the $^{12}\text{C}^{16}\text{O}$ molecule (recalculated by means of the standard isotopic relations to the examined $^{13}\text{C}^{17}\text{O}$ molecule, and constrained in the calculation giving the final equilibrium constants). The results are highlighted in Table 7.

Similarly, the vibrational equilibrium constants in the rare $^{13}\text{C}^{17}\text{O}$ molecule were determined for both the $B^1\Sigma^+$ and $A^1\Pi$ states in this work for the first time. To determine the vibrational equilibrium constants with a higher precision, the quantum $\Delta G_{1/2}$ for the regular $B^1\Sigma^+$ state was obtained by

Table 7. Equilibrium Molecular Constants of the $B^1\Sigma^+$ and $A^1\Pi$ States in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

constant	state	
	$B^1\Sigma^+$	$A^1\Pi$
σ_e	21 854.015 (51)	
ω_e	2076.04 (57) ^b	1463.340 (21)
$\omega_e x_e$	32.54 (28) ^b	16.46 ^c
$10^2 \omega_y$		2.24 ^c
B_e	1.824 678 (15)	1.499 02 (12)
$10^2 \alpha_e$	2.2967 (24)	1.7782 (49)
$10^3 \gamma_e$		−0.8684 ^d
$10^4 e_e$		2.255 ^d
$10^3 \eta_e$		−4.426 ^d
$10^6 Y_{51}$		4.359 ^d
$10^7 Y_{61}$		−2.434 ^d
$10^9 Y_{71}$		7.183 ^d
$10^{11} Y_{81}$		−8.773 ^d
$10^6 D_e$	5.226 (25)	7.36 (56)
$10^7 \beta_e$	6.71 (48)	1.27 ^e

^aIn cm^{-1} , 1 σ in parentheses. ^bThe value calculated on the basis of the derived $\Delta G_{1/2}$ vibrational quantum for the $^{13}\text{C}^{17}\text{O}$ molecule and all its already known values for other isotopologues of the CO. ^cThe value calculated from the $^{12}\text{C}^{16}\text{O}$ parameters of Kępa et al.¹³⁷ using the isotopic relationship within the Born–Oppenheimer approximation. ^dThe value calculated from the $^{12}\text{C}^{16}\text{O}$ parameters of Field¹⁰² using the isotopic relationship within the Born–Oppenheimer approximation. ^eThe value calculated from the $^{12}\text{C}^{16}\text{O}$ parameters of Kępa et al.¹¹³ using the isotopic relationship within the Born–Oppenheimer approximation.

solving equations based on the classic McKellar and Jenkins formulas,¹⁰³ and its value is

$$\Delta G_{1/2} = 2010.9622(69) \text{ cm}^{-1}$$

(As a result of this calculation, the following was also obtained: $B_0 - B_1 = 2.339 (36) \times 10^{-2} \text{ cm}^{-1}$.)

Next, on the basis of the derived $\Delta G_{1/2}$ value for the $B^1\Sigma^+$ state and using all of its already known values for the $^{12}\text{C}^{16}\text{O}$,⁷⁹ $^{13}\text{C}^{16}\text{O}$,⁸² $^{12}\text{C}^{18}\text{O}$,¹⁴ $^{14}\text{C}^{16}\text{O}$,¹³ $^{13}\text{C}^{18}\text{O}$,⁶⁶ and $^{14}\text{C}^{18}\text{O}$ ⁶⁹ isotopologues, by means of the weighted least-squares method, the ω_e and $\omega_e x_e$ constants for the $B^1\Sigma^+$ Rydberg state were calculated. Additional vibrational data published by Kępa et al.¹³⁷ in the $A^1\Pi$ state of $^{13}\text{C}^{16}\text{O}$, recalculated by means of the standard isotopic relations to the $^{13}\text{C}^{17}\text{O}$ molecule, were used. These values were constrained in the calculation of the rest of the vibrational equilibrium parameters. The results are presented in Table 7.

Because only the ($v = 0$)⁷³ and ($v = 1$) (this work) vibrational levels of the $B^1\Sigma^+$ state have been observed so far in the $^{13}\text{C}^{17}\text{O}$ molecule, the rotational equilibrium constants for this state were determined from a fit of the data in which the number of data equal the number of determined parameters. In that case standard deviations of equilibrium parameters were calculated by means of the Gauss error propagation method.

However, due to insufficient amount of experimental data and strong, multistate perturbations of the $A^1\Pi$ state, we did not manage to determine satisfactorily $\omega_e x_e$ equilibrium vibrational constants of the $A^1\Pi$ state. Also, due to predissociation appearing in the $B^1\Sigma^+$ state between the ($v = 1$) and ($v = 2$) vibrational levels, which dramatically shortens the $1-v''$ progression bands of the Ångström system, we were not able to satisfactorily determine the β_e centrifugal equilibrium rotational constant for the $A^1\Pi$ state.

The equilibrium constants included in Table 7 were then used to determine the RKR turning points, Y_{00} Dunham's factor, and zero point energy for the $B^1\Sigma^+$ as well as for the $A^1\Pi$ states for the first time in the rare $^{13}\text{C}^{17}\text{O}$ molecule. The results of these calculations are presented in Table 8. Also, for the first time for the $^{13}\text{C}^{17}\text{O}$ molecule, the Franck–Condon factors, relative intensities, and r centroids of the Ångström band system were determined and are presented in Table 9.

V. PERTURBATIONS IN THE ÅNGSTRÖM BAND SYSTEM FOR THE RARE $^{13}\text{C}^{17}\text{O}$ ISOTOPOLOGUE

A. Perturbations in the $A^1\Pi$ State. The $A^1\Pi$ singlet state in the CO molecule belongs to the most intensely and the most extensively perturbed electronic states among all electronic states of all known diatomic molecules. As the $A^1\Pi$ state is located in the 66 000 cm^{-1} region, there are no fewer than six other electronic states in its vicinity, which interact with it, that is, $1^1\Sigma^-$, $D^1\Delta$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $a^3\Pi_r$, and $d^3\Delta_r$.

The perturbations of the rotational structure are observed practically for each vibrational level of the $A^1\Pi$ state. The perturbations of the state under consideration in the $^{12}\text{C}^{16}\text{O}$ principal isotopologue were analyzed and described many times.^{41,50,59,61,76–79,102–126} Systematic classification of the perturbations appearing in this state in the $^{12}\text{C}^{16}\text{O}$ molecule was carried out by Krupenie.¹⁰⁵ Simmons et al.¹⁰⁶ made a critical analysis of this study as well as completed it. A conclusive analysis and deperturbational calculations for the $A^1\Pi$ state in the ordinary $^{12}\text{C}^{16}\text{O}$ molecule were carried out by Field et al.^{102,108} LeFloch et al.¹¹¹ conducted a comprehensive

Table 8. Vibrational Levels and RKR Turning Points of the $B^1\Sigma^+$ and $A^1\Pi$ States in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

vibrational level		$B^1\Sigma^+$	$A^1\Pi$
		$Y_{00} = -2.9025$	$Y_{00} = -0.9307$
	r_e	1.119 820 (5)	1.235 470 (49)
$\nu = 0$	$G(\nu) + Y_{00}$	1029.8850	727.5270
	r_{\min}	1.07597	1.18309
	r_{\max}	1.17035	1.29539
$\nu = 1$	$G(\nu) + Y_{00}$	3040.8450	2157.8095
	r_{\min}	1.04706	1.14882
	r_{\max}	1.21291	1.34529
$\nu = 2$	$G(\nu) + Y_{00}$	4986.7250 ^b	3555.2471
	r_{\min}	1.02841 ^b	1.12707
	r_{\max}	1.24554 ^b	1.38321
$\nu = 3$	$G(\nu) + Y_{00}$		4920.0440 ^c
	r_{\min}		1.11039 ^c
	r_{\max}		1.41648 ^c

^a $G(\nu)$ and Y_{00} are in cm^{-1} . All r values are in Å. ^bValues determined theoretically for the ($\nu = 2$) vibrational level of the $B^1\Sigma^+$ state, unobserved so far in the $^{13}\text{C}^{17}\text{O}$ molecule. ^cValues determined theoretically for the ($\nu = 3$) vibrational level of the $A^1\Pi$ state, unobserved so far in the $^{13}\text{C}^{17}\text{O}$ molecule.

Table 9. Franck–Condon Factors, Relative Intensities, and r Centroids for the Ångström ($B^1\Sigma^+ - A^1\Pi$) Band System in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

$A^1\Pi (\nu)$	$B^1\Sigma^+(\nu)$		
	0	1	2 ^b
0	8.1137×10^{-2}	0.2378	0.3122
	3.4669	10.0000	10.0000
	1.1839	1.2117	1.2404
1	0.1760	0.1810	1.3866×10^{-2}
	7.8011	7.1618	0.4199
	1.1640	1.1892	1.2026
2	0.2127	3.5599×10^{-2}	5.9497×10^{-2}
	10.0000	1.3866	1.7003
	1.1455	1.1672	1.2019
3 ^c	0.1898	3.1065×10^{-3}	0.1126
	9.4197	0.1284	3.0304
	1.1280	1.1637	1.1787

^aThe values represented in sequence one under the other stand for the Franck–Condon factor, relative intensities (in (energy/S) scaled to 10), and r centroids (in Å) for each band. ^bValues determined theoretically for the ($\nu = 2$) vibrational level of the $B^1\Sigma^+$ state, unobserved so far in the $^{13}\text{C}^{17}\text{O}$ molecule. ^cValues determined theoretically for the ($\nu = 3$) vibrational level of the $A^1\Pi$ state, unobserved so far in the $^{13}\text{C}^{17}\text{O}$ molecule.

study of perturbations emerging at the lowest ($\nu = 0$) vibrational level of the $A^1\Pi$ state. In his next work, LeFloch¹¹⁴ analyzed perturbations emerging at the ($\nu = 0-4$) level of the state under consideration of the $^{12}\text{C}^{16}\text{O}$ molecule. Ultimately,

LeFloch¹¹⁶ calculated very precise values of the terms for the $A^1\Pi$ ($\nu = 0-8$) state in the molecule under consideration.

Far fewer studies on the $A^1\Pi$ state have been carried out in other isotopologues of the CO molecule.^{66-73,80-86,107,125,127-137} What is worth noticing is the fact that observations and analyses of the perturbations of the $A^1\Pi$ state in isotopologues of the CO molecule allow confirmation of the accuracy of the previous theoretical analyses and verification of the quality of determined molecular constants of interacting states.

The first theoretical and experimental analysis of the perturbation of the $A^1\Pi$ state in the rarest natural and stable isotopologue of the CO molecule, that is, in the $^{13}\text{C}^{17}\text{O}$ molecule, has been recently carried out by Hakalla et al.⁷³ (perturbations appearing in $\nu = 1$ and 2). However, the present study shows for the first time for the $^{13}\text{C}^{17}\text{O}$ isotopologue the results of studies on perturbations of the $A^1\Pi$ ($\nu = 0$) vibrational level. It also presents the reanalysis of perturbations appearing in the ($\nu = 1$) vibrational level of the $A^1\Pi$ state, which confirms previous studies.⁷³

At the outset of the analysis concerning the perturbations mentioned above, their prevalence areas were theoretically calculated. It was performed by means of the rovibronic term crossing diagram of $I^1\Sigma^-$ ($\nu = 0-2$), $D^1\Delta$ ($\nu = 0-1$), $e^3\Sigma^-$ ($\nu = 1-3$), $a'^3\Sigma^+$ ($\nu = 9-11$), $a^3\Pi_r$ ($\nu = 11-12$), and $d^3\Delta_r$ ($\nu = 4-6$) states, together with the $A^1\Pi$ ($\nu = 0, 1$) state. The results are shown in Figure 4. Appropriate calculations were made on the basis of molecular constants of rovibronic structure of the $A^1\Pi$

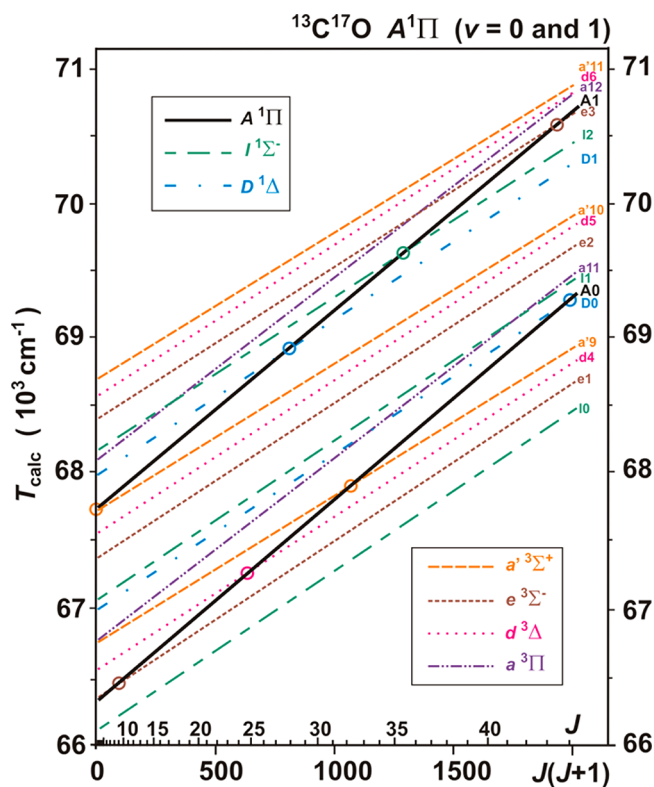


Figure 4. Rovibronic term crossing diagram of the perturbed $A^1\Pi$ ($\nu = 0, 1$) levels together with $I^1\Sigma^-$ ($\nu = 0-2$), $D^1\Delta$ ($\nu = 0-1$), $e^3\Sigma^-$ ($\nu = 1-3$), $a'^3\Sigma^+$ ($\nu = 9-11$), $a^3\Pi_r$ ($\nu = 11-12$), and $d^3\Delta_r$ ($\nu = 4-6$) states in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue. Points of intersection (marked by circles) correspond to the regions for which the strongest perturbations are expected. Compare this figure with Table 10.

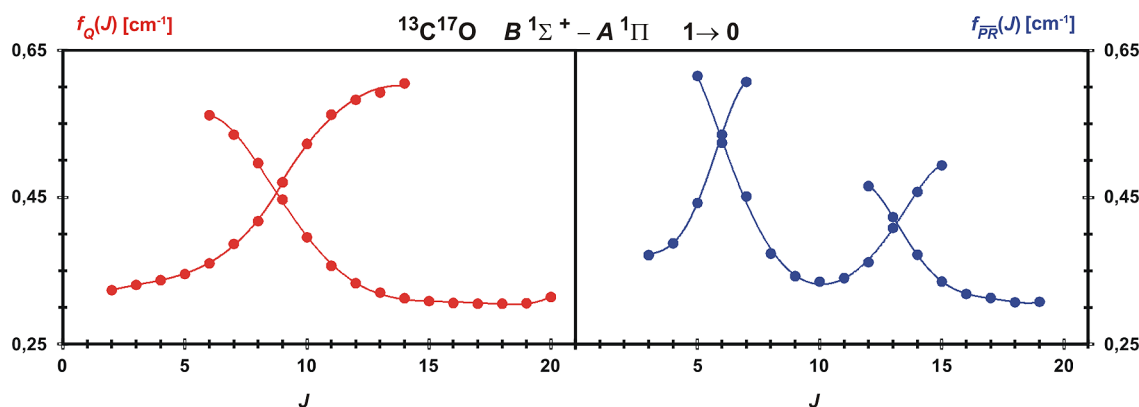


Figure 5. Perturbation in the $\nu = 0$ level of the $A^1\Pi$ state in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue illustrated by the $f_x(J)$ functions of Kovács,¹⁴⁰ where $x = Q$ or $\overline{P}\overline{R}$, plotted for the 1–0 band of the Ångström system. The reason for the appearance of additional curves is a strong rotational interaction between the $A^1\Pi$ ($\nu = 0$) and $e^3\Sigma^-$ ($\nu = 1$) states, which leads to the emergence of extra lines (see section VB and Table 2 with the description).

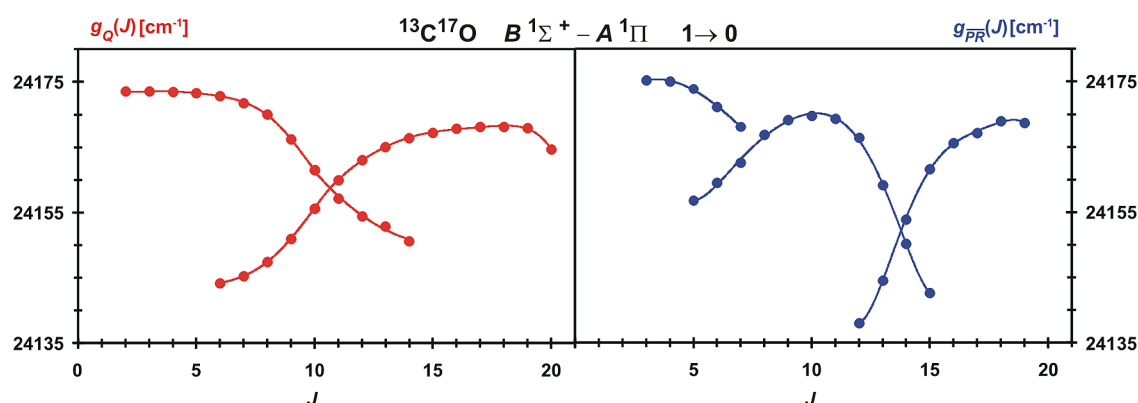


Figure 6. Perturbation in the $\nu = 0$ level of the $A^1\Pi$ state in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue illustrated by the $g_x(J)$ functions of Kovács,¹⁴⁰ where $x = Q$ or $\overline{P}\overline{R}$, plotted for the 1–0 band of the Ångström system. The reason for the appearance of additional curves is a strong rotational interaction between the $A^1\Pi$ ($\nu = 0$) and $e^3\Sigma^-$ ($\nu = 1$) states, which leads to the emergence of extra lines (see section VB and Table 2 with the description).

($\nu = 0$, and 1; $J = 0$ –40) state, determined in this work and in the work of Hakalla et al.⁷³ for the $^{13}\text{C}^{17}\text{O}$ molecule, as well as on the basis of constants of the I, D, e, a', a, d states, calculated by Field,¹⁰² and for the D state, calculated by Kittrell and Garetz¹³⁸ in the $^{12}\text{C}^{16}\text{O}$ molecule, and recalculated to the $^{13}\text{C}^{17}\text{O}$ molecule by means of standard isotopic relations.

The experimental classification and analysis of the observed perturbation of the $A^1\Pi$ ($\nu = 0, 1$) state, on the basis of wavenumbers of the $1-\nu''$ progression bands of the Ångström system in the $^{13}\text{C}^{17}\text{O}$ molecule, were carried out by means of $f_x(J)$ and $g_x(J)$ functions (where $x = Q$ and $\overline{P}\overline{R}$), as introduced by Gerö¹³⁹ and Kovács.¹⁴⁰ Detailed description of their properties and applications was presented in our previous work.⁷³ Figures 5 and 6 as well as Figures 7 and 8 present

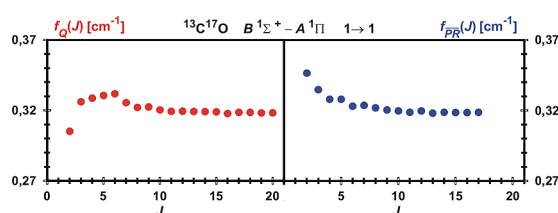


Figure 7. Perturbation in the $\nu = 1$ level of the $A^1\Pi$ state in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue illustrated by the $f_x(J)$ functions of Kovács,¹⁴⁰ where $x = Q$ or $\overline{P}\overline{R}$, plotted for the 1–1 band of the Ångström system.

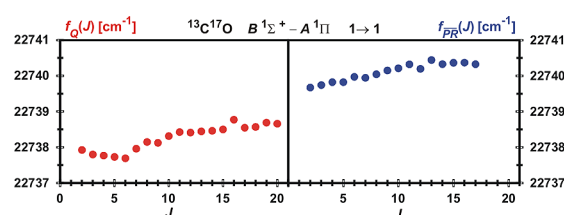


Figure 8. Perturbation in the $\nu = 1$ level of the $A^1\Pi$ state in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue illustrated by the $g_x(J)$ functions of Kovács,¹⁴⁰ where $x = Q$ or $\overline{P}\overline{R}$, plotted for the 1–1 band of the Ångström system.

functions: $f_Q(J)$ with $f_{\overline{P}\overline{R}}(J)$ and $g_Q(J)$ with $g_{\overline{P}\overline{R}}(J)$, for the $\nu = 0$ and 1 vibrational levels, respectively. Uncertainties of single measurements are negligibly small in the scales used in these graphs.

Identification of the perturbing states was conducted on the basis of relations displayed in Figures 5 and 6, and in Figures 7 and 8, as well as on the basis of the results of calculations presented in the rovibronic term crossing diagram in Figure 4. Already at this stage, one can observe close correspondence between the results received in this work for the $A^1\Pi$ ($\nu = 1$) state (Figures 7 and 8) on the basis of the (1–1) band, and the results obtained for the same vibrational level, which were reported by Hakalla et al.⁷³ (Figures 4 and 6) on the basis of the (0–1) band. This correspondence confirms the correctness

of interpretation and analysis performed in the $A^1\Pi$ ($\nu = 1$) state in the $J \leq 20$ range.

The occurrence and quantity of perturbations appearing in the rotational structure of the observed bands, for both the e and f components of the Λ -doubling, can be directly determined by means of a plot of the deviations of the observed (perturbed) $T(\nu, J)_{\text{obs}}$ term values from those of the calculated (unperturbed) $T(\nu, J)_{\text{calc}}$ ones, versus the rotational quantum number J . In Figure 9 we presented the results of the

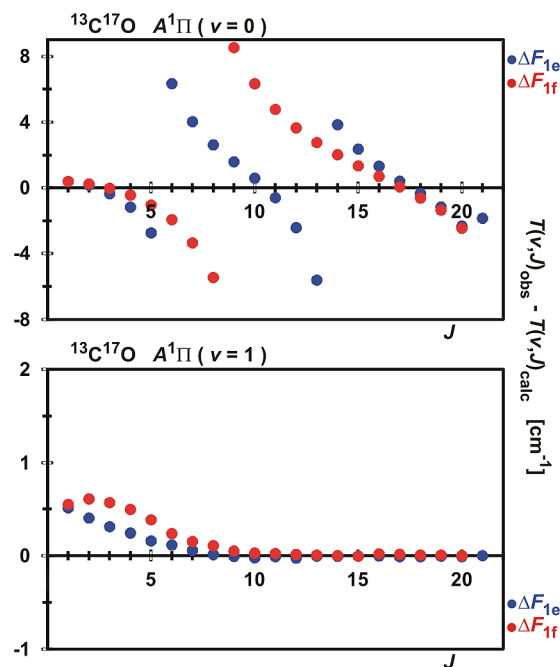


Figure 9. Differences between the observed and calculated term values of the $A^1\Pi$ ($\nu = 0$ and 1) rovibrational levels in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue.

rotational structure of both the $A^1\Pi$ ($\nu = 0$) vibrational level, not analyzed so far in the $^{13}\text{C}^{17}\text{O}$ molecule, and the reanalyzed $A^1\Pi$ ($\nu = 1$) state. Term values were calculated by means of the method described in section IV of this paper. As we can notice, there are extensive and strong rotational discontinuities in the structure of rotational terms of the $A^1\Pi$ ($\nu = 0$) vibrational level. The strongest perturbations fall on the $J = 5-6$ and $J = 13-14$ regions for the e component, and on the $J = 8-9$ region for the f component, and the values amount to about 6 and 9 cm^{-1} , respectively. Those perturbations are caused by a closely lying $e^3\Sigma^-$ electronic state (Figure 4). There are not many regular lines of the (1-0) band of B-A system of the $^{13}\text{C}^{17}\text{O}$ molecule (only about 17). Hence, serious difficulties arise in obtaining satisfactory effective rotational constants of the $A^1\Pi$ ($\nu = 0$) state. Comparison of the perturbations, observed in the $A^1\Pi$ ($\nu = 0$) state, with those that we predicted theoretically in the $^{13}\text{C}^{17}\text{O}$ molecule for both components of the Λ -doubling was presented in Table 10. On the basis of this table, it is worth noting that there is overall correspondence between experimental and theoretical results, with an exception of the perturbation of the e component of the $A^1\Pi$ ($\nu = 0$) caused by the $e^3\Sigma^-$ ($\nu = 1$) state, whose experimental maximum falls on $J = 13-14$.

B. The $e^3\Sigma^-$ State in the Rare $^{13}\text{C}^{17}\text{O}$ Molecule. As one can notice in Figure 2 showing the emission spectrum of the (1-0) band of the Ångström system for the $^{13}\text{C}^{17}\text{O}$ molecule,

Table 10. Observed and Predicted Perturbations of the $A^1\Pi$ ($\nu = 0$) State in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue

maximum perturbation (J) of the Λ -doubling component				perturbing state	
f		e			
obs	calc	obs	calc	triplet component	vibrational level
8-9	7-8	5-6	4-5	$F(1)$	$e^3\Sigma^-$ ($\nu = 1$)
		13-14	10-11	$F(2)$	
				$F(3)$	
a	20-21	a	20-21	$F(3)$	$d^3\Delta_i$ ($\nu = 4$)
a	24-25	a	24-25	$F(2)$	
a	28-29	a	28-29	$F(1)$	
a	29-30			$F(1)$	$a'^3\Sigma^+$ ($\nu = 9$)
		a	32-33	$F(2)$	
a	35-36			$F(3)$	

^aThe regions unverified by the experiment.

and also in Figures 5 and 6 presenting functions $f_Q(J)$ with $f_{\overline{P}\overline{R}}(J)$ and $g_Q(J)$ with $g_{\overline{P}\overline{R}}(J)$ of this band, the authors of this work have observed numerous extra lines appearing in the $J = 9$ region for the f component, as well as in the $J = 6$ and 14 regions for the e component of Λ -doubling. They result from rovibronic emission transitions from the regular $B^1\Sigma^+(\nu = 1)$ state to the state that strongly perturbs the lower $A^1\Pi$ ($\nu = 0$) state of the Ångström system in the $^{13}\text{C}^{17}\text{O}$ molecule. Theoretical calculations made in this work (represented in Figure 4 and Table 10), verified by our experiment (Figures 2, 5, and 6 and Table 10) show that the $e^3\Sigma^-$ ($\nu = 1$) state is this perturber in the molecule under consideration. The $F_{1e}(J)$ and $F_{3e}(J)$ components of the $e^3\Sigma^-$ ($\nu = 1$) state are the cause of perturbations emerging in the $P_{11ee}(J)$ and $R_{11ee}(J)$ branches, and the $F_{2f}(J)$ component of the $e^3\Sigma^-$ ($\nu = 1$) state perturbs the regularity of the $Q_{11ef}(J)$ branch of the $B^1\Sigma^+ - A^1\Pi$ transition.

Calculations of molecular constants of the perturbing state were performed by means of the methods described by Kovács,¹⁴⁰ which make use of the $f_x(J)$ and $g_x(J)$ functions, where $x = Q$ and $\overline{P}\overline{R}$. The analysis by means of the $f_x(J)$ function for the (1-0) band of the $B^1\Sigma^+ - A^1\Pi$ band system in the $^{13}\text{C}^{17}\text{O}$ molecule made it possible to obtain the rotational constant value for the $e^3\Sigma^-$ ($\nu = 1$) state in this molecule for the first time: $B_1^{e^3\Sigma^-} = 1.1582$ (31) cm^{-1} . This constant, however, is not satisfactory because it is not compatible with the value received by means of standard isotopic relations, which is based on the deperturbed rotational constant of the $e^3\Sigma^-$ ($\nu = 1$) state in the ordinary $^{12}\text{C}^{16}\text{O}$ molecule, published by Field.¹⁰² The reason for this is the extremely extensive, strong and complex perturbation, discussed here, which causes dramatic limitation of regular molecular lines of the (1-0) band of the B-A system in the $^{13}\text{C}^{17}\text{O}$ molecule, and by this leads to reduced accuracy of determining effective rotational constant $B_0 = 1.504$ 85 (78) cm^{-1} of the $A^1\Pi$ perturbed state, which is a component of the calculations. To check the accuracy of determining values of other quantities involved in the calculation of the $B_1^{e^3\Sigma^-}$ constant, in this method we used, instead of our effective constant B_0 of the $A^1\Pi$ ($\nu = 0$) state, the deperturbed one given

by Field¹⁰² for $^{12}\text{C}^{16}\text{O}$ and recalculated for the $^{13}\text{C}^{17}\text{O}$ molecule by means of standard isotopic relations. And here is the final result:

$$B_1^{e^3\Sigma^-} = 1.1698(31) \text{ cm}^{-1}$$

This result is compatible with both values assessed theoretically by means of standard isotopic relations on the basis of the data given by Field¹⁰² as well as by Tilford and Simmons¹⁴¹ for the $^{12}\text{C}^{16}\text{O}$ molecule.

The results of this comparison were presented in Table 11. This proved that the remaining values used in Kovács's

Table 11. Molecular Constants of the $e^3\Sigma^-$ State Derived from Analysis of the $A^1\Pi$ ($\nu = 0$) $\sim e^3\Sigma^-$ ($\nu = 1$) Perturbation in the Rare $^{13}\text{C}^{17}\text{O}$ Isotopologue^a

constant	this work	calculated ^b	calculated ^c
$B_1^{e^3\Sigma^-}$	1.1698 (31)	1.17066	1.171077
$(\nu_0)_{11}^{B^1\Sigma^+-e^3\Sigma^-}$	24 144.72 (30)	24 145.83	24 145.71

^aIn cm^{-1} , 1σ in parentheses. ^bValues determined by means of standard isotopic relation on the basis of the data concerning the $^{12}\text{C}^{16}\text{O}$ molecule, published by Field.¹⁰² To calculate the theoretical band origin, equilibrium vibrational constants of the $B^1\Sigma^+$ state (calculated in this work) were also used. ^cThe value determined on the basis of the data concerning the $^{12}\text{C}^{16}\text{O}$ molecule, published by Tilford and Simmons¹⁴¹ by using standard isotopic relations. To calculate the theoretical band origin, equilibrium vibrational constants of the $B^1\Sigma^+$ state (calculated in this work) were also used.

method¹⁴⁰ are correct within its uncertainties. Thus, the rotational assignments of extra lines appearing as a result of the $e^3\Sigma^-$ ($\nu = 1$) $\sim A^1\Pi$ ($\nu = 0$) perturbation in the $^{13}\text{C}^{17}\text{O}$ molecule are also correct.

Next, an analysis based on the $g_x(J)$ function was carried out; however, some formulas and results are presented by somewhat different means than the original ones.^{103,142} Using these formulas in relation to the $g_x(J)$ function and the (1–0) band origin of the B–A system in the $^{13}\text{C}^{17}\text{O}$ molecule, determined in this work, the B–e (1–1) band origin was calculated in the examined molecule for the first time: $\sigma_{11}^{B-e} = 24\,144.72$ (30) cm^{-1} , which also gives satisfactory agreement with the values calculated theoretically on the basis of the data given by Field¹⁰² and Tilford and Simmons¹⁴¹ from the $^{12}\text{C}^{16}\text{O}$ molecule, recalculated by means of standard isotopic relations. The results of this comparison and of the above analyses are presented in Table 11.

C. Perturbations in the $B^1\Sigma^+(\nu = 1)$ Rydberg State. For the first time Janjić et al.⁸⁰ wrote about a possible perturbation that appears in the $B^1\Sigma^+(\nu = 1)$ state, examining the 1–6 band of the Ångström (B–A) system in the $^{13}\text{C}^{16}\text{O}$ molecule. They claimed that they had found a rotational perturbation appearing in the $B^1\Sigma^+(\nu = 1)$ state between the $J = 7$ and $J = 8$ rotational levels. They also observed that the rotational constant of the perturbing state is larger than the rotational constant of the perturbed $B^1\Sigma^+(\nu = 1)$ state. These first reports were confirmed by Kępa et al.⁸² who at the same time calculated the maximum value of this perturbation on $T_{\text{obs}} - T_{\text{calc}} \approx -0.05 \text{ cm}^{-1}$ for $J = 7$ in the $B^1\Sigma^+(\nu = 1)$ state of the $^{13}\text{C}^{16}\text{O}$ molecule.

It is obvious that the place of occurrence and size of a perturbation change, very often significantly in different isotopologues. Therefore, our aim is not to verify the perturbation discovered by Janjić et al.⁸⁰ and by Kępa et al.⁸² (because to do this, we would need to deal with the analysis of

different transitions involving the $B^1\Sigma^+(\nu = 1)$ state exclusively in the $^{13}\text{C}^{16}\text{O}$ molecule), but rather to check if this type of perturbation also appears in the rare $^{13}\text{C}^{17}\text{O}$ molecule, studied by us, in the region close to $J \approx 7$ –8. In the 1– ν'' progression analysis of the Ångström (B–A) system carried out in the $^{13}\text{C}^{17}\text{O}$ molecule, within this work, we do not observe this type of perturbation appearing in the $B^1\Sigma^+(\nu = 1)$ state for the $J \approx 7$ –8 rotational levels. There may be a few reasons for this state of affairs. First, there is a perturbation in the $A^1\Pi$ ($\nu = 0$) state in the $^{13}\text{C}^{17}\text{O}$ molecule just in the $J = 8$ –9 region caused by the $e^3\Sigma^-$ ($\nu = 1$) state (Table 10 and Figure 9). Due to this fact, on the basis of the (1–0) band analysis we are not able to observe any possible perturbation in this area that could concern the $B^1\Sigma^+(\nu = 1)$ state. However, the $A^1\Pi$ ($\nu = 1$) state analysis on the basis of the (1–1) band of the Ångström system in $^{13}\text{C}^{17}\text{O}$ provides evidence that in the $^{13}\text{C}^{17}\text{O}$ molecule under consideration the $B^1\Sigma^+(\nu = 1)$ state is completely regular for $J \geq 8$, and the perturbation disrupting initial terms for $A^1\Pi$ ($\nu = 1$) (Figure 9) is caused by a well-known reason, namely $a^1\Sigma^+(\nu = 10)$ state (see Hakalla et al.,⁷³ Table 10). Also, graphs of the $f_x(J)$ and $g_x(J)$ functions for the (1–1) band of the B–A system in the $^{13}\text{C}^{17}\text{O}$ molecule (Figures 5 and 6) give evidence that in the $^{13}\text{C}^{17}\text{O}$ molecule there is not any perturbation, mentioned above, of the $B^1\Sigma^+(\nu = 1)$ state. Therefore, it is completely regular in this molecule. It seems that the rotational perturbation in the $B^1\Sigma^+(\nu = 1)$ state between the $J = 7$ and $J = 8$ levels, discovered by Janjić et al.⁸⁰ and Kępa et al.⁸² for the $^{13}\text{C}^{16}\text{O}$ molecule, either significantly becomes weaker in the heavier $^{13}\text{C}^{17}\text{O}$ molecule or considerably changes its location.

D. Predissociation of the $B^1\Sigma^+$ Rydberg State. Predissociation that appears in the $B^1\Sigma^+$ state, between $\nu = 1$ and $\nu = 2$ vibrational levels, in various isotopologues of the CO molecule has been described in both theoretical and experimental studies^{41,45,143,144} (and references therein). Because $B^1\Sigma^+(\nu > 1)$ vibrational levels are observed in absorption exclusively, following the authors of Eidelsberg et al.⁴⁵ one can quote a conclusion in which B state is probably predissociated by repulsive part of the $D^1\Sigma^+$ state. The impact of this interaction was also observed in this work as dramatic weakening of intensities of molecular lines of the examined 1– ν'' progression of the Ångström system in $^{13}\text{C}^{17}\text{O}$ molecule for the $J > 20$ region. Similar weakening was also observed by, for example, Klopotek and Vidal⁴¹ for the $^{12}\text{C}^{16}\text{O}$ molecule for $J > 17$ and for the $^{13}\text{C}^{16}\text{O}$ molecule for $J > 19$. As one can see, our result is satisfactory because for the heaviest molecule out of the three mentioned above, that is, for $^{13}\text{C}^{17}\text{O}$, the weakening region of intensities of spectral lines caused by this predissociation falls on the greatest values of the rotational quantum number $J > 20$. It is obviously caused by smaller energy-level spacing together with an increase in the reduced mass of the molecule.

We hope that the results presented in this work will certainly contribute not only to achieve a full deperturbation calculation for the greatly complicated $A^1\Pi$ state but also to derive a new precise value¹⁰⁴ of the first dissociation limit in the CO molecule.

VI. CONCLUSION

We believe that the first observation and analyses of the 1– ν'' progression bands of the Ångström ($B^1\Sigma^+ - A^1\Pi$) band system in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue, which allowed obtaining many molecular parameters for the first time such as: rotational

constants for the $B^1\Sigma^+(\nu = 1)$ state, equilibrium rotational and vibrational constants of the $B^1\Sigma^+$ state, the RKR turning points for the $B^1\Sigma^+$ as well as for the $A^1\Pi$ states, as well as the Franck–Condon factors, relative intensities, and r centroids of the Ångström band system, and also first molecular parameters for the $e^3\Sigma^-(\nu = 1)$ state in $^{13}\text{C}^{17}\text{O}$, will significantly broaden and improve the spectroscopic and quantum-mechanical information, not only on the first, lowest lying Rydberg $B^1\Sigma^+$ electronic state, and on the most perturbed electronic state of the CO molecule, that is, the $A^1\Pi$ state, but also on the entire set of isotopically related carbon monoxide species, which plays a crucial and important role both in environmental research and in innovative, industrial technologies, and above all in basic astrophysical research.

AUTHOR INFORMATION

Corresponding Author

*R. Hakalla: e-mail, hakalla@univ.rzeszow.pl; tel, (+48) 17-851-87-03; fax, (+48) 17-851-86-61.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We express our gratitude for the financial support for the European Regional Development Fund and the Polish state budget in the frame of the Regional Operational Program of the Carpathian (RPO WP) for the period 2007–2013 via the funding of the Center for Innovation and Transfer of Engineering and Natural Science Knowledge of the University of Rzeszów. We express our deepest gratitude to Professor Ryszard Kępa for helpful discussion.

REFERENCES

- Hall, D. N. B. Detection of the ^{13}C , ^{17}O , and ^{16}O Isotope Bands of CO in the Infrared Solar Spectrum. *Astrophys. J.* **1973**, *182*, 977–982.
- Encrenaz, P. J.; Wannier, P. G.; Jefferts, K. B.; Penzias, A. A.; Wilson, R. W. Interstellar OXYGEN-17. *Astrophys. J.* **1973**, *186*, L77–L80.
- Wannier, P. G.; Lucas, R.; Linke, R. A.; Encrenaz, P. J.; Penzias, A. A.; Wilson, R. W. The Abundance Ratio $[\text{O}^{17}]/[\text{O}^{16}]$ in Dense Interstellar Clouds. *Astrophys. J.* **1976**, *205*, L169–L171.
- Frerking, M. A.; Langer, W. D. Measurement of the Hyperfine Structure of C^{17}O . *J. Chem. Phys.* **1981**, *74*, 6990–6991.
- Frerking, M. A.; Langer, W. D.; Wilson, R. W. The Relationship Between Carbon Monoxide Abundance and Visual Extinction in Interstellar Clouds. *Astrophys. J.* **1982**, *262*, 590–605.
- Dame, T. M.; Hartmann, D.; Thaddeus, P. The Milky Way in Molecular Clouds: A New Complete CO Survey. *Astrophys. J.* **2001**, *547*, 792–813.
- Bensch, F.; Park, I.; Wouterloot, J. G. A.; Klapper, G.; Winnewisser, G. Detection of $^{13}\text{C}^{17}\text{O}$ and Observations of Rare CO Isotopomers toward the ρ Ophiuchi Molecular Cloud. *Astrophys. J.* **2001**, *562*, L185–L188.
- Ladd, E. F. On the Relative Abundance of C^{18}O and C^{17}O in the Taurus Molecular Cloud. *Astrophys. J.* **2004**, *610*, 320–328.
- Lellouch, E.; Moreno, R.; Paubert, G. A dual origin for Neptune's Carbon Monoxide? *Astron. Astrophys.* **2005**, *430*, L37–L40.
- Lupu, R. E.; Feldman, P. D.; Weaver, H. A.; Tozzi, G. P. The Fourth Positive System of Carbon Monoxide in the Hubble Space Telescope Spectra of Comets. *Astrophys. J.* **2007**, *670*, 1473–1484.
- Jewitt, D.; Garland, C. A.; Aussel, H. Deep Search for Carbon Monoxide in Cometary Precursors Using Millimeter Wave Spectroscopy. *Astron. J.* **2008**, *135*, 400–407.
- Rho, J.; Jarrett, T. H.; Reach, W. T.; Gomez, H.; Andersen, M. Carbon Monoxide in the Cassiopeia A Supernova Remnant. *Astrophys. J.* **2009**, *693*, L39–L43.
- Martin, S.; George, M. R.; Wilner, D. J.; Espada, D. Imaging Carbon Monoxide Emission in the Starburst Galaxy NGC 6000. *Astron. J.* **2010**, *139*, 2241–2248.
- Weaver, H. A.; Feldman, P. D.; A'Hearn, M. F.; Dello Russo, N.; Stern, S. A. The Carbon Monoxide Abundance in Comet 103p/Hartley 2 During the *Epoxi* Flyby. *Astrophys. J.* **2011**, *734*, L5–L10.
- Visscher, C.; Moses, J. I. Quenching of Carbon Monoxide and Methane in the Atmospheres of Cool Brown Dwarfs and Hot Jupiters. *Astrophys. J.* **2011**, *738*, 72–84.
- Schindhelm, E.; France, K.; Burgh, E. B.; Herczeg, G. J.; Green, J. C.; Brown, A.; Brown, J. M.; Valenti, J. A. Characterizing CO Fourth Positive Emission in Young Circumstellar Disks. *Astrophys. J.* **2012**, *746*, 97–111.
- Rho, J.; Onaka, T.; Cami, J.; Reach, W. T. Spectroscopic Detection of Carbon Monoxide in the Young Supernova Remnant Cassiopeia A. *Astrophys. J.* **2012**, *747*, L6–L11.
- Rodler, F.; Lopez-Morales, M.; Ribas, I. Weighing the Non-transiting Hot Jupiter τ Boo b. *Astrophys. J.* **2012**, *753*, L25–L30.
- Bally, J.; Langer, W. D. Isotope-selective photodestruction of carbon monoxide. *Astrophys. J.* **1982**, *255*, 143–148.
- Glassgold, A. E.; Huggins, R. J.; Langer, W. D. Shielding of CO from dissociating radiation in interstellar clouds. *Astrophys. J.* **1985**, *290*, 615–626.
- Viala, Y. P. Chemical equilibrium from diffuse to dense interstellar clouds. I - Galactic molecular clouds. *Astron. Astrophys. Suppl. Ser.* **1986**, *64*, 391–437.
- Bennett, C. J.; Jamieson, C. S.; Kaiser, R. I. Mechanical Studies on the Formation and Destruction of Carbon Monoxide (CO), Carbon Dioxide (CO_2), and Carbon Trioxide (CO_3) in Interstellar Ice Analog Samples. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4032–4050.
- Balser, D. S.; McMullin, J. P.; Wilson, T. L. CO Isotopes in Planetary Nebulae. *Astrophys. J.* **2002**, *572*, 326–334.
- Farrenq, R.; Guelachvili, G.; Sauval, A. J.; Grevesse, N.; Farmer, C. B. Improved Dunham Coefficients for CO from Infrared Solar Lines of High Rotational Excitation. *J. Mol. Spectrosc.* **1991**, *149*, 375–390.
- Greenwood, N.; Earnshaw, A. *Chemistry of the Elements*; Butterworth-Heinemann Press: Oxford, U.K., 1997.
- Weinstock, B.; Niki, H. Carbon Monoxide Balance in Nature. *Science* **1972**, *176*, 290–292.
- Li, L.; Hsu, A.; Moore, P. K. Actions and Interactions of Nitric Oxide, Carbon Monoxide and Hydrogen Sulphide in the Cardiovascular System and in Inflammation—a Tale of Three Gases. *Pharmacol. Ther.* **2009**, *123*, 386–400.
- Roberts, G. P.; Youn, H.; Kerby, R. L. CO-Sensing Mechanisms. *Microbiol. Mol. Biol. Rev.* **2004**, *68*, 453–473.
- Kormos, C. M.; Leadbeater, N. E. Alkoxycarbonylation of Aryl Iodides using Gaseous Carbon Monoxide and Pre-Pressurized Reaction Vessels in Conjunction with Microwave Heating. *Org. Biomol. Chem.* **2007**, *5*, 65–68.
- Du Plessis, A.; Strydom, C. A.; Uys, H.; Botha, L. R. Laser Induced and Controlled Chemical Reaction of Carbon Monoxide and Hydrogen. *J. Chem. Phys.* **2011**, *135*, 204303–204310.
- Le, H. T.; Lang, S. M.; De Haeck, J.; Lievens, P.; Janssens, E. Carbon Monoxide Adsorption on Neutral and Cationic Vanadium Doped Gold Clusters. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9350–9358.
- Keulks, G. W.; Ravi, A. Infrared Spectroscopic Study of Carbon Monoxide Adsorption on Hydrogen and Oxygen Treated Silver Surfaces. *J. Phys. Chem.* **1970**, *74*, 783–786.
- Den Besten, I. E.; Fox, P. G.; Selwood, P. W. J. The Mechanism of Chemisorption: Carbon Monoxide and Carbon Dioxide on Nickel. *Phys. Chem.* **1962**, *66*, 450–453.
- Zhou, D. D. Y.; Davis, M. J.; Skodje, R. T. Multitarget Global Sensitivity Analysis of n-Butanol Combustion. *J. Phys. Chem. A* **2013**, *117*, 3569–3584.

- (35) McKee, M. L. Moving Atoms and Small Molecules out of Open Containers. *J. Phys. Chem. A* **2013**, *117*, 2365–2372.
- (36) Kucernak, A. R.; Offer, G. J. The role of adsorbed hydroxyl species in the electrocatalytic carbon monoxide oxidation reaction on Platinum. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3699–3711.
- (37) Borba, A.; Gómez-Zavaglia, A.; Fausto, R. Molecular Structure, Infrared Spectra, and Photochemistry of Isoniazid under Cryogenic Conditions. *J. Phys. Chem. A* **2009**, *113*, 9220–9230.
- (38) Ceotto, M.; Dell'Angelo, D.; Tantardini, G. F. Multiple Coherent States Semiclassical Initial Value Representation Spectra Calculations of Lateral Interactions for CO on Cu(100). *J. Chem. Phys.* **2010**, *133*, 054701–054711.
- (39) Yan, N.; Chen, Q.; Wang, F.; Wang, Y.; Zhong, H.; Lin, H. High Catalytic Activity for CO Oxidation of CO₃O₄ Nanoparticles in SiO₂ Nanocapsules. *J. Mater. Chem. A* **2013**, *1*, 637–643.
- (40) Hadjiivanov, K.; Tsyntarski, B.; Venkov, Tz.; Daturi, M.; Saussey, J.; Lavalley, J.-C. New Types of Polycarbonyls of Co⁺ Formed After Interaction of Co with Co–Zsm-5: An FTIR Spectroscopic Study. *Phys. Chem. Chem. Phys.* **2003**, *5*, 243–245.
- (41) Klopotek, P.; Vidal, C. R. Two-Step Vacuum-Ultraviolet Visible Excitation Spectroscopy on the CO Molecule. *J. Opt. Soc. Am. B* **1985**, *2*, 869–876.
- (42) Rottke, H.; Zacharias, H. Sensitive Detection of CO by Tunable VUV Laser Excitation of the B¹Σ⁺ State. *Opt. Commun.* **1985**, *55*, 87–90.
- (43) Kępa, R. New Intercombination Bands in the Emission Spectrum of CO: the B¹Σ⁺ → d³Δ_i and C¹Σ⁺ → d³Δ_i Transitions. *Chem. Phys.* **1986**, *110*, 123–129.
- (44) Amiot, C.; Roncin, J.-Y.; Verges, J. First Observation of the CO E¹Π to B¹Σ⁺ and C¹Σ⁺ to B¹Σ⁺ Band Systems. Predissociation in the E¹Π(v=0) Level. *J. Phys. B: At. Mol. Phys.* **1986**, *19*, L19–L23.
- (45) Eidelsberg, M.; Roncin, J.-Y.; Le Floch, A.; Launay, F.; Letzelter, C.; Rostas, J. Reinvestigation of the Vacuum Ultraviolet Spectrum of CO and Isotopic Species: The B¹Σ⁺ ↔ X¹Σ⁺ Transition. *J. Mol. Spectrosc.* **1987**, *121*, 309–336.
- (46) Masaki, T.; Adachi, Y.; Hirose, C. Observation of Inter-Rydberg K¹Σ⁺–B¹Σ⁺ and L¹Π–B¹Σ⁺ Transitions of CO by Optogalvanic Spectroscopy. *Chem. Phys. Lett.* **1987**, *139*, 62–65.
- (47) Sekine, S.; Adachi, Y.; Hirose, C. Optogalvanic Observation of the CO W¹Π–B¹Σ⁺ Transition. *J. Chem. Phys.* **1989**, *90*, 5346–5349.
- (48) Hart, D. J.; Bourne, O. L. High-Resolution Coherent VUV Spectroscopy of NO [C²Π(1)–B²Π(10), B²Π(11)] and CO[B¹Σ(0)]. *Chem. Phys.* **1989**, *133*, 103–112.
- (49) Tjossem, P. J. H.; Smyth, K. C. Multiphoton Excitation Spectroscopy of the B¹Σ⁺ and C¹Σ⁺ Rydberg States of CO. *J. Chem. Phys.* **1989**, *91*, 2041–2049.
- (50) Choe, J.-I.; Lee, D.-K.; Le Floch, A. C.; Kukulich, S. G. Fourier Transform Spectroscopy of CO Intercombination Bands. *J. Mol. Spectrosc.* **1989**, *136*, 173–184.
- (51) Sekine, S.; Iwata, S.; Hirose, C. Optogalvanic Spectrum of the CO L¹Π–B¹Σ⁺(v=0) Band and Electronic Structure of the L¹Σ State. *Chem. Phys. Lett.* **1991**, *180*, 173–178.
- (52) Kanik, I.; Ratliff, M.; Trajmar, S. Electron-Impact Excitation of the B¹Σ⁺, C¹Σ⁺ and E¹Π States of CO at 100 eV. *Chem. Phys. Lett.* **1993**, *208*, 341–344.
- (53) Sekine, S.; Hirose, C. Perturbation on Intensity Profiles of the CO 4pσ K¹Σ⁺–3sσ B¹Σ⁺(0–0) and 4pπ L¹Π–3sσ B¹Σ⁺(0–0) bands. *Chem. Phys. Lett.* **1993**, *212*, 129–133.
- (54) Roncin, J.-Y.; Ross, A.; Boursey, E. The C → B(0–0) Band of Four Isotopes of Carbon Monoxide. *J. Mol. Spectrosc.* **1993**, *162*, 353–357.
- (55) Baker, J. The B¹Σ⁺(v = 2)–k³Π(v = 0) Interaction in CO. *J. Mol. Spectrosc.* **1994**, *167*, 323–333.
- (56) Baker, J.; Tchang-Brillet, W.-Ü. L.; Julianne, P. S. First Observation of the v = 3 Level of the B¹Σ⁺ Rydberg State of CO. *J. Chem. Phys.* **1995**, *102*, 3956–3962.
- (57) Komatsu, M.; Ebata, T.; Maeyama, T.; Mikami, N. Rotational Structure and Dissociation of the Rydberg States of CO Investigated by Ion-Dip Spectroscopy. *J. Chem. Phys.* **1995**, *103*, 2420–2436.
- (58) Hasegawa, H.; Tsukiyama, K. The C¹Σ⁺–B¹Σ⁺ Amplified Spontaneous Emission in CO. *Appl. Phys. B: Lasers Opt.* **1996**, *63*, 311–314.
- (59) Drabbe, M.; ter Meulen, J. J.; Meerts, W. L. High Resolution Pulsed-CW Double-Resonance Spectroscopy on the B¹Σ⁺(v' = 0) – A¹Π(v'' = 0) System of CO. *Chem. Phys. Lett.* **1997**, *267*, 127–131.
- (60) Di Teodoro, F.; Rehm, J. E.; Farrow, R. L.; Paul, P. H. Collisional Quenching of CO B¹Σ⁺(v' = 0) Probed by Two-Photon Laser-Induced Fluorescence using a Picosecond Laser. *J. Chem. Phys.* **2000**, *113*, 3046–3055.
- (61) Sakoda, A.; Mutoh, H.; Tsukiyama, K. Effect of Externally Injected Radiation on Amplified Spontaneous Emission in CO. *Appl. Phys. B: Lasers Opt.* **2001**, *72*, 411–415.
- (62) Katayanagi, H.; Matsumoto, Y.; de Lange, C. A.; Tsubouchi, M.; Suzuki, T. One- and Two-Color Photoelectron Imaging of the CO Molecule via the B¹Σ⁺ State. *J. Chem. Phys.* **2003**, *119*, 3737–3745.
- (63) Eidelsberg, M.; Sheffer, Y.; Federman, S. R.; Lemaire, J. L.; Fillion, J. H.; Rostas, F.; Ruiz, J. Oscillator Strengths and Predissociation Rates for Rydberg Transitions in ¹²C¹⁶O, ¹³C¹⁶O, and ¹³C¹⁸O Involving the E¹Π, B¹Σ⁺, and W¹Π States. *Astrophys. J.* **2006**, *647*, 1543–1548.
- (64) Eidelsberg, M.; Launay, F.; Ito, K.; Matsui, T.; Hinnen, P. C.; Reinhold, E.; Ubachs, W.; Huber, K. P. Rydberg-Valence Interactions of CO, and Spectroscopic Evidence Characterizing the C¹Σ⁺ Valence State. *J. Chem. Phys.* **2004**, *121*, 292–309.
- (65) Eidelsberg, M.; Lemaire, J. L.; Federman, S. R.; Stark, G.; Heays, A. N.; Sheffer, Y.; Gavilan, L.; Fillion, J.-H.; Rostas, F.; Lyons, J. R.; et al. High-Resolution Study of Oscillator Strengths and Predissociation Rates for ¹²C¹⁶O. W-X Bands and Rydberg Complexes Between 92.9 and 93.4 nm. *Astron. Astrophys.* **2012**, *543*, L69–L78.
- (66) Malak, Z.; Rytel, M.; Janjić, J.; Pešić, D. S. Ångström System of the ¹³C¹⁸O Molecule. *Acta Phys. Hung.* **1984**, *55*, 85–95.
- (67) Domin, J.; Domin, U.; Malak, Z.; Rytel, M. Ångström System of the ¹⁴C¹⁶O Molecule. *Acta Phys. Hung.* **1984**, *55*, 165–173.
- (68) Kępa, R. High Resolution Emission Spectra of the 0–0, 0–1 and 0–2 Bands of E¹Π – A¹Π and B¹Σ⁺ – A¹Π Transitions in ¹²C¹⁸O Molecule. *Acta Phys. Hung.* **1986**, *60*, 227–237.
- (69) Danielak, J.; Domin, J.; Domin, U.; Rytel, M. The Ångström (B¹Σ⁺–A¹Π) Band System of the ¹⁴C¹⁸O Molecule. *J. Mol. Spectrosc.* **1987**, *125*, 251–257.
- (70) Kępa, R.; Para, A.; Rytel, M.; Janjić, J. Analysis of the 0–7 Band of the Herzberg System of ¹³C¹⁶O. *Acta Phys. Hung.* **1990**, *68*, 205–214.
- (71) Prasad, C. V. V.; Reddy, S. P. Improved Molecular Constants of the A¹Π, B¹Σ⁺, and C¹Σ⁺ States of ¹³C¹⁸O. *J. Mol. Spectrosc.* **1988**, *130*, 62–68.
- (72) Haridass, C.; Reddy, S. P.; LeFloch, A. C. Precise Rovibronic Term Values of Some Vibrational Levels of the A¹Π, B¹Σ⁺, C¹Σ⁺, and E¹Π States of ¹²C¹⁸O and ¹³C¹⁸O. *J. Mol. Spectrosc.* **1994**, *168*, 429–441.
- (73) Hakalla, R.; Zachwieja, M. Rotational Analysis of the Ångström System (B¹Σ⁺–A¹Π) in the Rare ¹³C¹⁷O Isotopologue. *J. Mol. Spectrosc.* **2012**, *272*, 11–18.
- (74) Hakalla, R.; Szajna, W.; Zachwieja, M. Extended Analysis of the Ångström Band System (B¹Σ⁺ – A¹Π) in the Rare ¹²C¹⁷O Isotopologue. *J. Phys. B: At. Mol. Opt. Phys.* **2012**, *45*, 215102–215111.
- (75) Ångström, A. J.; Thalén, T. R. *Nova Acta Regiae Soc. Sci. Ups.* **1875**, *3*, 9.
- (76) Danielak, J.; Kępa, R.; Ojczyk, K.; Rytel, M. Weak Ångström Bands of ¹²C¹⁶O Molecule. *Acta Phys. Pol.* **1971**, *A39*, 29–32.
- (77) Kępa, R.; Rytel, M. On the Ångström Bands of ¹²C¹⁶O. *Acta Phys. Pol.* **1970**, *A37*, 585–590.
- (78) Le Floch, A. C.; Amiot, C. Fourier Transform Spectroscopy of the CO Ångström Bands. *Chem. Phys.* **1985**, *97*, 379–389.
- (79) Kępa, R.; Rytel, M. The Ångström (B¹Σ⁺–A¹Π) System of the CO Molecules: New Observations and Analyses. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, 3355–3362.
- (80) Janjić, J.; Danielak, J.; Kępa, R.; Rytel, M. Weak Ångström Bands of ¹³C¹⁶O and ¹²C¹⁸O Molecules. *Acta Phys. Pol.* **1972**, *A41*, 757–761.

- (81) Rytel, M. The Ångström System of the $^{13}\text{C}^{16}\text{O}$ Molecule. *Acta Phys. Pol.* **1970**, A37, 559–568.
- (82) Kępa, R.; Domin, U.; Porada, K. The Ångström ($B^1\Sigma^+-A^1\Pi$) Band System of $^{13}\text{C}^{16}\text{O}$: New Observations and Analyses. *Acta Phys. Pol., A* **2003**, 103, 441–451.
- (83) Hakalla, R.; Szajna, W.; Zachwieja, M.; Kępa, R. Reanalysis of the Ångström System ($B^1\Sigma^+-A^1\Pi$) in the $^{13}\text{C}^{16}\text{O}$ Isotopic Molecule. *Acta Phys. Pol., A* **2012**, 122, 674–683.
- (84) Kępa, R.; Rytel, M.; Janjić, J. D.; Pešić, D. S. Note on the Ångström Bands of the $^{13}\text{C}^{18}\text{O}$ Molecule. *Acta Phys. Pol.* **1972**, A41, 377–378.
- (85) Prasad, C. V. V.; Bhale, G. L.; Reddy, S. P. The Ångström ($B^1\Sigma^+-A^1\Pi$) Band System of $^{13}\text{C}^{18}\text{O}$. *J. Mol. Spectrosc.* **1984**, 104, 165–173.
- (86) Kępa, R. Analysis of the 1–2 Band of the Ångström ($B^1\Sigma^+-A^1\Pi$) System in the $^{14}\text{C}^{16}\text{O}$ Molecule. *Acta Phys. Hung.* **1994**, 74, 319–327.
- (87) Bacis, R. A New Source for the Search and Study of Electronic Molecular Spectra: the Composite Wall Hollow Cathode (CWHC). *J. Phys. E: Sci. Instrum.* **1976**, 9, 1081–1086.
- (88) Szajna, W.; Zachwieja, M. Emission Spectroscopy of the $A^1\Pi-X^1\Sigma^+$ System of AlH. *Eur. Phys. J. D.* **2009**, 55, 549–555.
- (89) Szajna, W.; Zachwieja, M. The Emission Spectrum of the $C^1\Sigma^+-X^1\Sigma^+$ System of AlH. *J. Mol. Spectrosc.* **2010**, 260, 130–134.
- (90) Szajna, W.; Zachwieja, M.; Hakalla, R.; Kępa, R. Emission Spectroscopy of AlH: the $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^+$ States Characteristics. *Acta Phys. Pol., A* **2011**, 120, 417–423.
- (91) Szajna, W.; Zachwieja, M. High-Resolution Emission Spectroscopy of the $A^2\Pi-X^2\Sigma^+$ System of AlH⁺. *J. Mol. Spectrosc.* **2011**, 269, 56–60.
- (92) Zachwieja, M.; Szajna, W.; Hakalla, R. The $A^2\Delta-X^2\Pi$ band system of the CD radical. *J. Mol. Spectrosc.* **2012**, 275, 53–60.
- (93) Palmer, B. A.; Engleman, R. *Atlas of the Thorium Spectrum Los Alamos National Laboratory*; Los Alamos, NM (unpublished).
- (94) Kępa, R. The Analysis of the Herzberg system in the $^{13}\text{C}^{16}\text{O}$ and partly in the $^{12}\text{C}^{16}\text{O}$ Molecules. *Acta Phys. Acad. Sci. Hung.* **1978**, 45, 133–147.
- (95) Dunham, J. L. The Energy Levels of a Rotating Vibrator. *Phys. Rev.* **1932**, 41, 721–731.
- (96) Brown, J. M.; Colbourn, E. A.; Watson, J. K. G.; Wayne, F. D. An Effective Hamiltonian for Diatomic Molecules: Ab Initio Calculations of Parameters of HCl⁺. *J. Mol. Spectrosc.* **1979**, 74, 294–318.
- (97) Curl, R. F.; Dane, C. B. Unbiased Least-Squares Fitting of Lower States. *J. Mol. Spectrosc.* **1988**, 128, 406–412.
- (98) Watson, J. K. G. On the Use of Term Values in the Least-Squares Fitting of Spectra. *J. Mol. Spectrosc.* **1989**, 138, 302–308.
- (99) Albritton, D. L.; Schmeltekopf, A. L.; Zare, R. N. A Method for Merging the Results of Separate Least-Squares Fits and Testing for Systematic Errors. *J. Mol. Spectrosc.* **1977**, 67, 132–156.
- (100) Coxon, J. A. Merging of Least-Squares Parameters: the Approach of Stepwise Merging. *J. Mol. Spectrosc.* **1978**, 72, 252–263.
- (101) Bembenek, Z.; Kępa, R.; Para, A.; Rytel, M.; Zachwieja, M.; Janjić, J. D.; Marx, E. Reinvestigations of the $A^2\Delta-X^2\Pi$ Band System in the CH Radical. *J. Mol. Spectrosc.* **1990**, 139, 1–10.
- (102) Field, R. W. *Ph.D. Thesis*; Harvard University: Cambridge, MA, 1971.
- (103) Herzberg, G. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*; Van Nostrand: Princeton, NJ, 1950.
- (104) Kępa, R.; Ostrowska-Kopeć, M.; Piotrowska, I.; Zachwieja, M.; Hakalla, R.; Szajna, W.; Kolek, P. The Ångström ($B^1\Sigma^+-A^1\Pi$) 0–1 and 1–1 Bands in Isotopic CO Molecules: Further Investigations. *J. Phys. B: At. Mol. Opt.* **2013**, submitted.
- (105) Krupenie, P. H. *The Band Spectrum of Carbon Monoxide*; National Bureau of Standards: Washington, DC, 1966.
- (106) Simmons, J. D.; Bass, A. M.; Tilford, S. G. The Fourth Positive System of Carbon Monoxide Observed in Absorption at High Resolution in the Vacuum Ultraviolet Region. *Astrophys. J.* **1969**, 155, 345–355.
- (107) Kępa, R. Note on the Herzberg System of the Isotopic Molecules. *Acta Phys. Pol.* **1969**, A36, 1109–1110.
- (108) Field, R. W.; Wicke, B. G.; Simmons, J. D.; Tilford, S. G. Analysis of Perturbations in the $a^3\Pi$ and $A^1\Pi$ States of CO. *J. Mol. Spectrosc.* **1972**, 44, 383–399.
- (109) Burnham, R. L.; Isler, R. C.; Wells, W. C. Zero-Field Level-Crossing Spectroscopy of the $A^1\Pi$ State of Carbon Monoxide. *Phys. Rev. A* **1972**, 6, 1327–1340.
- (110) Kłopotek, P.; Vidal, C. R. Frequency Selective Excitation Spectroscopy of the CO Intercombination Bands. *Can. J. Phys.* **1984**, 62, 1426–1436.
- (111) Le Floch, A. C.; Launay, F.; Rostas, J.; Field, R. W.; Brown, C. M.; Yoshino, K. Reinvestigation of the CO $A^1\Pi$ State and Its Perturbations: The $v = 0$ Level. *J. Mol. Spectrosc.* **1987**, 121, 337–379.
- (112) Le Floch, A. C.; Rostas, J.; Schamps, J. The $A^1\Pi \sim D^1\Delta$ Rotation-Electronic Interaction in CO. *Mol. Phys.* **1988**, 63, 677–684.
- (113) Kępa, R. New Spectroscopic Studies of the Herzberg Bands of the $^{12}\text{C}^{16}\text{O}$ Molecule. *J. Mol. Spectrosc.* **1989**, 135, 119–130.
- (114) Le Floch, A. C. *Ph.D. Thesis*; University Paris-Sud, Orsay, France, 1989.
- (115) Hallstadius, H.; Lundberg, H. Investigation of the $A^1\Pi v' = 13$ Level in CO Using VUV Radiation Generated by Resonant Sum-Frequency Mixing in Hg Vapour. *Phys. Scr.* **1989**, 40, 652–655.
- (116) Le Floch, A. C. Accurate Energy Levels for the $C^1\Sigma^+ (v = 0)$ and $E^1\Pi (v = 0)$ States of $^{12}\text{C}^{16}\text{O}$. *J. Mol. Spectrosc.* **1992**, 155, 177–183.
- (117) Stark, G.; Lewis, B. R.; Gibson, S. T.; England, J. P. High-Resolution Oscillator Strength Measurements for High- v' Bands of the $A^1\Pi(v') - X^1\Sigma^+(v'' = 0)$ System of Carbon Monoxide. *Astrophys. J.* **1998**, 505, 452–458.
- (118) Zetner, P. W.; Kanik, I.; Trajmar, S. Electron Impact Excitation of the $a^3\Pi$, $a'^3\Sigma^+$, $d^3\Delta$ and $A^1\Pi$ States of CO at 10.0, 12.5 and 15.0 eV Impact Energies. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, 31, 2395–2413.
- (119) Jolly, A.; Lemaire, J. L.; Belle-Oudry, D.; Edwards, S.; Malmasson, D.; Vient, A.; Rostas, F. High Resolution 'VUV Laser' Measurements of the Band Oscillator Strengths of the CO $A^1\Pi (9 \leq v' \leq 17) - X^1\Sigma^+ (v'' = 0)$ Transition. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, 30, 4315–4337.
- (120) Sykora, T.; Vidal, C. R. Interaction of a Magnetic Field with the $a'^3\Sigma^+-A^1\Pi$ Complex in CO. *J. Chem. Phys.* **1998**, 108, 6320–6331.
- (121) Borges, I.; Caridade, P. J. S. B.; Varandas, A. J. C. Potential Energy Curves for $X^1\Sigma^+$ and $A^1\Pi$ States of CO: the $A^1\Pi(v'=1-23) \leftarrow X^1\Sigma^+(v''=0, 1)$ Transitions. *J. Mol. Spectrosc.* **2001**, 209, 24–29.
- (122) Sun, M.; Liu, J.; Sun, W.; Chen, X.; Jiang, B.; Sha, G. Collision-Induced Rotational Energy Transfer of CO ($A^1\Pi, v = 3$) with He, Ne and Ar: Experiment Via Two-Color 2 + 1 REMPI Technique. *Chem. Phys. Lett.* **2002**, 365, 244–250.
- (123) Cyrul, B.; Darlak, K.; Domin, J. Vibrational Analysis of the Fourth Positive System in $^{12}\text{C}^{18}\text{O}$ Isotope Molecule. *Proc. SPIE* **2003**, 5125, 345–348.
- (124) Liu, J.; Sun, M.; Jiang, B.; Sha, G. Quantum Interference in Collision-Induced Energy Transfer for CO ($A^1\Pi, v = 0/e^3\Sigma^+, v = 1$)–HCl ($X^1\Sigma^+$) System Studied by OODR-MPI Spectroscopy. *Chem. Phys. Lett.* **2004**, 388, 306–311.
- (125) Du Plessis, A.; Rohwer, E. G.; Steenkamp, C. M. Investigation of Four Carbon Monoxide Isotopomers in Natural Abundance by Laser-Induced Fluorescence in a Supersonic Jet. *J. Mol. Spectrosc.* **2007**, 243, 124–133.
- (126) Bartels, N.; Schfer, T.; Hhnert, J.; Field, R. W.; Wodtke, A. M. *J. Chem. Phys.* **2012**, 136, 214201.
- (127) Kępa, R.; Rzeszut, Z. The Analysis of the $E^1\Pi-A^1\Pi$ Transition in $^{14}\text{C}^{16}\text{O}$ Molecule. *Acta Phys. Acad. Sci. Hung.* **1981**, 50, 237–245.
- (128) Kępa, R.; Rytel, M.; Rzeszut, Z. The $E^1\Pi-A^1\Pi$ System Bands in $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ Molecules. *Acta Phys. Pol.* **1978**, A54, 355–361.
- (129) Kępa, R. The Herzberg System $C^1\Sigma^+-A^1\Pi$ Transition in $^{14}\text{C}^{16}\text{O}$ Isotopic Molecule. *Acta Phys. Pol.* **1982**, A62, 467–472.
- (130) Prasad, C. V. V.; Reddy, S. P.; Sandys-Wunsch, M. The Herzberg ($C^1\Sigma^+-A^1\Pi$) Band System of $^{13}\text{C}^{18}\text{O}$. *J. Mol. Spectrosc.* **1985**, 114, 436–444.

- (131) Kępa, R. The 0–1 and 0–2 Bands of the $E^1\Pi-A^1\Pi$ System of the $^{13}\text{C}^{18}\text{O}$ Molecule. *J. Mol. Spectrosc.* **1988**, *132*, 545–549.
- (132) Haridass, C.; Reddy, S. P.; LeFloch, A. C. The Fourth Positive ($A^1\Pi-X^1\Sigma^+$) System of $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{18}\text{O}$: Perturbations in the $A^1\Pi$ State. *J. Mol. Spectrosc.* **1994**, *167*, 334–352.
- (133) Kępa, R.; Jarosz, M.; Kocan, A.; Piotrowska-Domagala, I.; Porada, K. The Herzberg ($C^1\Sigma^+-A^1\Pi$) System in the $^{14}\text{C}^{18}\text{O}$ Molecule: Observations and Analysis of 0–1, 0–2 and 0–3 Bands. *Acta Phys. Hung. Heavy Ion Phys.* **1998**, *8*, 207–216.
- (134) Steinmann, C. M.; Rohwer, E. G.; Stafast, H. Accurate Laboratory Wavelengths of the Vacuum Ultraviolet $A(v' = 3)-X(v'' = 0)$ Band of $^{12}\text{C}^{17}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. *Astrophys. J.* **2003**, *590*, L123–L126.
- (135) Domin, J.; Fran, M.; Ploskon, B. Is the level $v' = 6$ of $A^1\Pi$ state perturbed in origin at $^{13}\text{C}^{16}\text{O}$ molecule? *Proc. SPIE* **2004**, *5484*, 346–349.
- (136) Plessis, A.; Rohwer, E. G.; Steenkamp, C. M. Accurate Laboratory Wavelengths of the $A^1\Pi(v' = 0-5)-X^1\Sigma^+(v'' = 0)$ Vibronic Bands of $^{12}\text{C}^{17}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. *Astrophys. J. Suppl. S.* **2006**, *165*, 432–437.
- (137) Kępa, R.; Ostrowska-Kopeć, M.; Piotrowska, I. New Spectroscopic Investigations of the Fourth-Positive ($A^1\Pi \rightarrow X^1\Sigma^+$) System Bands in the $^{13}\text{C}^{16}\text{O}$ Molecule. *J. Mol. Spectrosc.* **2011**, *266*, 104–112.
- (138) Kittrell, C.; Garetz, B. A. Analysis of the $D^1\Delta-X^1\Sigma^+$ Transition in CO Observed by Two-Photon Excitation. *Spectrochim. Acta, Part A* **1989**, *45*, 31–40.
- (139) Gerö, L. Über den $A^1\Pi$ - Zustand des CO. *Z. Phys.* **1935**, *93*, 669–675.
- (140) Kovács, I. *Rotational Structure in the Spectra of Diatomic Molecules*; Akadémiai Kiadó: Budapest, and Hilger: London, 1969.
- (141) Tilford, S. G.; Simmons, J. D. Atlas of the Observed Absorption Spectrum of Carbon Monoxide Between 1060 and 1900 Å. *J. Phys. Chem. Ref. Data* **1972**, *1*, 147–189.
- (142) Rytel, M.; Siwiec, T. Perturbations in the Spectra of CO Isotopic Molecules I. Partial Analysis of ($e^3\Sigma^- - A^1\Pi$) Perturbations. *Acta Phys. Pol.* **1973**, *A44*, 67.
- (143) Li, Y.; Buenker, R. J.; Hirsch, G. Theoretical Treatment of Predissociation of the CO ($3s\sigma$) B and ($3p\sigma$) $C^1\Sigma^+$ Rydberg States Based on a Rigorous Adiabatic Representation. *Theor. Chem. Acc.* **1998**, *100*, 112–116.
- (144) Lefebvre-Brion, H.; Field, R. W. *The Spectra and Dynamics of Diatomic Molecules*; Elsevier: Amsterdam, 2004.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper posted ASAP on November 13, 2013. A correction was made to Table 11 and the revised version was reposted on November 14, 2013.