The 1-v'' bands progression of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of $^{12}C^{17}O^+$

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Abstract

The $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ (0–1, 2, 3, 4 progression) electronic transition of $^{12}C^{17}O^+$ was first observed and analyzed by Szajna and Kępa [Spectrochim. Acta A 65 (2006) 1014–1020]. We have now extended our previous studies. The use of high resolution conventional spectroscopic techniques has allowed first rotational analysis of the 1–2, 1–3, 1–4 and 1–5 bands of the first negative system in the 37,000–43,000 cm^{-1} spectral region. Approximately 500 transition wavenumbers were measured with an estimated accuracy of 0.005 cm^{-1}. The present data were combined with the previous measurements to yield an improved set of molecular constants for the $B^2\Sigma^+(v' = 0, 1)$ and $X^2\Sigma^+(v'' = 1, 2, 3, 4, 5)$. The $v' = 1$ and $v'' = 5$ vibrational levels were observed for the first time and the main molecular constants are (in cm^{-1}, one standard deviation in parentheses)

$B^2\Sigma^+$	$X^2\Sigma^+$
$B_1 = 1.710792(20)$	$B_5 = 1.825694(23)$
$D_1 = 7.799(15) \times 10^{-6}$	$D_5 = 6.085(21) \times 10^{-6}$
$\gamma_1 = 1.9491(37) \times 10^{-2}$	$\gamma_5 = [8.381] \times 10^{-3}$

The principal equilibrium molecular constants for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states have also been derived and the vibrational terms values for the ground and excited states have been calculated.
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1. Introduction

Carbon monoxide ion is of considerable astrophysical interest because its occurrence in interstellar medium and in many different astrophysical objects: interstellar clouds [1], comets [2,3] and probably in extragalactic source Cygnus A [4]. The emission spectrum of the CO$^+$ molecule consists of four band systems, arising as a result of the transitions between the excited $A^2\Pi_i$, $B^2\Sigma^+$, $C^2\Delta_r$ electronic states and the ground $X^2\Sigma^+$ state. In the laboratory $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ of CO$^+$ has been extensively studied for

many years beginning with Jevons [5] in 1924. From this time many measurements have been made on $^{12}C^{16}O^+$ [6–14] and other isotopic species: $^{13}C^{16}O^+$ [12,15–17], $^{12}C^{18}O^+$ [18–20] and $^{13}C^{18}O^+$ [21,22]. There has been only one previous observation of the $B \rightarrow X$ system in emission spectrum of CO$^+$ with the ^{17}O isotope, which natural abundance is about 0.04%. Szajna and Kępa [23] observed the $0 - v''(v'' = 1, 2, 3, 4)$ bands progression and provided first spectroscopic constants for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states.

We report here analysis of the four new bands (1–2, 1–3, 1–4 and 1–5) of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of $^{12}C^{17}O^+$, with origins at 43011.8106(22), 40914.4874(21), 38846.7183(13) and 36808.5250(17) cm^{-1}, recorded by conventional spectroscopic techniques. The present data, when combined in

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merge calculations with previous results, provided an improved set of molecular constants for $B^2\Sigma^+(v'=0)$ and $X^2\Sigma^+(v''=1, 2, 3, 4)$ state and first constants for $v'=1$ and $v''=5$ vibrational levels. Also some major equilibrium molecular parameters for excited $B^2\Sigma^+$ state were obtained for the first time.

2. Experimental details

The experimental details were the same as described in our previous paper [23]. Briefly, the spectrum of $^{12}C^{17}O^+$ was excited in a standard discharge tube with a graphite cathode and filled with 1.0 Torr of molecular oxygen (enriched in 45% of $^{17}O_2$ isotope). The lamp was operated with about 600 V and 50 mA dc. The emission from the discharge was observed with the 2-m Ebert plane grating PGS-2 spectrograph in the 10th order. The reciprocal linear dispersion varied from 0.033 to 0.043 nm/mm. The exposure time on the ORWO WU2 plates was about 10 h. The thorium atomic lines were used for absolute wavenumber calibration using the measurements of Palmer and Engelman [24].
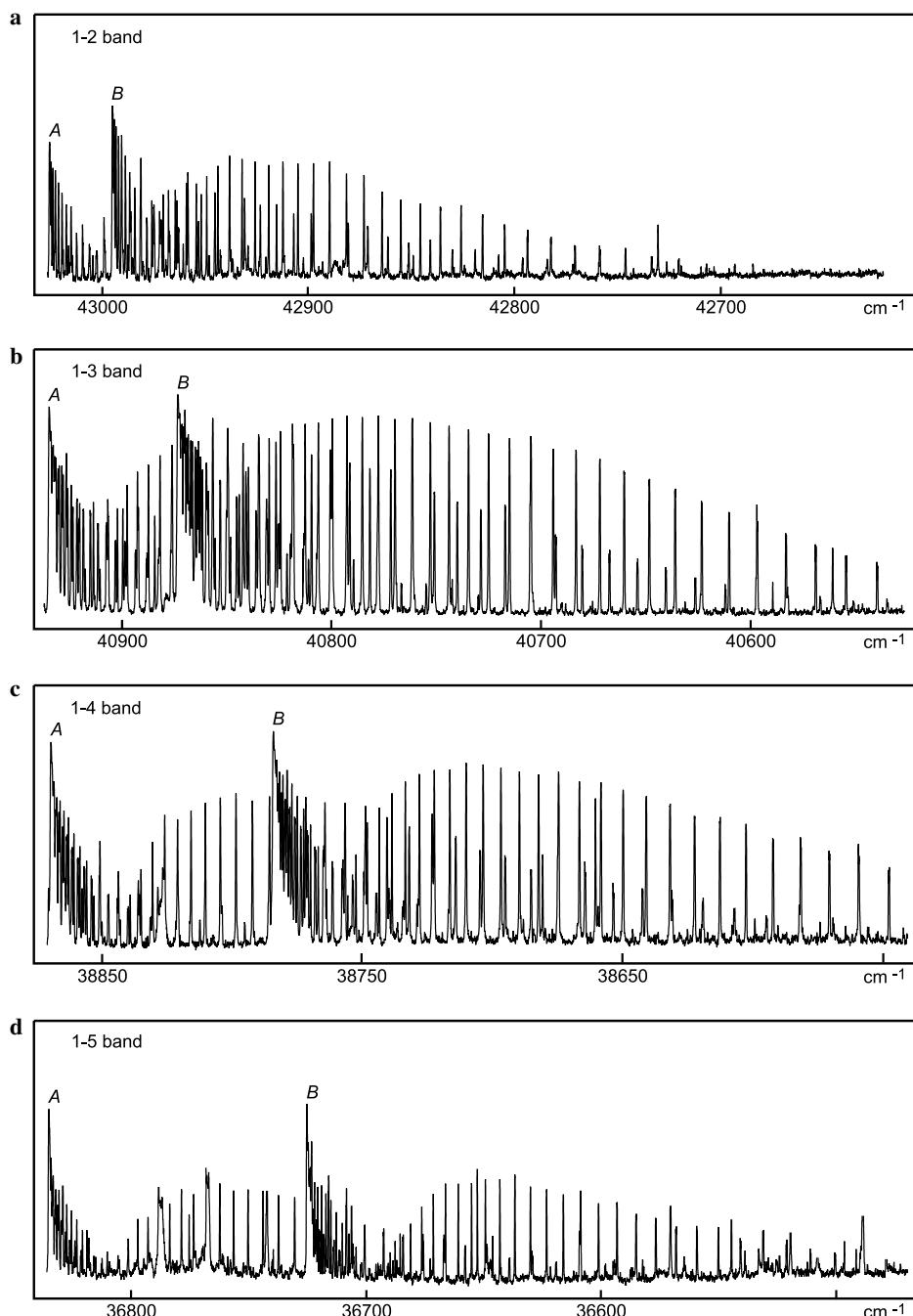

Fig. 1. A compressed portion of the low-resolution spectrum of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of CO^+ showing the $^{12}C^{17}O^+$ (A) and $^{12}C^{16}O^+$ (B) isotope shifts.

The positions of the line centers were calculated by using the least-squares procedure and assuming Gaussian line-shape to each spectral contour. The CO^+ lines have spectral widths of about 0.15–0.20 cm^{-1} and appear with a maximum signal-to-noise ratio of about 50:1, so that 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}. Since oxygen used in our experiments was a mixture of $^{17}O_2$ and $^{16}O_2$ isotope (almost 1:1), the bands of the $^{12}C^{16}O^+$ molecule have appeared too. Because

of that, a few isotopic lines were overlapped from the lines of the major isotopomer, and the accuracy of measurements for the blended and weaker lines is reduced to 0.010–0.020 cm^{-1}. However, due to large vibrational isotope effect, the overlapping spectral regions of both isotopomers involved a small part of the bands. The observed wavenumbers of lines of the 1–2, 1–3, 1–4 and 1–5 bands of the $B^2\Sigma^+ \to X^2\Sigma^+$ system of $^{12}C^{17}O^+$ are deposited in the Electronic Depository of the Supplementary Material of the journal. The observed isotope shifts of the bands
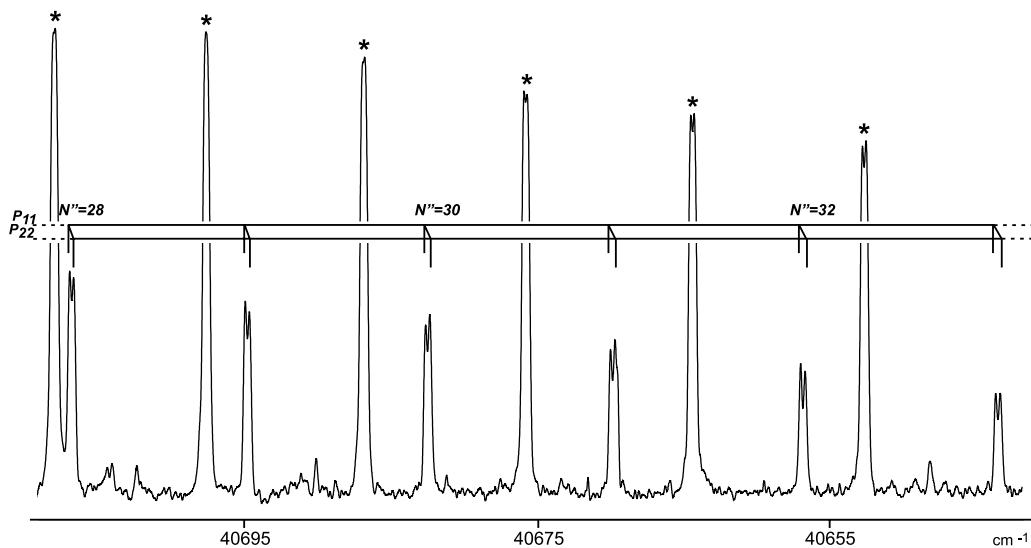

Fig. 2. A portion of P branch of the 1–3 band of $^{12}C^{17}O^+$. The doublet structure is caused by the spin–rotation interaction. The lines marked with asterisks are from the $^{12}C^{16}O^+$ major isotope.

Table 1
Individual band fits in the $B^2\Sigma^+ \to X^2\Sigma^+$ system of $^{12}C^{17}O^+$

Band	Remarks	$\sigma_{v'-v''}$ (cm^{-1})	n	f	J_{max}	$\sigma \times 10^2$ (cm^{-1})
1–2	First obs.	43011.8106(22)	129	82	39.5	0.89
1–3	First obs.	40914.4874(21)	131	86	39.5	0.75
1–4	First obs.	38846.7183(13)	128	93	35.5	0.46
1–5	First obs.	36808.5250(17)	108	63	29.5	0.51

$\sigma_{v'-v''}$ denotes band origin (value from final merging). n is a total number of observed lines. f is the number degrees of freedom, $f = n_f - 6$. J_{max} is the maximum values of the quantum number J for observed lines. σ is the standard deviation of the fit.

Table 2
Molecular constants[a,b] for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of $^{12}C^{17}O^+$

v	$B^2\Sigma^+$			$X^2\Sigma^+$		
	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	1.739728(21)	7.605(16)	2.0520(50)			
1	1.710792(20)	7.799(15)	1.9491(37)	1.899567(21)	6.048(15)	[8.823]
2				1.881224(14)	6.075(14)	[8.746]
3				1.862758(20)	6.066(15)	[8.647]
4				1.844278(20)	6.098(15)	[8.526]
5				1.825694(23)	6.085(21)	[8.381]

[a] In cm^{-1}, one standard deviation in parentheses.
[b] Values in square brackets were fixed during the calculations.

head, defined as $\sigma_{\text{band head}}^{^{12}\text{C}^{16}\text{O}^+} - \sigma_{\text{band head}}^{^{12}\text{C}^{17}\text{O}^+}$, for 1–2 to 1–5 bands were estimated as: -35.80, -61.80, -86.60 and -101.80 cm^{-1}, respectively. An overview spectrum of the transition observed between 37,000 and 43,000 cm^{-1} is displayed in Fig. 1.

3. Analyses and calculations

Both combining electronic states are $^2\Sigma^+$, in which $e(F_1)$ and $f(F_2)$ spin components are split by the spin–rotation interaction. Here, symbols e/f refer to the parities of the rotational levels [25]. According to the theory, structure of each band of the $^2\Sigma^+ \to {}^2\Sigma^+$ transition consists of two main doublet branches: R (R_{11ee}, R_{22ff}) and P (P_{11ee}, P_{22ff}),

Table 3
Equilibrium molecular constants[a,b] for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of $^{12}\text{C}^{17}\text{O}^+$

Constant	$B^2\Sigma^+$	$X^2\Sigma^+$
σ_e	45876.542(17)	
ω_e	1712.2191(46)	2186.0155(99)
$\omega_e x_e$	[27.3597]	14.7818(14)
$\omega_e y_e$	[0.3356]	
$\omega_e z_e \times 10^3$	[3.015]	
B_e	1.754196(33)	1.926985(55)
$\alpha_e \times 10^2$	2.8936(29)	1.8222(35)
$\gamma_e \times 10^5$		$-3.53(49)$
$D_e \times 10^6$	7.508(26)	6.038(16)
$\beta_e \times 10^7$	1.94 (22)	0.108(44)
$\gamma_e \times 10^2$	2.1035(78)	
$\alpha_{\gamma e} \times 10^3$	$-1.029(63)$	

[a] In cm^{-1}, one standard deviation in parentheses.
[b] Values in square brackets were fixed during the calculations.

respectively. The doublet structure is shown in Fig. 2, where the lines of the P branch ($N'' = 28, 29, \ldots, 33$) of the 1–3 band are splits into $P_{11}\left(J'' = N'' + \frac{1}{2}\right)$ and $P_{22}\left(J'' = N'' - \frac{1}{2}\right)$ components, respectively.

Initially, each band observed was fitted separately via a nonlinear least-squares procedure and using the customary effective Hamiltonian proposed by Brown et al. [26]. An explicit listing of the Hamiltonian matrix elements employed for the $^2\Sigma^+$ state can be found in papers Amiot et al. [27] and Douay et al. [28]. Table 1 presents the statistical data of the least-squares fits for individual bands. For each band the band origin $\sigma_{v'-v''}$ value, B_v, D_v rotational constants, spin–rotation interaction constants γ_v, for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states, were required to obtain a satisfactory fit. Due to the fact that the $B^2\Sigma^+$ and $X^2\Sigma^+$ electronic states of CO$^+$ both belong to the Hund's (b) coupling case, the existence of a very strong correlation between $\gamma_{v'}$ and $\gamma_{v''}$ parameters has been discovered. For these constants diagonal and above-diagonal elements of the freedom matrix [29] had values near zero. Therefore, we have chosen to fix the ground state $\gamma_{v''}$ constant to very precise values calculated from equilibrium parameters of $^{12}\text{C}^{16}\text{O}^+$ given by Bogey et al. [30] and to vary the corresponding constant in the upper state. The molecular constants obtained from individual bands fit were subsequently used as an input data for the merge calculus described by Albritton et al. [31] and Coxon [32], to provide the molecular constants of Table 2. The estimated variance of this merging was $\sigma_M^2 = 1.50$ and the number of degrees of freedom was $f = 24$. The value of variance is satisfactory and lies within the 95 percent confidence limits.

When the Born–Oppenheimer approximation holds strictly, which is quite well fulfilled for heavy molecules,

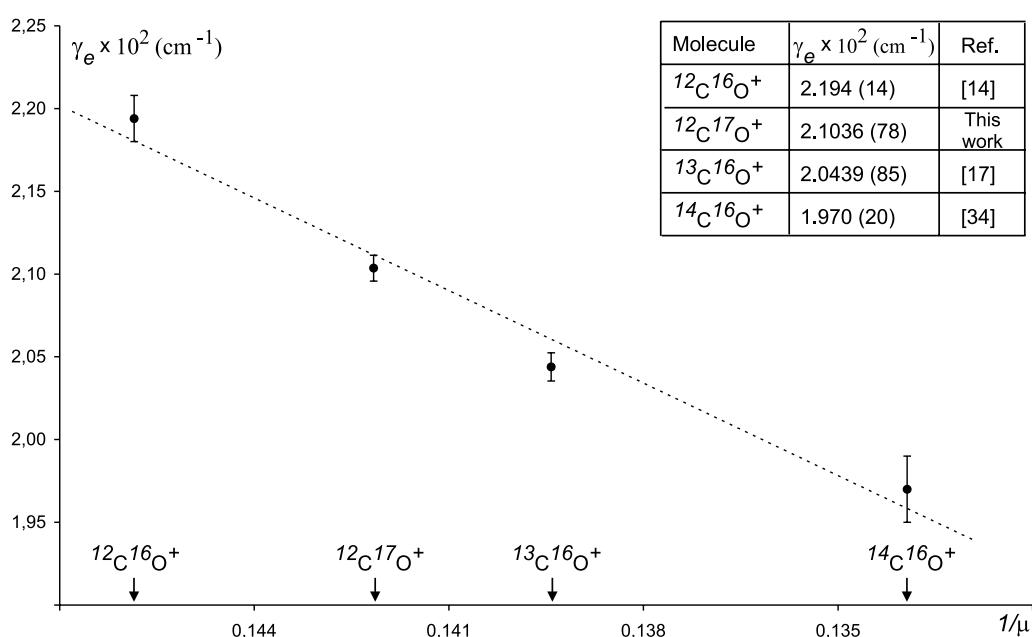| Molecule	$\gamma_e \times 10^2$ (cm^{-1})	Ref.
$^{12}\text{C}^{16}\text{O}^+$	2.194 (14)	[14]
$^{12}\text{C}^{17}\text{O}^+$	2.1036 (78)	This work
$^{13}\text{C}^{16}\text{O}^+$	2.0439 (85)	[17]
$^{14}\text{C}^{16}\text{O}^+$	1.970 (20)	[34]

Fig. 3. Experimental values of the spin–rotation interaction parameters of the $B^2\Sigma^+$ state for four isotopomers of CO$^+$.

Table 4
Vibrational terms values for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of $^{12}C^{17}O^+$

v	$G_v^{B^2\Sigma^+} + Y_{00}$(cm^{-1})	$G_v^{X^2\Sigma^+} + Y_{00}$(cm^{-1})
0	848.4219	1089.361[a]
1	2507.0274	3245.8130
2	4114.021[a]	5372.7013
3		7470.0260
4		9537.7871
5		11575.9846
6		13584.618[a]

$Y_{00}^{B^2\Sigma^+} = -0.8898$cm^{-1}, $Y_{00}^{X^2\Sigma^+} = 0.0488$cm^{-1}.
[a] Extrapolated for unobserved vibrational levels.

the equilibrium molecular constants can be derived from observed parameters for different vibrational levels by using the usual expressions:

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

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

$$\gamma_v = \gamma_e + \alpha_{\gamma_e}\left(v + \frac{1}{2}\right) + \ldots \quad (1)$$

Because only two vibrational levels have been observed in the $B^2\Sigma^+$ state, the equilibrium rotational and spin–rotation interaction constants for this state were determined from an exact fit to the data, providing values featured in Table 3. From the band origin values the vibrational equilibrium parameters can be derived from the following equation:

$$\sigma_{v'v''} = \sigma_e + \omega'_e\left(v' + \frac{1}{2}\right) - \omega_e x'_e\left(v' + \frac{1}{2}\right)^2 + \omega_e y'_e\left(v' + \frac{1}{2}\right)^3 + \ldots$$
$$\ldots - \omega''_e\left(v'' + \frac{1}{2}\right) + \omega_e x''_e\left(v'' + \frac{1}{2}\right)^2 - \ldots \quad (2)$$

The present $\sigma_e = 45876.542(17)$ cm^{-1} and $\omega_e = 1712.2191(46)$ cm^{-1} constants for the excited state have been calculated on the basis 0–1, 2, 3, 4 and 1–2, 3, 4, 5 bands origins and $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$ constants, for the $B^2\Sigma^+$ state, recalculated from equilibrium parameters of the $^{13}C^{16}O^+$ ion [17] and fixed in calculation.

The experimental equilibrium spin–rotation interaction constants γ_e and $\alpha_{\gamma e}$ for the B state, are in perfect compatibility with values recalculated from $^{12}C^{16}O^+$. By using customary isotopic relationship: $\gamma_e^i = \rho^2 \gamma_e$ and $\alpha_{\gamma e}^i = \rho^3 \alpha_{\gamma e}$, the predicted values of these constants for $^{12}C^{17}O^+$ are $\gamma_e = 2.1382 \times 10^{-2}$ cm^{-1} and $\alpha_{\gamma e} = -9.824 \times 10^{-4}$ cm^{-1}, respectively. The experimental values of these constants were found to be $\gamma_e = 2.1035(78) \times 10^{-2}$ cm^{-1} and $\alpha_{\gamma e} = -1.029(63) \times 10^{-3}$ cm^{-1}. The mass reduced dependence of the γ_e constants for the $B^2\Sigma^+$ state could be analyzed from our data. Brown and Watson [33] have discussed the isotopic dependence of the spin–rotation interaction, and predicted that the γ parameter is inversely proportional to the reduced mass of molecule ($\gamma \sim \mu^{-1}$).

Carbon has three natural isotopes (^{12}C, ^{13}C and ^{14}C), together with three isotopes of oxygen (^{16}O, ^{17}O and ^{18}O)

nine different isotopomers of CO^+ can be anticipated. Using experimental data from this work and from previous studies [14,17,34], the reduced mass dependence of the γ_e constants for the four isotope species, have been graphically presented in Fig. 3. The less precise data for $^{12}C^{18}O^+$ [20] and $^{13}C^{18}O^+$ [22] have not been used. The linear form of the plot of γ_e against $1/\mu$ implies that to model the isotopic dependence of the $Y_{\gamma,kl}$ parameter following expression can be used:

$$Y_{\gamma,kl} = \mu^{-(k+2l)/2} U_{\gamma,kl}, \quad (3)$$

where $U_{\gamma,kl}$ parameter is isotopically invariant. Fitting isotopic data to Eq. (3), gave a value for $U_{\gamma,kl}$ for the $B^2\Sigma^+$ state of $14.778(72) \times 10^{-2}$ cm^{-1}.

The equilibrium B_e constants have been used to evaluate the values of the equilibrium bond lengths for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states which are found to be: 1.168820(11) Å for and 1.115187(16) Å, respectively. Also the vibrational terms values for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states have been calculated and results are featured in Table 4.

4. Conclusion

Four new bands (1–2, 1–3, 1–4 and 1–5) of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ electronic transitions of $^{12}C^{17}O^+$ have been recorded in high spectral resolution conditions. A conventional hollow cathode discharge tube has been used as a source of radiation. Over 500 rotational lines were measured with an estimated precision of 0.005 cm^{-1} and a maximum J value up to 39.5. An improved set of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states constants was obtained from merge calculations of our present data together with the previous measurements [23]. Prior to the present work no information about equilibrium parameters of excited state of $^{12}C^{17}O^+$ were available. Our investigation derived first values of the following constants for the B state: $\omega_e = 1712.2191(46)$ cm^{-1}, $B_e = 1.754196(33)$ cm^{-1}, $\alpha_e = 2.8936(29) \times 10^{-2}$ cm^{-1}, $D_e = 7.508(26) \times 10^{-6}$ cm^{-1}, $\beta_e = 1.94\ (22) \times 10^{-7}$ cm^{-1}, $\gamma_e = 2.1035(78) \times 10^{-2}$ cm^{-1} and $\alpha_{\gamma e} = -1.029(63) \times 10^3$ cm^{-1}. Moreover, the isotopic dependence of the spin–rotation interaction γ_e constants for the four isotopomers of CO^+ was analyzed and discussed.

Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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