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Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) 0–1 and 1–1 bands in isotopic CO molecules: further investigations

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Abstract

In the emission spectrum of six $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$, $^{13}\text{C}^{18}\text{O}$ and $^{14}\text{C}^{18}\text{O}$ isotopologues of the carbon monoxide molecule, new recordings and analyses or new reanalyses of the selected and strongest bands belonging to the Ångström ($B^1\Sigma^+ - A^1\Pi$) system were carried out. Under high resolution, emission spectra of the 0–1 and 1–1 bands were recorded and reanalysed, representing both the $0 - v''$ and $1 - v''$ progressions of this system. Unobserved so far, new spectral lines were identified, and for the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{18}\text{O}$ molecules new parameters of the rovibronic structure B_0 , B_1 , D_0 and D_1 of the $v = 0$ and $v = 1$ levels of the $B^1\Sigma^+$ state and band origins ν_0 of the 0–1 and 1–1 bands of the $B - A$ transition were determined. A detailed analysis included the predissociation regions of the spectra observed in all analysed bands and isotopologues. The values of rotational quantum numbers and rovibronic terms of the highest nonpredissociated J^h as well as the first, already predissociated J^f levels were determined. On that basis, a new and more precise value of dissociation energy of the CO molecule was determined: $D_e = (90\,679.1 \pm 6.0) \text{ cm}^{-1}$. Also, atomic states of the dissociation products of this molecule, which correspond to this energy, were identified as $\text{C}(^3\text{P}_0) + \text{O}(^3\text{P}_2)$ i.e. as both triplet ground atomic sublevels.

Keywords: carbon monoxide, perturbations, fourth-positive, Ångström system, CO molecule

 Online supplementary data available from stacks.iop.org/JPhysB/47/045101/mmedia

1. Introduction

The role of the CO molecule in astrophysics and cosmology has been well known and documented. It is the second most abundant molecule, after H_2 , in the universe. Also, here on earth, this molecule plays a crucial role in physical chemistry, environmental research, materials engineering, and it also belongs to the group of the most researched diatomic molecules. The research, apart from the most thoroughly studied natural $^{12}\text{C}^{16}\text{O}$ molecule, has also included isotopologues created as a result of combination of ^{12}C , ^{13}C , ^{14}C with ^{16}O , ^{17}O and ^{18}O isotopes.

The Ångström system as a result of the $B^1\Sigma^+ \rightarrow A^1\Pi$ transitions, being the subject of present analyses during the last half a century, has been studied in the following isotopomers: $^{12}\text{C}^{16}\text{O}$ [1–4], $^{13}\text{C}^{16}\text{O}$ [5–10], $^{12}\text{C}^{18}\text{O}$ [8, 11, 12], $^{14}\text{C}^{16}\text{O}$ [13, 14], $^{13}\text{C}^{18}\text{O}$ [15, 16], $^{14}\text{C}^{18}\text{O}$ [17], and recently in $^{12}\text{C}^{17}\text{O}$ [18] and $^{13}\text{C}^{17}\text{O}$ [19]. The result of studies of the CO molecule to date, carried out by means of experimental and theoretical methods, is a more thorough knowledge of its spectrum, parameters of energy structure and quantum properties, and among them, dissociation energy of this molecule. Dissociation energy D_e of carbon monoxide is a quantity that is of great and intriguing importance, not only because of the fact that its value belongs to the

highest ones among diatomic molecules [20] but it is also connected with other physicochemical quantities, for example with the latent heat of sublimation of carbon. An in-depth discussion of methods of calculation and the D_e values determined earlier are presented in monographs [21, 22]. A brief presentation of the latest results is included in section 3.3 of this paper. Undoubtedly, the most precise method of determining D_e , among others, is the one which is based on the predissociation analysis observed in spectra with the involvement of predissociated rovibronic levels. In the CO molecule this is enabled by the predissociations of the $B^1\Sigma^+$ ($v = 0, J > 37$ and $v = 1, J > 17$) as well as $b^3\Sigma^+$ ($v = 0, J > 55$ and $v = 1, J > 43$) levels observed in the $^{12}\text{C}^{16}\text{O}$ spectrum. The predissociation of the $B^1\Sigma^+$ ($v = 0$ and 1) levels was most often observed and analysed in the bands of the $B^1\Sigma^+ \rightarrow A^1\Pi$ transition [6, 23, 24], and less frequently in the $B^1\Sigma^+ - X^1\Sigma^+$ transition (Hopfield–Birge system) [25, 26]. In turn, the predissociation of the $b^3\Sigma^+$ ($v = 0$ and 1) levels was observed in the $b^3\Sigma^+ \rightarrow a^3\Pi$ transition (third positive) [27–30] but because it occurs at higher J values than in the B – A bands, it is not so valuable in this method.

The aim of this work is reanalyses in isotopomers: $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$, and new analyses in $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{18}\text{O}$ of the selected 0–1 and 1–1 bands of the Ångström system, paying special attention to the predissociation regions of the $B^1\Sigma^+$ ($v = 0$ and 1) levels. On the basis of new, extended and detailed information about the spectrum and energy of these levels, a new limiting curve of dissociation was plotted as well as a new value of dissociation energy of the CO molecule was determined. Also, atomic states of the dissociation products of this molecule were identified.

2. Experimental details

As in earlier studies of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) emission system of CO and its isotopic molecules, spectra were excited in a water-cooled Geissler-type tube. The experimental details were very similar to the ones used in the investigation of individual isotopomers and described in earlier papers from our laboratory: by Kępa and Rytel [1, 4]—for $^{12}\text{C}^{16}\text{O}$; by Rytel [7] and Kępa *et al* [9]—for $^{13}\text{C}^{16}\text{O}$; by Kępa [12]—for $^{12}\text{C}^{18}\text{O}$; by Domin *et al* [13] and Kępa [14]—for $^{14}\text{C}^{16}\text{O}$ and by Danielak *et al* [17]—for $^{14}\text{C}^{18}\text{O}$. Briefly, tubes were filled with gaseous carbon monoxide of spectral purity—for the natural $^{12}\text{C}^{16}\text{O}$ and with carbon monoxide enriched with carbon ^{13}C (about 90% of the ^{13}C isotope) for $^{13}\text{C}^{16}\text{O}$ and with radiocarbon ^{14}C (about 80% of the ^{14}C isotope) for the $^{14}\text{C}^{16}\text{O}$ spectra, respectively. In order to obtain the $^{12}\text{C}^{18}\text{O}$ molecule, a graphite element was used as one of the electrodes, and the tube was filled with oxygen that was enriched in 90% with the ^{18}O isotope. The $^{14}\text{C}^{18}\text{O}$ molecule, in turn, was synthesized from carbon ^{14}C deposited on the electrodes of the tube during a controlled discharge in gaseous $^{14}\text{C}^{16}\text{O}$ (80% of ^{14}C) and oxygen $^{18}\text{O}_2$ (90% of ^{18}O). The pressure in the tubes was 0.1 kPa during the exposure of all 1–1 bands and about 0.5 kPa during the exposure of 0–1 bands. The tubes were operated at about 6 kV and 40 mA ac. The spectra were photographed in the fifth (the 0–1 bands) and sixth (1–1 bands) orders of

a 2 m plane grating Ebert spectrograph equipped with 651 grooves mm^{-1} grating (total number of grooves was 45 600) blazed at $1.0 \mu\text{m}$. The observed resolving power was near the theoretical value and was 228 000 and 273 000 for the fifth and sixth orders and the reciprocal linear dispersion was 0.092 and 0.064 nm mm^{-1} , respectively. The exposure time on ORWO UV-1 spectral plates varied from 10 min to 2 h depending on the band and isotopomer. The emission spectral lines obtained from several overlapped orders of the spectrum and emitted from a hollow-cathode type tube were used as a calibration spectrum [31]. The relative position of the lines was measured using an automatic comparator built in our laboratory. The position of the lines on the plate was controlled interferometrically and the line profiles were scanned photoelectrically. The position of the line centres was calculated by using the least-squares procedure and assuming Gaussian profiles for the lines. The typical standard deviation of the least-squares fit by fifth or sixth order polynomials for the 30–50 calibration lines was about $(2\text{--}4) \times 10^{-3} \text{ cm}^{-1}$. Consequently, the precision of wavenumbers of molecular lines is, however, considered to be $0.005\text{--}0.010 \text{ cm}^{-1}$ excluding the blended lines marked by an asterisk. A list of experimental wavenumbers of rotational lines of the 0–1 band of the Ångström system in $^{13}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{16}\text{O}$ and the 1–1 band in $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{18}\text{O}$, and their rotational assignments are available in the electronic depository of the supplementary material (available at stacks.iop.org/JPhysB/47/045101). Additional information concerning the 0–1 and 1–1 bands in the isotopologues of CO, recorded in this work and obtained earlier, is collected in table 1.

3. Analyses and calculations

3.1. Analyses of the bands

Analyses of the bands of the Ångström system in the CO molecule have been carried out in our laboratory since the beginning of the 1970s, and they have already included most of the isotopic molecules derived from a combination of isotopes ^{12}C , ^{13}C and ^{14}C and ^{16}O , ^{18}O , and also recently ^{17}O . Therefore, our previous recordings and analyses were partly used where it was possible considering the range of a recorded spectrum and a possibility of observing predissociation. In the 0–1 bands of molecules: $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{13}\text{C}^{18}\text{O}$ and in the 1–1 band in $^{13}\text{C}^{18}\text{O}$, recorded earlier, including spectral regions that were close to the predissociation, only reexamination of their spectral lines was performed. However, for the 0–1 bands of $^{13}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{16}\text{O}$, and for the 1–1 bands of $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{18}\text{O}$, some spectra obtained earlier did not include predissociation regions; new and more extended recording of the spectra and new analyses as well as calculations of molecular constants were therefore carried out. Detailed information about the analysed spectra is provided in table 1.

3.2. Calculation of molecular constants

Reduction of the spectrum lines and calculation of the molecular constants were performed in several stages and

Table 1. Statistical details of the analysed Ångström ($B^1\Sigma^+ - A^1\Pi$) 0–1 and 1–1 bands in isotopic CO molecules.

Isotopomer	Band	Band head (cm^{-1})	$J_{\text{obs}}^{\text{max}}$			Total number of lines	$\sigma_f \cdot 10^3$ (cm^{-1}) *	Remarks
			$R(J)$	$Q(J)$	$P(J)$			
$^{12}\text{C}^{16}\text{O}$	0–1	20 675.66 ^{a,b}	36 ^{a,b}	39 ^{a,b}	39 ^{a,b}	123 ^{a,b}		Reexamined the Keça and Rytel spectrum [1]
	1–1	20 757.40 ^a	21 ^a	23 ^a	22 ^a	66 ^a	6.2 ^a	Rephotographed, recalibrated and refitted
$^{12}\text{C}^{17}\text{O}$	1–1	22 748.65 ^d	18 ^d	19 ^d	20 ^d			New observation and analysis
$^{13}\text{C}^{16}\text{O}$	0–1	20 704.46 ^a	39 ^a	40 ^a	40 ^a	118 ^a	6.8 ^a	Rephotographed, recalibrated and refitted
		20 704.46 ^c	29 ^e	34 ^e	33 ^e	96 ^e		
	1–1	22 741.24 ^a	21 ^a	21 ^a	21 ^a	61 ^a	7.9 ^a	Rephotographed, recalibrated and refitted
$^{12}\text{C}^{18}\text{O}$	0–1	20 706.52 ^{a,g}	39 ^{a,g}	40 ^{a,g}	40 ^{a,g}	109 ^{a,g}		Reexamined the Rytel [11] spectrum
			37 ^h	39 ^h	40 ^h	106 ^h		
	1–1	22 739.58 ^a	16 ^a	20 ^a	22 ^a	58 ^a	5.6 ^a	Rephotographed, recalibrated and refitted
		22 739.60 ^f	9 ^h	14 ^h	14 ^h	23 ^h		
$^{13}\text{C}^{17}\text{O}$	1–1	22 729.97 ⁱ	17 ⁱ	21 ⁱ	20 ⁱ			New observation and analysis
$^{14}\text{C}^{16}\text{O}$	0–1	20 727.49 ^a	40 ^a	41 ^a	40 ^a	121 ^a	4.7 ^a	Rephotographed, recalibrated and refitted
		20 727.47 ^j	11 ^j	19 ^j	18 ^j	47 ^j		
	1–1	22 725.03 ^a	22 ^a	23 ^a	22 ^a	66 ^a	6.4 ^a	Rephotographed, recalibrated and refitted
		22 725.10 ^j	15 ^j	20 ^j	17 ^j	49 ^j		
$^{13}\text{C}^{18}\text{O}$	0–1	20 733.58 ^{a,k}	36 ^{a,k}	40 ^{a,k}	40 ^{a,k}	111 ^{a,k}		Reexamined the Malak <i>et al</i> [15] spectrum
		20 733.58 ^l	35 ^l	39 ^l	40 ^l	109 ^l		
	1–1	22 720.50 ^{a,k}	20 ^{a,k}	21 ^{a,k}	19 ^{a,k}	58 ^{a,k}		Reexamined the Malak <i>et al</i> [15] spectrum
		22 720.50 ^l	19 ^l	20 ^l	19 ^l	56 ^l		
$^{14}\text{C}^{18}\text{O}$	1–1	20 703.86 ^a	22 ^a	24 ^a	24 ^a	69 ^a	9.8 ^a	Rephotographed, recalibrated and refitted
		20 704.08 ^m	18 ^m	21 ^m	21 ^m	59 ^m		

*Standard deviation of the fit; ^athis work; ^bafter Keça and Rytel [1a]; ^cafter Le Floch and Amiot [3]; ^dafter Hakalla *et al* [40]; ^eafter Hakalla *et al* [10]; ^fafter Rytel [7]; ^gafter Rytel [11a]; ^hafter Rytel [11]; ⁱafter Hakalla *et al* [41]; ^jafter Domin *et al* [13]; ^kafter Malak *et al* [15a]; ^lafter Malak *et al* [15]; ^mafter Danielak *et al* [17].

by using the well-known Hamiltonians of both rovibronic states involved in this transition. The upper $B^1\Sigma^+$ state was represented by

$$\langle H \rangle = T^B + B_v \cdot J(J+1) - D_v J^2(J+1)^2 + \dots, \quad (1)$$

and the lower $A^1\Pi$ state by

$$\langle H \rangle = T^A + B_v \cdot [J(J+1) - 1] - D_v \cdot [J(J+1) - 1]^2 + \dots, \quad (2)$$

where T^B and T^A are the rotationless energies calculated with respect to the lowest rovibrational level in the ground $X^1\Sigma^+$ state for the $B^1\Sigma^+$ and $A^1\Pi$ states, respectively, and B_v and D_v rotational constants.

For the calculation of B_v and D_v , rotational constants of the $v = 0$ and $v = 1$ levels of the $B^1\Sigma^+$ state, the linear least-squares method proposed by Curl and Dane [32], and Watson [33] was applied. By this method, there is a possibility of separating information about the upper $B^1\Sigma^+$ state, which is considered to be regular in all analysed isotopologues, and information about the lower perturbed $A^1\Pi$ ($v = 1$) level. Currently calculated and previously determined rotational constants B_v and D_v of the $v = 0$ and $v = 1$ levels of the $B^1\Sigma^+$ state are gathered in table 2. On the basis of currently determined rotational constants: B_0 and B_1 and D_0 and D_1 of the $B^1\Sigma^+$ state and derived from previous analyses constants B_1 and D_1 of the lower $A^1\Pi$ state for $^{12}\text{C}^{16}\text{O}$ [34], $^{13}\text{C}^{16}\text{O}$ [10], $^{12}\text{C}^{18}\text{O}$ [35], $^{14}\text{C}^{16}\text{O}$ [36] and $^{14}\text{C}^{18}\text{O}$ [37], and using

equations (1) and (2) by means of the least-squares method band origins: $\nu_0(0-1)$ and $\nu_0(1-1)$ of the Ångström system were calculated in the analysed isotopologues of CO. Currently determined as well as previously obtained values are also gathered in table 2.

3.3. Predissociation of $B^1\Sigma^+$ and calculation of the dissociation energy of CO

The effect of predissociation of the $B^1\Sigma^+$ state appears as a sudden drop of intensity observed in emission lines in the $B^1\Sigma^+ \rightarrow A^1\Pi$ and $B^1\Sigma^+ \rightarrow X^1\Sigma^+$ transitions for lines above certain critical values of the rotational number which we denote as J^h . For the lines involved in the $v = 0$ level, $J^h = 37$, and for the $v = 1$ level, $J^h = 17$, there was no observation of emission lines originating from the $v > 1$ levels in $^{12}\text{C}^{16}\text{O}$. For the first time sudden weakening of the intensity of emission lines in the 0–1 Ångström band in $^{12}\text{C}^{16}\text{O}$ had been observed by Coster and Brons [23]. Schmid and Gerö [24] confirmed these observations, and they also observed a similar effect in the 1–0 and 1–1 band lines originating in the $v^B = 1$ level. After two decades Douglas and Møller [6] confirmed all the previous observations concerning the weakening of lines in the $^{12}\text{C}^{16}\text{O}$ molecule. They also observed similar effects in the corresponding bands in $^{13}\text{C}^{16}\text{O}$. In the $B - X$ transition Read [25] observed the predissociation of the $B(v = 0)$ level in $^{12}\text{C}^{16}\text{O}$, and Eidelberg *et al* [26] expanded and documented

Table 2. Molecular constants (in cm^{-1}) of the $B^1\Sigma^+$ ($v = 0$ and 1) levels for isotopic CO molecules^a.

	$^{12}\text{C}^{16}\text{O}$	$^{13}\text{C}^{16}\text{O}$	$^{12}\text{C}^{18}\text{O}$	$^{14}\text{C}^{16}\text{O}$	$^{14}\text{C}^{18}\text{O}$
B_0		1.862 520(43) ^b 1.862 5054(67) ^c 1.862 517(55) ^e 1.862 58(14) ^g		1.789 349(30) ^b 1.789 24(16) ^d 1.789 343(14) ^f	
$D_0 \cdot 10^6$		6.135(21) ^b 6.1384(52) ^c 6.142(28) ^e 6.178(48) ^g		5.648(15) ^b 5.593(22) ^d 5.6573(60) ^f	
$\nu_0(0-1)$		20 711.0541(64) ^b 20 711.0586(98) ^c 20 711.067(12) ^e		20 733.801(20) ^b 20 735.236 ^d	
B_1	1.921 833(11) ^b 1.921 87(10) ^h 1.921 902(20) ^g 1.921 620(152) ^f	1.837 729(69) ^b 1.838 234(49) ^e 1.838 10(20) ^g	1.830 743(95) ^b 1.830 85(28) ⁱ 1.831 00(42) ^g	1.766 689(93) ^b 1.766 98(39) ^d	1.675 45(18) ^b 1.6763(5) ^j
$D_1 \cdot 10^6$	7.21(15) ^b 7.28(32) ^h 7.36(15) ^g 5.979(692) ^f	6.695(89) ^b 6.748(67) ^e 6.69(13) ^g	6.15(29) ^b 6.35(54) ^g	6.13(17) ^b 7.337(67) ^d	5.06(27) ^b 5.9(10) ^j
$\nu_0(1-1)$	22 765.7940(62) ^b 22 765.17(2) ^k	22 748.2228(39) ^b 22 748.185(19) ^e 22 749.75(3) ^l	22 746.5446(24) ^b 22 747.98(5) ⁱ	22 731.7932(76) ^b 22 733.307 ^d	22 710.2847(38) ^b 22 710.33(3) ^j

^a Values in parentheses denote one standard deviation, excluding Eidelsberg *et al* [26] data (3σ), in units of the last quoted digit; ^bthis work; ^cafter Hakalla *et al* [10]; ^dafter Domin *et al* [13]; ^eafter Keřa *et al* [9]; ^fafter Amiot *et al* [53]; ^gafter Eidelsberg *et al* [26]; ^hafter Le Floch and Amiot [3]; ⁱafter Rytel [11]; ^jafter Danielak *et al* [17]; ^kafter Keřa and Rytel [1]; ^lafter Rytel [7].

these observations for the $v = 0$ and 1 levels in molecules: $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ and $v = 1$ in $^{13}\text{C}^{18}\text{O}$. The weakening of rotational lines involved in $B(v = 1)$ with $J > 17$ in $^{12}\text{C}^{16}\text{O}$ and with $J > 19$ in $^{13}\text{C}^{16}\text{O}$ has also been observed by Klopotek and Vidal [38], and Rottke and Zacharias [39] in their laser VUV excitation experiments.

In this work we observed the predissociation in the $v = 0$ and $v = 1$ or only in the $v = 1$ levels of the $B^1\Sigma^+$ state in eight isotopologues of the CO molecule on the basis of the spectra of the Ångström bands:

- previously recorded 0–1 bands of $^{12}\text{C}^{16}\text{O}$ [1a], $^{12}\text{C}^{18}\text{O}$ [11a], $^{13}\text{C}^{18}\text{O}$ [15a] and the 1–1 band of $^{13}\text{C}^{18}\text{O}$ [15a],
- currently recorded and analysed 0–1 bands of $^{13}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{16}\text{O}$ and the 1–1 bands of $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{18}\text{O}$,
- recorded and reanalysed by Hakalla *et al* the 1–1 bands of $^{12}\text{C}^{17}\text{O}$ [40] and $^{13}\text{C}^{17}\text{O}$ [41]. Figure 1 presents microdensitometer trace of the overexposed 1–1 band of $^{12}\text{C}^{16}\text{O}$ with a sudden drop of intensity of lines in regions of predissociation in $P(J)$, $Q(J)$ and $R(J)$ branches.

On the basis of the analysed spectra of all isotopologues, the information about the quantum numbers of the highest nonpredissociated J^h level was obtained as well as the information about the wavenumbers of lines: $P(J^h + 1)$, $Q(J^h)$, and $R(J^h - 1)$ as well as the first predissociated J^f level, and the wavenumbers of lines connected with them. Next, the wavenumbers of lines were recalculated to term values of the

$B^1\Sigma^+$ state, namely $T^B(v, J)$ for $v = 0$ and J^h , $v = 0$ and J^f , as well as $v = 1$ and J^h and $v = 1$ and J^f , relative to the potential curve minimum of the ground $X^1\Sigma^+$ state of $^{12}\text{C}^{16}\text{O}$. The values of rotational constants B_1 and D_1 of the $A^1\Pi$ state, necessary for the above calculations, were taken from the previous analyses in $^{12}\text{C}^{16}\text{O}$ [34], $^{12}\text{C}^{17}\text{O}$ [18], $^{13}\text{C}^{16}\text{O}$ [10], $^{12}\text{C}^{18}\text{O}$ [35], $^{13}\text{C}^{17}\text{O}$ [19], $^{14}\text{C}^{16}\text{O}$ [36], $^{13}\text{C}^{18}\text{O}$ [42] and $^{14}\text{C}^{18}\text{O}$ [37] isotopologues. The source of vibronic constants of the $A^1\Pi$ state in $^{12}\text{C}^{16}\text{O}$ was, however, the work by Field [43], and for the $X^1\Sigma^+$ state the data of Le Floch [44] and their standard isotopic recalculations for all analysed isotopologues. The information obtained about the highest nonpredissociated and the first already predissociated rovibronic levels for each isotopic molecule is collected in table 3. Next, the determined term values corresponding to these levels are plotted against $J(J + 1)$, and are presented in figure 2. From this plot we were able to draw a new limiting curve of dissociation for the CO molecule, developed by Schmid and Gerö [45]. An analogous assumption was made as in the previous calculations of the dissociation energy of the CO molecule that the limiting curve is a straight line and that it was extrapolated to $J = 0$. By means of the weighted least-squares method and taking into account Watson's suggestion [46] concerning so-called outliers, a new value of the dissociation energy was determined, which is now: $\mathcal{D}_e = (90\,679.1 \pm 6.0) \text{ cm}^{-1}$. The values of dissociation energy of CO, currently determined and obtained from the previous analyses of the predissociation of the $B^1\Sigma^+$ state, are collected in table 4.

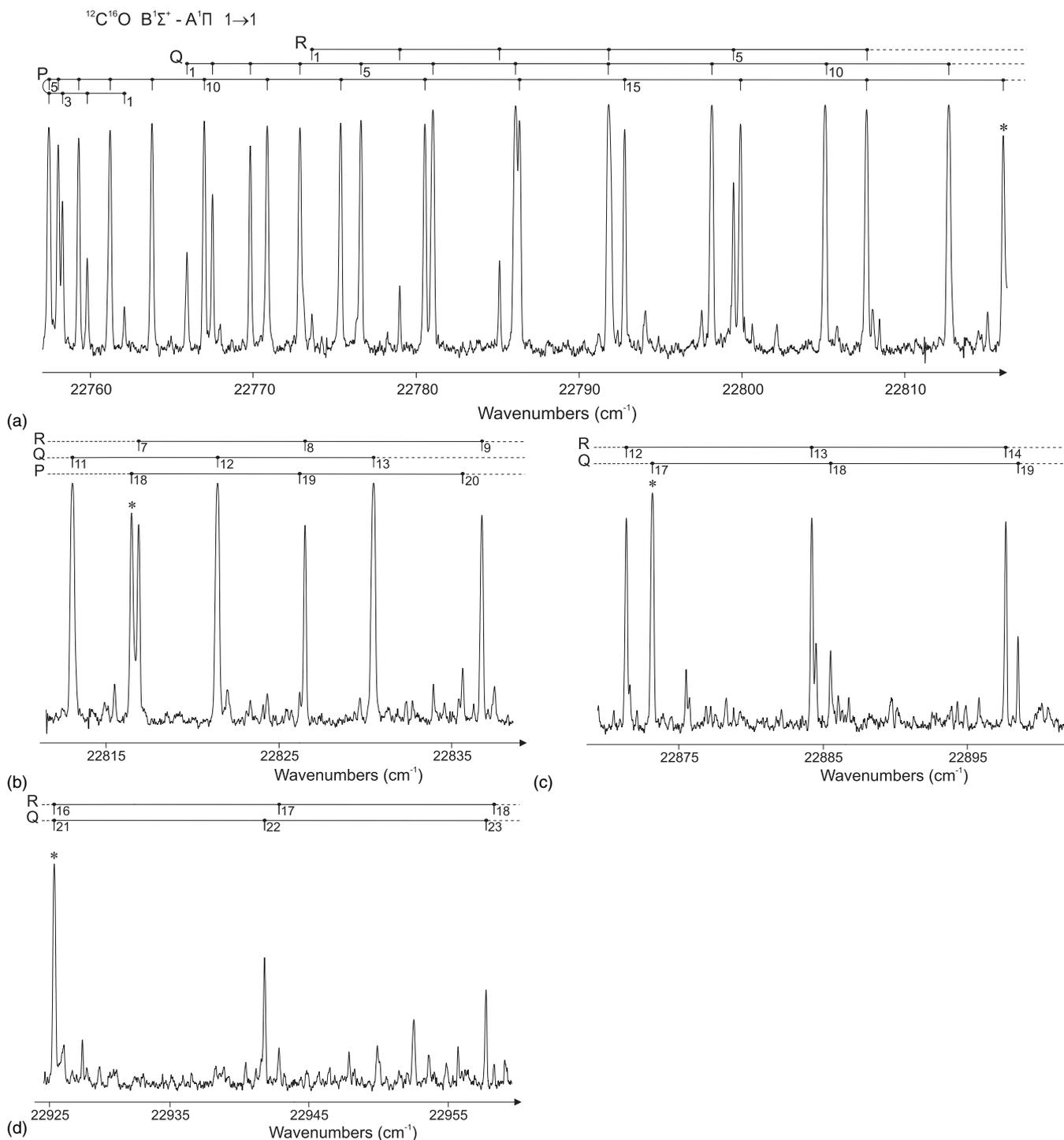


Figure 1. Densitometer trace and the rotational assignments of the 1–1 band spectrum of the Ångström system of $^{12}\text{C}^{16}\text{O}$: (a) general view of the band; the region of predissociation of: (b) $P(J)$ branch, (c) $Q(J)$ branch, (d) $R(J)$ branch. Lines marked by an asterisk are the last nonpredissociated lines observed in $P(J)$, $Q(J)$ and $R(J)$ branches.

4. Discussion and conclusions

The analyses of high resolution spectra of the Ångström ($B^1\Sigma^+ \rightarrow A^1\Pi$) 0–1 and 1–1 bands carried out currently in the most numerous group of isotopologues of the CO molecule provide the most extensive and precise information on the rovibronic structure, especially in regions of predissociation of the $B^1\Sigma^+(v = 1)$ level in the analysed isotopomers.

Inclusion of five new isotopologues in the analysis of regions of predissociation of the $v^B = 1$ level increases the weight of experimental data and precision of the determined value of dissociation energy. However, the lack of information on the predissociation of the $v^B = 2$ level, which even in the heaviest $^{14}\text{C}^{18}\text{O}$ isotopomer lies more than 1000 cm^{-1} above the dissociation energy limit and which for all rotational levels J is quasibound, does not allow for determining the

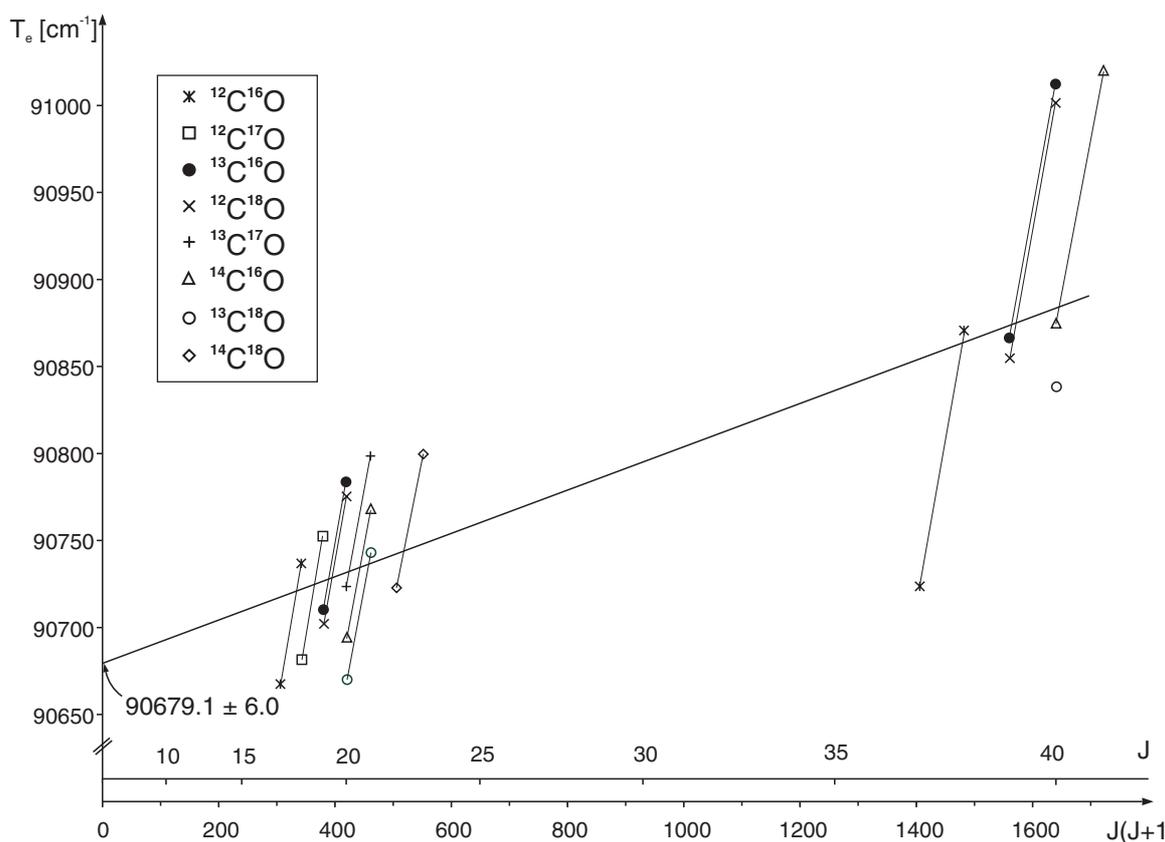


Figure 2. Limiting curve of dissociation for the $X^1\Sigma^+$ ground state of the CO molecule.

Table 3. Term values (in cm^{-1}) of the highest (h) nonpredissociated and first (f) predissociated rovibronic levels of the $B^1\Sigma^+$ state in isotopic CO molecules.

Isotopomer	v	J^h	J^f	$T_e^h(J)$	$T_e^f(J)$	Remarks
$^{12}\text{C}^{16}\text{O}$	0	37	38	90 723.71 ^a	90 870.68 ^a	Reanalysis of predissociation
				90 723.46 ^b	90 870.33 ^b	
	1	17	18	90 667.52 ^a	90 736.92 ^a	
$^{12}\text{C}^{17}\text{O}$	1	18	19	90 681.60 ^{a,c}	90 752.50 ^{a,c}	First observation of predissociation
				90 667.19 ^b	90 736.19 ^b	
$^{13}\text{C}^{16}\text{O}$	0	39	40	90 866.36 ^a	91 012.28 ^a	Reanalysis of predissociation
				90 864.91 ^b	91 012.33 ^b	
	1	19	20	90 710.34 ^a	90 783.70 ^a	
$^{12}\text{C}^{18}\text{O}$	0	39	40	90 854.74 ^a	91 001.38 ^a	First observation of predissociation
				90 702.14 ^a	90 775.26 ^a	
$^{13}\text{C}^{17}\text{O}$	1	20	21	90 723.61 ^{ad}	90 798.55 ^{ad}	First observation of predissociation
$^{14}\text{C}^{16}\text{O}$	0	40	41	90 874.91 ^a	91 020.11 ^a	First observation of predissociation
				90 694.52 ^a	90 768.47 ^a	
$^{13}\text{C}^{18}\text{O}$	0	40	41*	90 838.27 ^a		First observation of predissociation
				90 670.06 ^a	90 743.21 ^a	
	90 668.52 ^b	90 741.67 ^b				
$^{14}\text{C}^{18}\text{O}$	1	22	23	90 722.83 ^a	90 799.65 ^a	First observation of predissociation

^a This work.

^b After Eidelsberg *et al* [26].

^c Calculated from Hakalla *et al* [40] results.

^d Calculated from Hakalla *et al* [41] results.

* Predicted.

Table 4. Dissociation energy of the CO molecule (in cm^{-1}) obtained from predissociation of the $B^1\Sigma^+$ state.

	\mathcal{D}_e^a	\mathcal{D}_0^b	n^c
This work	$90\,679.1 \pm 6.0^d$	$89\,597.3 \pm 6.0^d$	12
After Eidelsberg <i>et al</i> [26]	$90\,674 \pm 15^e$	$89\,592 \pm 15^e$	5
After Douglas and Møller [6]	$90\,677 \pm 30^e$	$89\,595 \pm 30^e$	4
After Schmid and Gerö [45]	$90\,702 \pm 50^e$	$89\,620 \pm 50^e$	2
After Coster and Brons [23]	$90\,822^f$	$89\,740^f$	1

^a Above the potential curve minimum of the $X^1\Sigma^+$ ground state.

^b Above the $v = 0$ level of the ground state.

^c Number of pairs of experimental data.

^d One standard deviation.

^e Estimated error.

^f Estimated value.

real shape of the limiting curve of dissociation and it also makes us assume that this limiting curve is a straight line. Dissociation energy calculation based on the data obtained for eight isotopologues of CO, apart from the above assumption, was based on a more general limitation, that is, on the Born–Oppenheimer approximation. Consequently, the dissociation energy \mathcal{D}_e can be assumed to be isotopically invariant. The fact that it was possible to pass one smooth line through 12 pairs in experimental points derived from eight isotopologues can indicate that the interpretation of the observed weakening of the rotational lines as a predissociation effect is a reasonable one and it also excludes the possibility that the observed effects were due to perturbations. Also, the constant tangent of an inclination angle of the limiting curve line indicates that the potential curve of the $B^1\Sigma^+$ state has a maximum even without taking the rotation into account. The currently determined value of dissociation energy $\mathcal{D}_e = (90\,679.1 \pm 6.0) \text{ cm}^{-1}$ confirms that the $B^1\Sigma^+$ state predissociates towards the lowest dissociation limit of CO and its $C(^3P) + O(^3P)$ atomic products, and also the remaining possibilities of combinations of the atomic states, i.e. $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ [6, 22] are excluded. Higher precision of the determined value \mathcal{D}_e enables us to identify triplet splitting components of both carbon and oxygen atoms as $C(^3P_0) + O(^3P_2)$ i.e. as their respective triplet ground sublevels.

Identification of the state predissociating the $B^1\Sigma^+$ state still remains an open question. The consequence of the interaction of the $C(^3P)$ and $O(^3P)$ states is, however, the possibility of forming 18 bound molecular states including: two states of the $^1\Sigma^+$ type and one $^1\Sigma^-$; two states $^1\Pi$ and one $^1\Delta$; two $^3\Sigma^+$ and one $^3\Sigma^-$; two $^3\Pi$ and one $^3\Delta$; two states of the $^5\Sigma^+$ type, two $^5\Pi$ and one $^5\Delta$ [47, 48]. According to Mulliken's [49] considerations and our observations confirming the decrease of rotational quantum number of the highest nonpredissociated level J^h with increasing vibrational level v and decreasing reduced mass of the isotopologue, the state which predissociates the $B^1\Sigma^+$ state crosses it on the right-hand side of its potential curve. Therefore, we should exclude all known low-lying states of

CO, i.e., $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, $e^3\Sigma^-$, $a^3\Sigma^+$, $I^1\Sigma^-$ and $D^1\Delta$ [50, 51] as the ones involved in the process of predissociation of the B state. Also, the $D^1\Sigma^+$ state, considered previously as the one that predissociates the B state according to the theoretical and quantitative calculation of Tchang-Brillet *et al* [52], should be excluded as responsible for this process. In conclusion, the weakening of the emission lines observed in the bands, in which the $B^1\Sigma^+$ state is involved as the upper one and in $v = 0$, $J > 37$ and $v = 1$ and $J > 17$ levels of $^{12}\text{C}^{16}\text{O}$, is highly likely to be caused by predissociation of a still unknown mechanism of interaction and still unidentified states of this molecule.

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