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Reinvestigation of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system in the CO$^+$ molecule

The $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system in CO$^+$

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Abstract. Conventional, high resolution molecular spectroscopy has been employed to record emission spectra of the first negative bands system in the ^{12}C^{16}O$^+$ molecule. Twenty two bands form the $0-v'', 1-v'', 2-v'', 3-v'', 4-v'', 5-v''$ progressions and 6-10 band were photographed in the 34000−46000 cm^{-1} spectral region. The reduction of the spectrum for the individual bands has been performed via a nonlinear least-squares fit with the effective Hamiltonians of Brown et al. [J. Mol. Spectrosc. **74**, 294 (1979)]. The final molecular constants for both the $B^2\Sigma^+$ ($v = 0-6$) and $X^2\Sigma^+$ ($v = 0-10$) states were obtained from global merge calculations of the present data of the $B \rightarrow X$ system and previously obtained in our laboratory data for $A \rightarrow X$ and $B \rightarrow A$ systems in the CO$^+$ molecule. Merged molecular parameters have been used in order to the determine the equilibrium constants for both considered states. The $\gamma_e = 2.194(14) \times 10^{-2}$ cm^{-1} and $\alpha_{\gamma e} = -1.021(64) \times 10^{-4}$ cm^{-1} constants for the $B^2\Sigma^+$ state were obtained for the first time. The RKR potentials have been calculated for both combining states, as well as Franck-Condon factor and r-centroids for the first negative system in the ^{12}C^{16}O$^+$ molecule. Furthermore, we report the value of the electronic isotopic shift $\Delta\nu_e = -0.395$ cm $^{-1}$ of the $B \rightarrow X$ system in ^{13}C^{16}O$^+$, calculated on the basis the presents results and those obtained by us previously for the ^{13}C^{16}O$^+$ molecule.

PACS. 33.20.Lg Ultraviolet spectra

1 Introduction

The carbon monoxide positive ion is one of the basic diatomic cations and has a very important place in the history of spectroscopic studies of diatomic molecules, and its importance in astrophysics research is generally known. Its presence has been revealed in a number of different objects: stars, molecular clouds, atmosphere of planets and tails of comets. The four bands systems are observed in the emission spectrum of the CO$^+$ molecule as a result of the transitions between the: $X^2\Sigma^+$, $A^2\Pi_i$, $B^2\Sigma^+$ and $C^2\Delta_r$ electronic states. These systems have been distinguished as Comet-Tail ($A^2\Pi_i \rightarrow X^2\Sigma^+$), first negative ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$), Baldet-Johnson ($B^2\Sigma^+ \rightarrow A^2\Pi_i$) and Marschand-D'Incan-Janin ($C^2\Delta_r \rightarrow A^2\Pi_i$) systems respectively.

Many experimental investigations on the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system in the CO$^+$ molecule have been carried out: Blacburn [1], Schmid [2], Coster et al. [3], Schmid and Gerö [4], Woods [5]. In 1950 Rao [6] reanalysed fifteen bands of this system with $v' = 0-4$ and $v'' = 0-7$. The experimental conditions he applied allowed him to record in the spectrum lines with very high values of the quantum number J (J up to 40).

Misra et al. [7], in 1987, reexamined the 0-0, 0-1 and 0-2 bands of the $B \rightarrow X$ system, at a linear dispersion of about 0.069 Å/mm. In this work they performed global merge calculations, including their data and Rao's earlier data [6] and recent microwave observations [9–11].

In 1992, Haridass et al. [8] investigated the Comet-Tail system made in the same manner, global fit for the CO$^+$ molecule including all experimental data from optical [6,7,12], infrared [14] and microwave [10,11] studies.

Consistence between the results achieved in the works quoted does not takes place in case of values of γ_v constants for both $B^2\Sigma^+$ and $X^2\Sigma^+$ states. Despite applying a similar calculation method and partly identical experimental data, the values obtained for the γ_v constants show significant differences, far beyond 3σ limits (see Tabs. 2 and 3). A similar situation arise while comparing these values with those obtained from $B^2\Sigma^+ \rightarrow A^2\Pi_i$ system analysis [12,13].

Recently, the present authors [15] carried out an analysis of the six bands, 4-6, 4-7 (reanalysis), 4-8, 5-8, 5-9 and 6-10, deriving new molecular parameters for the unobserved levels of the $B^2\Sigma^+$ ($v = 5, 6$) and $X^2\Sigma^+$

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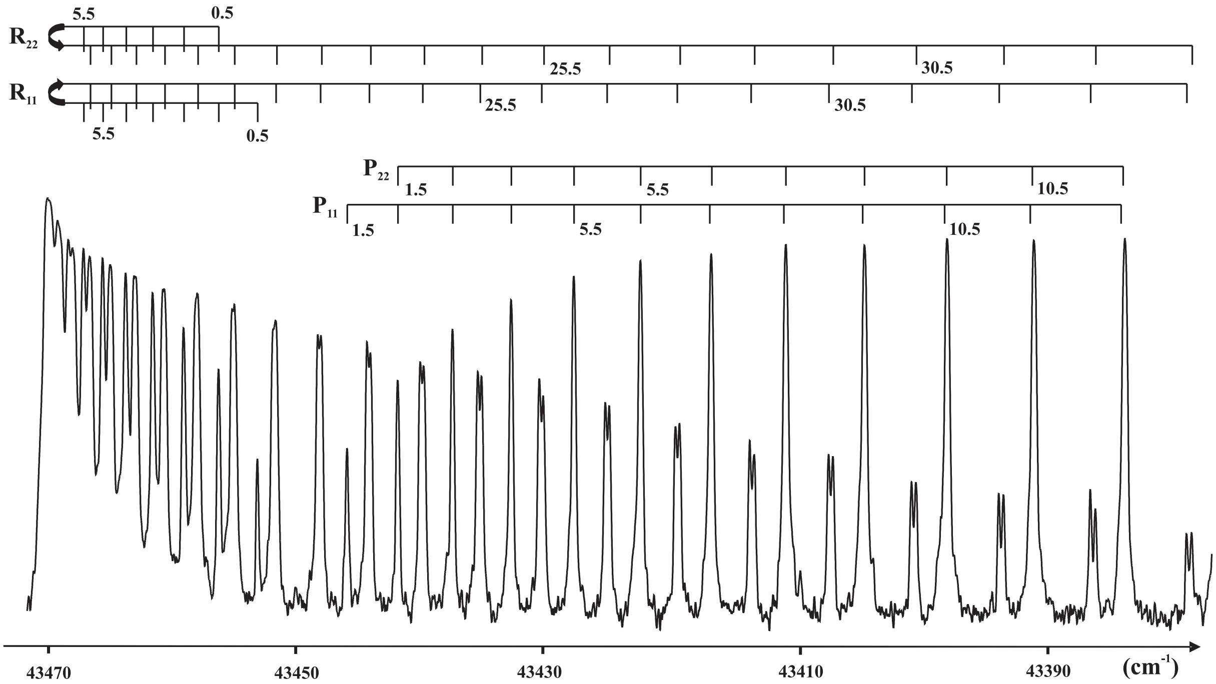

Fig. 1. A portion of the 0-1 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system in the emission spectrum of the CO$^+$ molecule.

(v = 8, 9, 10) states of ^{12}C^{16}O$^+$. In this work, we remark significant differences between the constants obtained from experimental data and those calculated on the basis of equilibrium parameters given by Haridass et al. [8]. It demonstrate the unreliability of the extrapolation of molecular constants for higher vibrational levels.

The present reinvestigations of the first negative bands system were undertaken in order to broaden, generalize and make the spectroscopic and quantum-mechanical information about the second excited $B^2\Sigma^+$ state more precise. With this end in view, we recorded 22 bands of the first negative system under high resolution conditions again. In the global calculations, we merged all of the experimental data concerning CO$^+$ molecule obtained in our laboratory in recent years. From this global fit, a unique set of molecular parameters for the $X^2\Sigma^+$, $A^2\Pi_i$ and $B^2\Sigma^+$ states and band origins of all the bands used in the analysis of ^{12}C^{16}O$^+$ were obtained. The results for $B^2\Sigma^+$ and $X^2\Sigma^+$ states, are summarized in Section 3. Experimental details are given in Section 2, the summary is presented in Section 4.

2 Experimental details

The emission spectrum of the first negative band system of CO$^+$ has been obtained from an air cooled hollow cathode tube. The lamp was filled with ^{12}C^{16}O$_2$ gas at the total pressure of about 0.1 kPa. The lamp was operated at about 600 V and 50 mA dc. Spectra were obtained by using a 2-m Ebert plane grating PGS-2 spectrograph equipped with a 651-grooves/mm grating with a total number of grooves of 45 600, blazed at 1.0 μm. The observations were made in the 10th, 11th and 12th orders, which permitted obtaining a spectrum with a linear dispersion in the range from 0.033 to 0.043 nm/mm and with a theoretical resolving power of 450 000–500 000. The exposure time on the ORWO UV - 1 plates varied from 6 to 12 hours, depending on the band intensity and the grating order used. The applied experimental conditions permitted one to record spectra with the resolution sufficient to observe a very small value of the spin splitting of the lines. The spectra were calibrated by the Th lines (Palmer and Engleman [16]) emitted from a water-cooled hollow-cathode lamp. The measurements were carried out carefully using an automatic interferometric comparator assembled in our laboratory. The positions of the line centers were calculated by using the least-squares procedure and assuming Gaussian profiles for the lines. For the wavenumber calculations seventh-order interpolation polynomials were used. The typical standard deviation of the least-squares fit for the 40-60 calibration lines was about $(1.4–1.9)\times10^{-3}$ cm^{-1}. Consequently, the precision of the fully resolved lines with a good line/background ratio was estimated to be 0.005–0.020 cm^{-1}. Lines whose deviations were higher than three standard deviation and unresolved lines, with low J values ($J \leq 6.5$), were excluded from the calculations of molecular constants. A portion of the rotational structure of the 0-1 band of the $B \rightarrow X$ system of the ^{12}C^{16}O$^+$ molecule is shown in Figure 1. A complete list of experimental wavenumbers rotational lines and their assignments for all bands of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system analyzed in this work is available from: `http://www.fonon.univ.rzeszow.pl/zfam/12c16o_plus/bx/`.

Table 1. Summary of observations and analyses of the first negative ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) system of the CO$^+$ molecule.

band	band origin[a] (cm^{-1})	number of lines		f	J_{max}	$\sigma \times 10^2$ (cm^{-1})
		b	c			
0-0	47281.9095(20)	156	(70)	84	42.5	1.34
0-1	43499.750(13)	158	(111)	73	41.5	1.75
0-2	41296.1483(86)	148	(111)	85	40.5	1.77
0-3	39172.8956(57)	153	(120)	39	39.5	1.51
0-4	37080.015(21)	119	(60)	46	33.5	1.96
1-2	42975.5150(86)	139	(121)	73	36.5	1.65
1-3	40852.2623(57)	150	(110)	33	42.5	0.95
1-4	38759.381(21)	162	(106)	53	41.5	1.55
1-5	36696.807(24)	159	(93)	49	41.5	1.65
2-3	42478.7288(57)	74	(68)	41	22.5	1.84
2-4	40385.848(21)	132	(119)	77	39.5	1.28
2-5	38323.247(24)	167	(119)	69	43.5	1.36
2-6	36291.100(33)	118	(99)	57	30.5	1.35
3-5	39898.915(24)	97	(91)	46	37.5	1.17
3-6	37866.742(33)	130	(92)	69	36.5	1.34
3-7	35864.954(45)	92	–	49	27.5	1.62
4-6	39394.049(33)	102	–	54	27.5	1.30
4-7	37392.262(45)	128	(78)	66	33.5	1.51
4-8	35421.012(83)	91	–	33	29.5	2.73
5-8	36902.493(83)	114	–	72	33.5	0.91
5-9	34961.591(27)	67	–	32	22.5	2.14
6-10	34489.433(14)	45	–	27	30.5	2.22

[a] Values from final merging: number in parentheses represents one standard deviation in units of the last quoted digit. [b] Present investigations. [c] From Rao [6]. f is the number degrees of freedom. J_{max} is the maximum values of the quantum number J for the observed lines. σ is the standard deviation of the fit.

3 Analysis and calculations

The first negative system in the CO$^+$ molecule spectrum is formed as a result of transitions between the second excited $B^2\Sigma^+$ state and the $X^2\Sigma^+$ ground state. Both the states involved belong to Hund's case (b). All bands of the first negative system form a simple and regular structure doublet R (R_{11ee}, R_{22ff}) and P (P_{11ee}, P_{22ff}) branches. Here the subscripts 1 and 2 refer to the F_1 and F_2 components respectively, and e/f refer to the parities of the rotational level. The notation used is in agreement with that introduced by Brown et al. [17].

3.1 Band by band rotational analysis

In the first step of analysis, the experimental wavenumbers of lines were reduced to rotational parameters for individual bands. For this purpose the non-linear least-squares procedure has been used. In this method both analyzed states are represented by effective Hamiltonian from Brown et al. [19]. Amiot et al. [20] gave a complete list of the matrix elements of this Hamiltonian for the $^2\Sigma^+$ state, which were used in this work. Table 1 presents the statistical data of the least-squares fits for individual bands. In this way each band has been described by a set of the molecular parameters: the rotational constants B_v, D_v and the spin-rotation interaction constant γ_v as well as origins ν_0 of the bands.

The large correlation between the γ'_v and γ''_v parameters did not allow up to compute values for these constants simultaneously. For these constants diagonal and above-diagonal elements of the freedom matrix [21] had values near zero. For this reason, during the individual reduction of the bands, the values of the γ''_v for the lower state were constrained to very precise values obtained from equilibrium constants given by Bogey et al. [11].

3.2 Global fit

To obtain a precise set of molecular constants, we performed a global least-squares analysis using the method proposed by Albritton et al. [22] and by Coxon [23]. This fit included 39 vibrational transitions of the: $A \rightarrow X$ systems [24] (11 bands), $B \rightarrow A$ system [13] (7 bands) and $B \rightarrow X$ system (21 bands) in the emission spectrum of the $^{12}C^{16}O^+$ molecule. As this method requires that the bands have at least one vibrational level in common, the 6-10 band of the $B \rightarrow X$ system had to be excluded from the fit. In this merged calculation, 295 initial molecular parameters were reduced to 125 parameters (39 band origins + 86 molecular constants) describing altogether 26 vibrational levels in the $X^2\Sigma^+$ ($v = 0 - 10$), $A^2\Pi_i$ ($v = 0{-}4, 6, 7, 8$) and $B^2\Sigma^+$ ($v = 0{-}6$) states of $^{12}C^{16}O^+$. The estimated variance of the merging was $\sigma_M^2 = (1.78)^2$ and the number of degrees of freedom was $f_M = 170$.

Table 2. Molecular constants (in cm^{-1}) of the $B^2\Sigma^+$ state of CO^{+a}.

v	B_v	$D_v \times 10^6$	$\gamma_v \times 10^2$
0	1.784661(15)	7.975(16)	2.1339(92)
	1.784770(3)^b	8.051(1)^b	1.918(5)^b
	1.784787(45)^c	8.078(37)^c	1.664(66)^c
1	1.754589(17)	8.150(19)	2.065(12)
	1.754607(5)^b	8.249(3)^b	1.857(6)^b
	1.75466(10)^c	8.274(58)^c	1.51(13)^c
2	1.724232(22)	8.422(25)	1.936(12)
	1.724234(9)^b	8.448(6)^b	2.041(13)^b
	1.72433(11)^c	8.496(71)^c	1.23(14)^c
3	1.693906(34)	8.608(31)	1.824(16)
	1.693822(49)^b	8.560(26)^b	1.785(18)^b
	1.69393(20)^c	8.63(13)^c	1.35(22)^c
4	1.663777(47)	8.717(51)	1.843(22)
	1.664088(121)^b	8.977(97)^b	0.94(35)^b
5	1.634137(89)	8.929(92)	1.815(19)
6	1.60690(27)	9.181^d	1.534(42)

^{a} Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. ^{b} After Haridass et al. [8]. ^{c} After Misra et al. [7]. ^{d} The D_v value recalculated from the $^{13}\mathrm{C}^{16}\mathrm{O}^+$ equilibrium parameters of Kępa et al. [18] using the isotopic relationship within the Born-Oppenheimer approximation.

The rotational constants obtained from the merged calculation for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states are summarized in Tables 2 and 3, respectively.

The spin-rotation interaction constants γ_v, for $B^2\Sigma^+$ (see Tab. 2), show differences from those obtained earlier [7,8]. We also think that thanks to the method described above, the constants we have obtained are more reliable. Figure 2 presents the dependence of the γ_v constants on vibrational quantum number v for $B^2\Sigma^+$ and their comparison with previous data. For the calculations of equilibrium rotational parameters the B_v, D_v and γ_v values listed in Tables 2 and 3 have been fitted to the standard spectroscopic relations:

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \varepsilon_e\left(v+\frac{1}{2}\right)^3, \tag{1}$$

$$D_v = D_e + \beta_e\left(v+\frac{1}{2}\right), \tag{2}$$

$$\gamma_v = \gamma_e + \alpha_{\gamma e}\left(v+\frac{1}{2}\right). \tag{3}$$

It should be noted, that the values $\gamma_e = 2.194(14) \times 10^{-2}\ \mathrm{cm}^{-1}$ and $\alpha_{\gamma e} = -1.021(64) \times 10^{-4}\ \mathrm{cm}^{-1}$ for the $B^2\Sigma^+$ state have been obtained for the first time. In this calculations the γ_v constants for the $v = 4$ and 5 levels were excluded from the fit. The results and their standard deviation are collected in Table 4.

Table 3. Molecular constants (in cm^{-1}) of the $X^2\Sigma^+$ state of CO^{+a}.

v	B_v	$D_v \times 10^6$	$\gamma_v \times 10^3$
0	1.967459(13)	6.317(14)	[9.105]
	1.96746255(3)^b	6.330(26)^b	9.1052(3)^b
	1.9674656(31)^c	6.354(38)^c	9.1051(89)^c
1	1.948449(18)	6.346(19)	[9.045]
	1.94843464(9)^b	5.916(26)^b	9.0485(4)^b
	1.9484388(43)^c	6.344(47)^c	9.048(12)^c
2	1.929399(16)	6.371(16)	[8.965]
	1.9293521(1)^b	6.380(3)^b	8.9730(5)^b
	1.929479(63)^c	6.437(41)^c	8.46(25)^c
3	1.910240(13)	6.424(17)	[8.862]
	1.910234(5)^b	6.404(3)^b	9.72(8)^b
	1.910331(97)^c	6.464(58)^c	9.7(1.2)^c
4	1.890945(23)	6.390(24)	[8.734]
	1.890976(6)^b	6.422(4)^b	11.98(12)^b
	1.89107(11)^c	6.468(70)^c	4.9(1.6)^c
5	1.871708(24)	6.450(24)	[8.582]
	1.87170(2)^b	6.424(4)^b	10.70(12)^b
	1.87176(13)^c	6.466(84)^c	6.3(1.7)^c
6	1.852381(36)	6.433(37)	[8.406]
	1.85247(1)^b	6.562(11)^b	13.58(20)^b
	1.85255(17)^c	6.59(12)^c	4.9(2.0)^c
7	1.833008(54)	6.515(61)	[8.200]
	1.83332(12)^b	6.710(95)^b	5.5(3.5)^b
8	1.813645(82)	6.647(80)	[7.982]
9	1.79361(39)	5.95(75)	[7.734]
10	1.77620(30)	6.419^d	[7.461]

^{a} Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. Values in square brackets were fixed during the fits. ^{b} After Haridass et al. [8]. ^{c} After Misra et al. [7]. ^{d} The D_v value recalculated from the $^{13}\mathrm{C}^{16}\mathrm{O}^+$ equilibrium parameters of Kępa et al. [18] using the isotopic relationship within the Born-Oppenheimer approximation.

Table 4. Equilibrium molecular constants (in cm^{-1}) for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of CO^{+a}.

Constant	$B^2\Sigma^+$	$X^2\Sigma^+$
ν_e	45876.724(48)	
ω_e	1734.626(86)	2214.2219(79)
$\omega_e x_e$	28.272(38)	15.1509(31)
$\omega_e y_e$	0.3951(41)	−0.00221(30)
B_e	1.799526(20)	1.976949(26)
$\alpha_e \times 10^2$	2.9579(37)	1.8948(18)
$\gamma_e \times 10^4$	$\underline{-3.17(18)}$	−3.32(26)
$\varepsilon_e \times 10^5$	$\underline{4.15(23)}$	
$D_e \times 10^6$	7.868(27)	6.3009(97)
$\beta_e \times 10^7$	2.06(14)	0.308(33)
$\gamma_e \times 10^2$	$\underline{2.194(14)}$	
$\alpha_{\gamma e} \times 10^4$	$\underline{-1.021(64)}$	

^{a} Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. The underlined values were obtained for the first time.

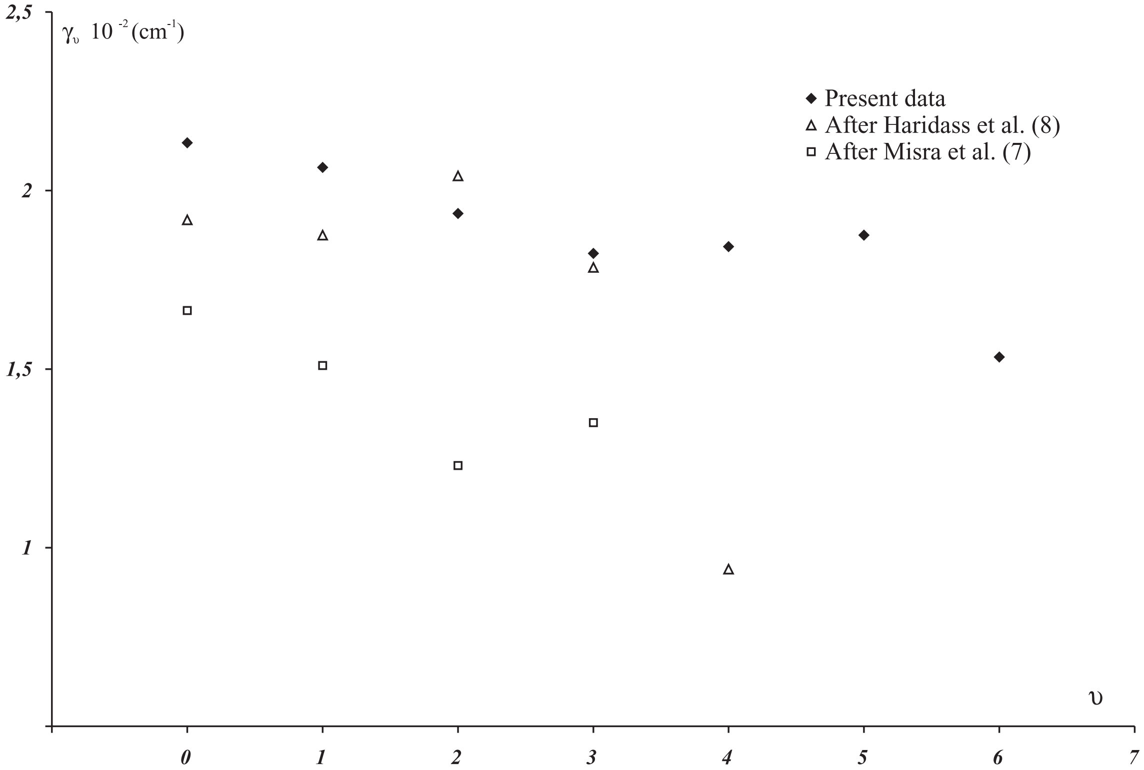

Fig. 2. The v-dependence of the γ_v constants for the $B^2\Sigma^+$ state of the ^{12}C^{16}O$^+$ molecule. Standard deviation, which was less a 3%, was impossible to show because of scale of the plot.

3.3 Vibrational analysis

The knowledge of the ν_0 band origins (see Tab. 1) for 22 bands of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ allowed one to calculate the ν_e, ω_e, $\omega_e x_e$ and $\omega_e y_e$ equilibrium vibrational constants, assuming their traditionally recognized polynomial dependence on the $(v + 1/2)$ argument. The results with their standard deviations are collected in Table 4.

These constants were subsequently used to calculate the RKR potential curves for $B^2\Sigma^+$ and $X^2\Sigma^+$ states, see Table 5. The RKR potential curves with vibrational energy levels of $B^2\Sigma^+$, $A^2\Pi_i$ and $X^2\Sigma^+$ states are shown in Figure 3. The more precise equilibrium molecular constants used in the calculations make the RKR potential and vibrational energy levels more accurate and reliable. Finally the Franck-Condon factors and r-centroids for the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions have been calculated and are listed in Table 6.

The ν_e values from Table 4 and Y'_{00} and Y''_{00} values from Table 5 for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of ^{12}C^{16}O$^+$ and ^{13}C^{16}O$^+$ (from Kępa et al. [18]), made it possible to derive an isotope shift, as described in detail by Bunker [25], for the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of ^{13}C^{16}O$^+$ using the expression:

$$\Delta\nu_e = \nu_e^i - Y_{00}'^{\,^{13}\mathrm{CO}^+} + Y_{00}''^{\,^{13}\mathrm{CO}^+} - \left(\nu_e - Y_{00}'^{\,^{12}\mathrm{CO}^+} + Y_{00}''^{\,^{12}\mathrm{CO}^+}\right). \tag{4}$$

The electronic isotopic shift derived in this way is $\Delta\nu_e = -0.395$ cm^{-1}, the accuracy of the derivation being

Table 5. Vibrational levels and RKR turning points for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of CO$^+$.

v	$G_v + Y_{00}$ (cm^{-1})	r_{min} (Å)	r_{max} (Å)
	$B^2\Sigma^+$		
0	859.1895	1.11978	1.22693
1	2538.5556	1.08841	1.27658
2	4164.9335	1.06882	1.31503
3	5740.6941	1.05402	1.34919
4	7268.2076	1.04197	1.38103
5	8749.8449	1.03174	1.41139
6	10187.9764	1.02281	1.44071
$Y_{00} = -1.1049$ cm^{-1}		$r_e = 1.16889$ Å	
	$X^2\Sigma^+$		
0	1103.3801	1.07074	1.16526
1	3287.2930	1.04131	1.20597
2	5440.8842	1.02243	1.23626
3	7564.1405	1.00788	1.26239
4	9657.0485	0.99585	1.28618
5	11719.5951	0.98552	1.30844
6	13751.7670	0.97642	1.32964
7	15753.5509	0.96828	1.35007
8	17724.9335	0.96089	1.36993
9	19665.9016	0.95414	1.38935
10	21576.4420	0.94792	1.40844
$Y_{00} = 0.0571$ cm^{-1}		$r_e = 1.11521$ Å	

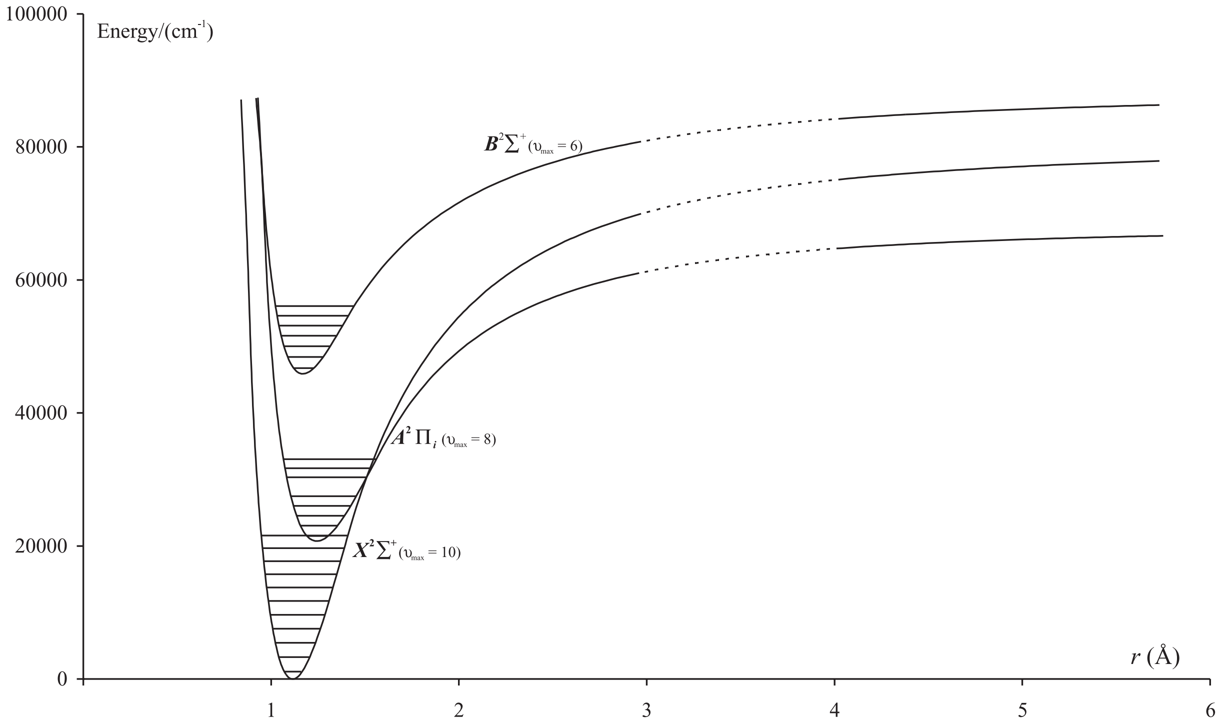

Fig. 3. RKR potential curves of the $B^2\Sigma^+$, $A^2\Pi_i$ and $X^2\Sigma^+$ states in the $^{12}C^{16}O^+$ molecule. The progress of the curves, beyond the analyzed area, is only approximate.

Table 6. Franck-Condon factors and r-centroids for the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of CO^{+a}.

$v'' \setminus v'$	0	1	2	3	4	5	6
0	5.3808×10^{-1}	3.1529×10^{-1}	1.0869×10^{-1}	2.9318×10^{-2}	6.9358×10^{-3}	1.5265×10^{-3}	3.2132×10^{-4}
	1.1449	1.1061	1.0672	1.0286	0.9904	0.9529	0.9151
1	3.3563×10^{-1}	6.4774×10^{-2}	2.7302×10^{-1}	1.9961×10^{-1}	8.6490×10^{-2}	2.8981×10^{-2}	8.4096×10^{-3}
	1.1956	1.1536	1.1185	1.0816	1.0447	1.0081	0.9713
2	1.0223×10^{-1}	3.1928×10^{-1}	1.0880×10^{-2}	1.1496×10^{-1}	2.0468×10^{-1}	1.4240×10^{-1}	6.7133×10^{-2}
	1.2432	1.2051	1.1786	1.1304	1.0961	1.0610	1.0254
3	2.0552×10^{-2}	2.1189×10^{-1}	1.5994×10^{-1}	1.0509×10^{-1}	1.0746×10^{-2}	1.3106×10^{-1}	1.6310×10^{-1}
	1.2877	1.2519	1.2144	1.1835	1.1364	1.1103	1.0768
4	3.1025×10^{-3}	7.0337×10^{-2}	2.5466×10^{-1}	2.9024×10^{-2}	1.6116×10^{-1}	1.3848×10^{-2}	4.3439×10^{-2}
	1.3291	1.2955	1.2609	1.2209	1.1941	1.1691	1.1219
5	3.7662×10^{-4}	1.5495×10^{-2}	1.3786×10^{-1}	2.0825×10^{-1}	3.6454×10^{-3}	1.2354×10^{-1}	7.3047×10^{-2}
	1.3677	1.3362	1.3037	1.2702	1.2579	1.2049	1.1783
6	3.7619×10^{-5}	2.5523×10^{-3}	4.3510×10^{-2}	1.9367×10^{-1}	1.0901×10^{-1}	5.8088×10^{-2}	4.4414×10^{-2}
	1.4061	1.3747	1.3437	1.3123	1.2794	1.2542	1.2264
7	3.1102×10^{-6}	3.3126×10^{-4}	9.5908×10^{-3}	8.7813×10^{-2}	2.0631×10^{-1}	2.3676×10^{-2}	1.1412×10^{-1}
	1.4449	1.4127	1.3817	1.3518	1.3212	1.2874	1.2643
8	2.1312×10^{-7}	3.5296×10^{-5}	1.5866×10^{-3}	2.5773×10^{-2}	1.3844×10^{-1}	1.6419×10^{-1}	9.6422×10^{-4}
	1.4873	1.4483	1.4198	1.3892	1.3604	1.3304	1.3023
9	1.4531×10^{-8}	2.9781×10^{-6}	2.0785×10^{-4}	5.4239×10^{-3}	5.4419×10^{-2}	1.7571×10^{-1}	8.9105×10^{-2}
	1.4962	1.4904	1.4562	1.4269	1.3971	1.3693	1.3397
10	4.9315×10^{-10}	1.9431×10^{-7}	2.2089×10^{-5}	8.7561×10^{-4}	1.4642×10^{-2}	9.4725×10^{-2}	1.7923×10^{-1}
	1.6267	1.5390	1.4940	1.4636	1.4343	1.4057	1.3770

[a] The upper and lower entries for each band are the Franck-Condon factors and r-centroids (in Å), respectively.

impossible to determine for reason discussed in detail in [25]. In the same work Bunker has shown that $\Delta\nu_e$ can be written in the form:

$$\Delta\nu_e = \Delta U(1 - \rho^2)/\mu \qquad (5)$$

where ΔU is independent of the nuclear masses and $\rho = (\mu/\mu_i)^{\frac{1}{2}}$. On the basis of the value $\Delta\nu_e$ obtained from the equation (4), the value $\Delta U = -61.5$ cm^{-1} was derived. Equation (5) can be applied to future analyses of other isotopic species of this molecule for a more precise determination of ΔU and for an estimation of the precision of electronic isotopic shifts of all species of this molecule.

4 Discussion and conclusion

Precise reinvestigations of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system in the ^{12}C^{16}O$^+$ molecule have been carried out. Due to the high resolution of the spectra and the high precision of the calculated wavenumbers of lines, more reliable values of the spin-rotation interaction constants γ_v for the $B^2\Sigma^+$ state have been determined. The comparison of our results with those obtained previously [7,8] is graphically presented in Figure 2. Subsequently, this made it possible to derive for the first time the equilibrium parameters γ_e and $\alpha_{\gamma e}$ for this state. A grand merged calculation all experimental data obtained in our laboratory for the CO$^+$ transitions, have been made. In this way we obtained a set of precise molecular parameters describing altogether 18 vibrational levels of $B^2\Sigma^+(v = 0 - 6)$ and $X^2\Sigma^+(v = 0 - 10)$, as well as band origins values for the 22 transitions of the first negative system (see Tab. 1). From the band origins, the equilibrium vibrational parameters were also estimated. In addition, the RKR potential curve parameters for both states and Franck-Condon factors, and r-centroids for the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions have been determined. The $\Delta\nu_e = -0.340$ cm^{-1} value, defined in equation (4), of electronic isotopic shift of the $B \rightarrow X$ transition in ^{13}C^{16}O$^+$ has been determined for the first time in this work.

Therefore, we consider that the results presented significantly widen and improve the spectroscopic and quantum-mechanical information about the spectrum and energetic structure of the CO$^+$ molecule, especially about the $B^2\Sigma^+$ state.

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