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Emission spectroscopy of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of $^{12}C^{18}O^+$

The $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of $^{12}C^{18}O^+$ ⋆

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Abstract. The emission spectrum of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of $^{12}C^{18}O^+$ has been investigated by using conventional spectroscopic techniques. The 0–1, 0–3, 1–2, 1–4 and 2–5 bands were recorded with high resolution (reciprocal linear dispersion was about 0.030–0.040 nm/mm) and spin splitting of the spectral lines has been precisely studied. Approximately 700 transition wavenumbers were measured with an estimated accuracy of 0.005 cm^{-1}. The rotational analysis has been performed and molecular constants, for the ground $X^2\Sigma^+$ and excited $B^2\Sigma^+$ states, have been extracted. In particular, more reliable values of the spin-rotation interaction constants for the $B^2\Sigma^+$ $(v = 0, 1, 2)$ state were found to be: $\gamma_0 = 2.0415(37) \times 10^{-2}$ cm^{-1}, $\gamma_1 = 1.9495(30) \times 10^{-2}$ cm^{-1} and $\gamma_2 = 1.8554(59) \times 10^{-2}$ cm^{-1}, respectively. Also new values of the principal equilibrium parameters and vibrational terms values for $B^2\Sigma^+$ and $X^2\Sigma^+$ states have been provided.

PACS. 33.20.Lg Ultraviolet spectra

1 Introduction

Spectroscopic studies of electronic transitions of the CO$^+$ molecule were started in the 1920s. Because of the considerable importance in several areas of science, including astrophysics and chemistry, it has still remained a subject of numerous investigations. Many of works, dealing with $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system, have been done in several isotopic species of CO$^+$: $^{12}C^{16}O^+$ [1–10], $^{13}C^{16}O^+$ [8,11–13] and $^{13}C^{18}O^+$ [14,15]. However, only three papers concerning the first negative system of $^{12}C^{18}O^+$ have been published, up to now. Pure vibrational analysis of this system was first done in 1974 by Pešić et al. [16]. They have measured a vibrational isotope shift of the bands head of the $^{12}C^{18}O^+$ relative to those observed in $^{12}C^{16}O^+$. The low-resolution (1.2 Å/mm) spectrum of the following ten bands: 0–1, 2, 3, 4; 1–4, 5; 2–4, 5, 6 and 3–5 were studied by Janić et al. [17], but the spin splitting of the spectral lines has been not observed. The analysis of four bands, with observation of doublet structure of lines, was first done by Antic-Jovanovic et al. [18]. In spite of high resolution of registration (0.012 nm/mm) obtained in that work values of the rotational constants together with the spin-rotation interaction parameters γ_v $(v = 0, 1, 2)$ of the $B^2\Sigma^+$ state are extremely questionable. In view of these conclusions further careful investigation of this system is essential.

The main goals of the work presented have been to register, measure and analyse five (0–1, 0–3, 1–2, 1–4 and 2–5) bands of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ electronic transition in the $^{12}C^{18}O^+$ molecule again. All bands were recorded in high resolution and the detailed study of the spin splitting of the spectral lines was carried out. Present results have provided a significant improvement of the molecular constants for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of the $^{12}C^{18}O^+$ isotopic molecule.

2 Experimental details

The experimental details were almost the same as provided in our previous papers [9,10,12,13]. Briefly, the bands of the first negative system were excited in a conventional hollow cathode type lamp, equipped with a graphite cathode and filled with molecular oxygen (enriched ∼45% of the $^{18}O_2$ isotope) under 0.1 kPa pressure. The lamp was operated at 500 V with 50 mA current. The spectra were recorded in the 10th order (dispersion 0.030–0.040 nm/mm) with the 2-m Ebert plane grating spectrograph, on the ORWO WU-2 type plates. The atomic thorium lines [19], emitted from water-cooled hollow cathode lamp, have been used for calibration of

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⋆ A supplementary table (Tab. I) is only available in electronic form at `http://www.eurphysj.org`

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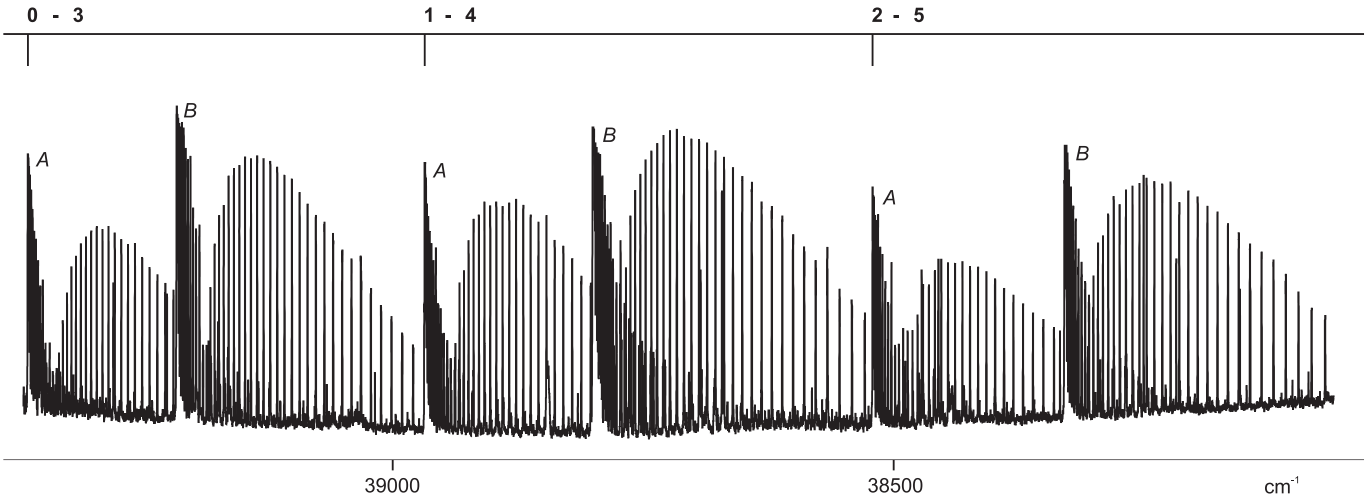

Fig. 1. A compressed portion of the low-resolution spectrum of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CO$^+$. A and B indicate the bands head of the ^{12}C^{18}O$^+$ and ^{12}C^{16}O$^+$ isotopomer, respectively (see description in Sect. 2).

our CO$^+$ spectra. The plates were measured automatically using interferometric comparator designed in our laboratory. The peak positions of the spectral lines were calculated by using the least-squares procedure and assuming Gaussian line-shape to each spectral contour. For the wavenumber calculations seventh-order interpolation polynomials were used. The typical standard deviation of the least-squares fit for the 60–80 calibration lines was about (1.5–2.0) $\times 10^{-3}$ cm^{-1}. The CO$^+$ lines have a spectral widths of about 0.20 cm^{-1} and appear with a maximum signal-to-noise ratio of about 50:1 in the strong 1–4 band. Therefore, the absolute accuracy and precision of measurements of strong and unblended molecular lines are expected to be of the order of ± 0.005 cm^{-1}. Because a few ^{12}C^{18}O$^+$ lines and the lines of the major ^{12}C^{16}O$^+$ isotopomer overlapped, the accuracy of measurements for the weaker and blended lines is reduced to $\pm(0.010–0.020)$ cm^{-1}. A compressed portion of the low-resolution spectrum of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CO$^+$ has been presented in Figure 1.

3 Analysis and calculations

As expected for the $^2\Sigma^+ \rightarrow ^2\Sigma^+$ transition, each band consists of four main branches: double R (R_{11ee}, R_{22ff}) and double P (P_{11ee}, P_{22ff}) (two week satellite branches $^QR_{21fe}$ and $^QP_{12ef}$ were not observed). 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 [20]. The doublet structure is shown in Figure 2 where the lines of the R branch of the 0–1 band are clearly split by the spin-rotation interaction into R_{11} and R_{22} components, respectively.

In total, almost 700 lines belonging to five bands of ^{12}C^{18}O$^+$ have been measured and their wavenumbers are provided in Table I (see the *Supplementary Online Material*). The effective Hamiltonian for diatomic molecules, introduced by Brown et al. [21], was used to reduce the experimental wavenumbers of lines to rovibronic parameters via a non-linear least-squares fitting procedure. Explicit matrix elements of this Hamiltonian for the $^2\Sigma^+$ state were taken in forms proposed by Amiot et al. [22] and completed by Douay et al. [23]. The following energy level expression has been applied in the present work in order to determine the molecular constants:

$$^2\Sigma^+_{e,f} = T_v + B_v x(x \mp 1) - D_v x^2(x \mp 1)^2 \pm 0.5\gamma_v(x \mp 1). \tag{1}$$

The B_v and D_v are the rotational and centrifugal distortion constants, γ_v is the spin-rotation interaction constant, $x = (J + 0.5)$ and upper and lower signs ($\pm$ or $\mp$) refer to the e/f levels, respectively [20]. The statistical data of individual bands fit are presented in Table 1.

During individual band-by-band calculations, the existence of very strong correlation between spin-rotation interaction parameters, $\gamma_{v'}$ and $\gamma_{v''}$, has been found out. For these constants diagonal and above-diagonal elements of the freedom matrix [24] had values near zero. For this reason, we have decided to fix the ground state $\gamma_{v''}$ constants to very precise values calculated from equilibrium parameters of ^{12}C^{16}O$^+$ given by Bogey et al. [25] from microwave studies, and to vary the corresponding constant in the upper state. The molecular constants obtained as output from individual fit of the bands served as input data for the merge calculations [26,27], giving a final set of molecular constants for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states. As the merge program requires that the bands to have at least one common vibrational level, the calculations have been performed in two stages. Firstly we merged the 0–1 and 0–3 bands (variance of this merging $\sigma^2_M = 1.31$) and secondly the 1–2 and 1–4 bands were merged (variance of this merging $\sigma^2_M = 1.17$). This way we obtained precise molecular constants for the $B^2\Sigma^+$ ($v = 0, 1$) and $X^2\Sigma^+$ ($v = 1, 2, 3, 4$) states. Because the 2–5 band had to be excluded from the merge calculation, all values of the molecular parameters for the $v' = 2$ and $v'' = 5$ levels come from the

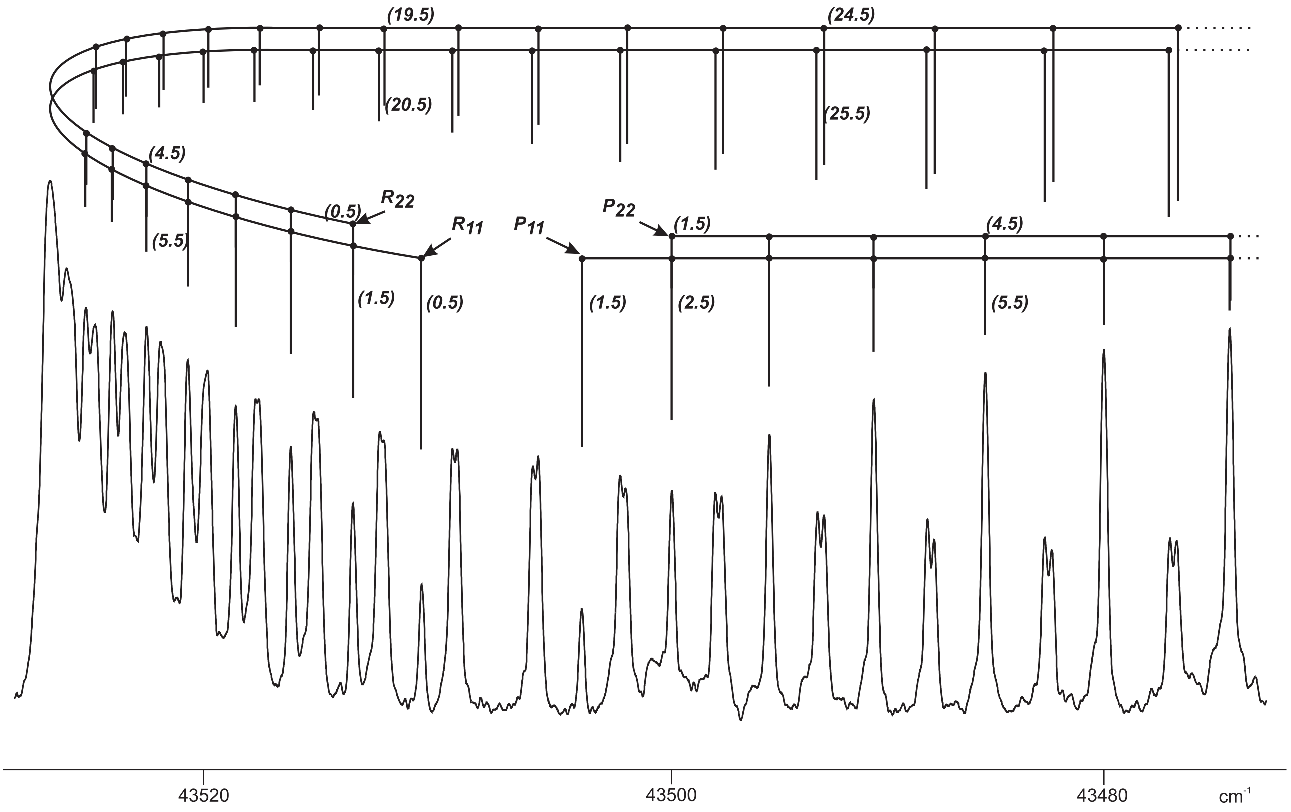

Fig. 2. An expanded view of the 0–1 band of the $B^2\Sigma^+ \to X^2\Sigma^+$ transitions of $^{12}C^{18}O^+$.

Table 1. Individual bands fits in the $B^2\Sigma^+ \to X^2\Sigma^+$ system of $^{12}C^{18}O^+$.

Band	σ_{head} (cm^{-1})	n^a	J_{max}	f^b	$\sigma \times 10^3$ (cm^{-1})
0–1	43527.80	150	41.5	118	5.87
0–3	39356.15	141	36.5	109	9.54
1–2	43063.09	126	36.5	91	5.41
1–4	38948.41	150	38.5	114	4.95
2–5	38519.47	124	32.5	87	6.07

[a] Total number of observed lines. [b] Number of degrees of freedom of the fit for the individual band analysis.
[c] Standard deviation of the fit for the individual band analysis.

individual band fit. The final molecular constants for the $B^2\Sigma^+$ ($v = 0,1,2$) and $X^2\Sigma^+$ ($v = 1,2,3,4,5$) states of $^{12}C^{18}O^+$ are summarized and compared in Table 2.

The previous [18] values of the B_v and D_v constants, for ground and excited state, are in limited compatibility with the present values, which are more accurate by at least two orders of magnitude. Our γ_v constants for $B^2\Sigma^+$ ($v = 0,1,2$) state differ substantially from previous experimental constants [18]. There are probably three reasons for such differences: (i) we have observed and measured spin splitting in a larger amount of lines; (ii) the precision of our wavenumbers is more than one order better than the previous ones; (iii) in the previous band fit the γ_v for the $X^2\Sigma^+$ ($v = 1,3,4,5$) state were constrained to almost the same value (see Tab. 2).

As it was pointed out in the work [18], the significant difference between the band origin of the 0–1 band given in work [17], has been verified in present investigations. The isotope shift of the bands origins of the first negative system of $^{12}C^{18}O^+$ relative to those of $^{12}C^{16}O^+$ are calculated as the differences of values taken from [10] for $^{12}C^{16}O^+$ and values for $^{12}C^{18}O^+$ obtained in these studies.

The molecular constants from Table 2 and band origins from Table 3 have been used to evaluate the equilibrium constants for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states. When the Born-Oppenheimer approximation holds strictly, the following equations can be applied:

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \ldots, \qquad (2)$$

$$D_v = D_e + \beta_e(v + \tfrac{1}{2}) + \ldots, \qquad (3)$$

$$\gamma_v = \gamma_e + \alpha_{\gamma e}(v + \tfrac{1}{2}) + \ldots, \qquad (4)$$

$$\begin{aligned}\sigma_{v'-v''} &= \sigma_e + \omega_e'(v' + \tfrac{1}{2}) - \omega_e x_e'(v' + \tfrac{1}{2})^2 + \ldots \\ &\ldots - \omega_e''(v'' + \tfrac{1}{2}) + \omega_e x_e''(v'' + \tfrac{1}{2})^2 - \ldots \qquad (5)\end{aligned}$$

The results are provided and compared in Table 4. Some valuable conclusions can be drawn from the spectroscopic

Table 2. Molecular constants (in cm^{-1}) of the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of $^{12}\text{C}^{18}\text{O}^+$.

	$B^2\Sigma^+$			$X^2\Sigma^+$			
v	B_v	$D_v \times 10^6$	$\gamma_v \times 10^2$	B_v	$D_v \times 10^6$	$\gamma_v \times 10^3$	
0	1.699741(23)	7.171(11)	2.0415(37)				[a]
	1.7002(6)	8.21(2)	1.55				[b]
1	1.671759(19)	7.305(10)	1.9495(30)	1.856082(22)	5.700(11)	[8.619]	[a]
	1.6757(7)	10.72(6)	1.65	1.8563(1)	6.27(3)	8.7	[b]
2	1.643649(39)	7.583(27)	1.8554(59)	1.838273(20)	5.662(11)	[8.546]	[a]
	1.6395(5)	4.98(40)	1.60	——	——	——	[b]
3				1.820506(24)	5.692(13)	[8.452]	[a]
				1.8238(7)	9.84(6)	8.7	[b]
4				1.802666(19)	5.709(11)	[8.335]	[a]
				1.8062(6)	8.57(5)	8.7	[b]
5				1.784858(40)	5.862(28)	[8.196]	[a]
				1.7805	3.07(5)	8.0	[b]

[a] This work, one standard deviation is given in parentheses. Values in squares brackets were fixed during the fit. [b] After Antic-Jovanovic et al. [18].

Table 3. Band origins (in cm^{-1}) of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of $^{12}\text{C}^{18}\text{O}^+$.

Band	This work[a]	After [18]	After [17]	Isotope shift[b]
0–1	43507.5952 (12)	43507.68(2)	43510.23	–57.845(14)
0–3	39330.5621 (22)	39330.72(2)	39330.66	–157.667(8)
1–2	43044.6157 (15)	———	———	–69.101(10)
1–4	38925.3882 (11)	38925.39(2)	38925.32	–166.007(22)
2–5	38498.6816 (17)	38498.62(3)	38498.66	–175.435(26)

[a] One standard deviation is given in parentheses. [b] Calculated as $\sigma^{^{12}\text{C}^{16}\text{O}^+}_{\text{band origin}} - \sigma^{^{12}\text{C}^{18}\text{O}^+}_{\text{band origin}}$ experimental values.

constants listed in Table 4. The present σ_e and ω_e constants for the $B^2\Sigma^+$ state and ω_e and $\omega_e x_e$ for the $X^2\Sigma^+$ state were derived on the basis of the 0–1, 0–3, 1–2, 1–4 and 2–5 band origins, and the vibrational constants obtained by Kępa et al. [13] for $^{13}\text{C}^{16}\text{O}^+$ and recalculated from isotopic relations. The $B \rightarrow X$ bands system origin value is over 5 cm^{-1} smaller than the one given in work [17] and can be compared with the σ_e value of $^{12}\text{C}^{16}\text{O}^+$ presented by Szajna et al. [10], which is 45876.724(48) cm^{-1}. When used in the customary isotopic relationship, $\gamma_e^i = \rho^2\gamma_e$ and $\alpha^i_{\gamma_e} = \rho^3\alpha_{\gamma_e}$, equilibrium constants for $B^2\Sigma^+$ state of $^{12}\text{C}^{16}\text{O}^+$ [10][1] predicted γ_e and α_{γ_e} values of $^{12}\text{C}^{18}\text{O}^+$ are 2.0891×10^{-2} cm^{-1} and -9.487×10^{-4} cm^{-1}, respectively. The experimental values of these constants were found to be: $\gamma_e = 2.0882(11) \times 10^{-2}$ cm^{-1} and $\alpha_{\gamma_e} = -9.279(75) \times 10^{-4}$ cm^{-1}. This excellent compatibility confirms the theoretical result of Brown and Watson [28]. They have discussed the isotopic dependence of the spin-rotation interaction and have predicted that the γ parameter is inversely proportional to the reduced mass of molecule. However, when the large set of highly accurate isotopic data is accessible the dimensionless mass correction terms, introduced by Watson [29], can be determined. These small deviations are often calculated only for the light molecules. For molecules with relatively big reduced masses (like CO^+) a simple formula [28] are

Table 4. Equilibrium molecular constants (in cm^{-1}) of the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of $^{12}\text{C}^{18}\text{O}^+$.

	$B^2\Sigma^+$	
Constant	This work[a]	After [17]
σ_e	45876.6721(55)	45881.85
ω_e	1692.3786(22)	1691.81
$\omega_e x_e$	[26.7307]	26.09
$\omega_e y_e$	[0.32502]	——
$\omega_e z_e \times 10^3$	[2.878]	——
B_e	1.713774(65)	1.7074(4)
$\alpha_e \times 10^2$	2.8028(46)	2.2
$D_e \times 10^6$	7.072(63)	7.0
$\beta_e \times 10^7$	1.71(48)	——
$\gamma_e \times 10^2$	2.0882(11)	——
$\alpha_{\gamma e} \times 10^4$	–9.279(75)	——
	$X^2\Sigma^+$	
ω_e	2160.7469(36)	2163.10
$\omega_e x_e$	14.44090(56)	14.71
$\omega_e y_e \times 10^3$	[–1.257]	——
B_e	1.882791(22)	1.8778(5)
$\alpha_e \times 10^2$	1.78041(64)	1.7
$D_e \times 10^6$	5.841(71)	6.5
$\beta_e \times 10^7$	1.71(48)	——
$\delta_e \times 10^8$	2.25(77)	——

[a] One standard deviation is given in parentheses. Values in squares brackets are that recalculated from equilibrium parameters of the $^{13}\text{C}^{16}\text{O}^+$ ion [13] and were kept fixed in calculation.

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[1] Table 4 of the work [10] inadvertently contains erroneous of α_{γ_e} constant, which correct value is $-1.021(64) \times 10^{-3}$ cm^{-1}.

Table 5. Vibrational terms values (in cm^{-1}) of the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of $^{12}C^{18}O^+$.

	$B^2\Sigma^+$	$X^2\Sigma^+$
v	$G(v) + Y_{00}$	$G(v) + Y_{00}$
0	838.7039^a	1076.891^b
1	2478.6918^a	3208.8021
2	4068.2270^a	5311.8199
3		7358.9372
4		9431.1463
5		11447.4396

^{a} Values expressed above the minimum of the $B^2\Sigma^+$ state which is 45876.6721(55) cm^{-1}. ^{b} Extrapolated for unobserved in this work $v'' = 0$ vibrational level. $Y_{00}^{B^2\Sigma^+} = -0.8435$ cm^{-1}. $Y_{00}^{X^2\Sigma^+} = 0.1030$ cm^{-1}.

quite sufficient to model the isotopic dependence of the spin-rotation interaction constants. From the B_e values the equilibrium bond distances of 1.168851(22) Å for the $B^2\Sigma^+$ state and 1.1151544(65) Å for $X^2\Sigma^+$ are computed. The equilibrium constants, presented in Table 4, were subsequently used to determine the vibrational terms values for both electronic states. The results are collected in Table 5.

4 Conclusion

The previous analysis of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ bands system in the $^{12}C^{18}O^+$ isotopic molecule were performed on the basis of observations carried out in low resolutions [16,17] or low precision of wavenumbers of spectral lines [18]. In the present study the high resolution spectrum of the first negative system of $^{12}C^{18}O^+$ has been observed using conventional spectroscopic techniques. A rotational analysis of the 0–1, 0–3, 1–2, 1–4 and 2–5 bands provide improved spectroscopic constants, especially more reliable values of the spin-rotation interaction constants for the $B^2\Sigma^+$ ($v = 0, 1, 2$) state have been derived. Moreover, much improved set of equilibrium vibrational and rotational constants for the two electronic states of $^{12}C^{18}O^+$ was determined.

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