Global analysis of the Comet-tail system of $^{12}C^{16}O^{+}$*

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A global analysis of the ro-vibrational spectra of 19 bands in the comet-tail ($A^2\Pi_i - X^2\Sigma^+$) system of the $^{12}C^{16}O^+$ cation is presented, and the precise molecular constants of the vibrational levels involved are obtained via a weighted nonlinear least-squares fitting procedure. Furthermore, the resultant precise equilibrium molecular constants enable us to achieve accurate Rydberg–Klein–Rees (RKR) potential curves for both the A and X states, yielding the accurate Franck–Condon factor and band origin of each band in this system.

Keywords: CO^+, molecular constants, comet-tail ($A^2\Pi_i - X^2\Sigma^+$) system

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1. Introduction

The CO^+ cation is one of the most important molecules in the study of atmospheric physics, astrophysics, plasma physics, and combustion science. The studies of $^{12}C^{16}O^+$ by various spectroscopes lasted for over a century. Among the four observed systems, the comet-tail ($A^2\Pi_i - X^2\Sigma^+$) system has been studied most intensively. The comet-tail system of $^{12}C^{16}O^+$ was first observed in the tail of the comet Morehouse by Pluvinel and Baldet[1] in 1908. Thereafter a number of laboratory studies of this system were performed.[2–6] In 1992, Haridass *et al.*[7] recorded 17 bands in this system with $v' = 0$–8 and $v'' = 0$–4 by using emission spectroscopy. They[8] re-investigated 10 bands of the comet-tail system and obtained a set of revised constants for the A and X states eight years later. Most recently, Coxon *et al.*[9] reported their study of the A – X interaction in CO^+ including its isotopes.

High resolution, high precision, and high sensitivity absorption spectrum of CO^+ could not be recorded until Gudeman and Saykally[10] developed the velocity modulation spectroscopy (VMS) in 1983. Wang *et al.*[11] combined optical phase modulation and magnetic rotation with VMS in order to further improve the sensitivity in 1999. In the last decade, ro-vibrational spectra of some bands were studied employing this novel spectroscopy by Yang and his co-workers.[12–17]

The molecular structures and constants can be studied by pure precise theoretical computations,[18–21] and the theoretical predictions can also help us to analyze the experimental data. However, it can hardly reach the precision of the analysis based on the modern experimental spectral data. Therefore, in the present work, a global rotational analysis is performed to obtain more precise molecular constants of the vibrational levels in the comet-tail system of $^{12}C^{16}O^+$ based on the available experimental data. In detail, 1588-rotational lines of the (0, 2), (4, 2), (6, 0), (7, 0), (7, 1), and (8, 1) bands observed by Kępa *et al.*,[22] 1745 lines of the (4, 0), (3, 0), (2, 0), (1, 0), (2, 1), (1, 1), and (0, 1) bands observed by Haridass *et al.*,[8] and 1187 lines of the (2, 3), (0, 3), (1, 2), (1, 4), (3, 6), and (4, 6) bands observed by Yang and his coworkers[12–17] are involved in the present global analysis. Additionally, the Rydberg–Klein–Rees (RKR) potential curves of the two electronic states, the band origin, and the Franck–Condon factor of each band in the comet-tail system of $^{12}C^{16}O^+$ are calculated.

2. Theory

The lower $X^2\Sigma^+$ state belongs to Hund's case (b), and the upper $A^2\Pi_i$ state belongs to either Hund's case (a) for low J values or to Hund's case (b) for high J values. In the present analysis, Hund's case (a) is a good approximation for the upper state due to low J values observed in the experiments. Each band of this transition resolves into two sub-bands: $^2\Pi_{1/2} - ^2\Sigma^+$ and $^2\Pi_{3/2} - ^2\Sigma^+$, which combine into 12 branches designated as R_{21ee}, R_{22ff}, Q_{21fe}, Q_{22ef}, P_{21ee}, P_{22ff}, R_{11ee}, R_{12ff}, Q_{11fe}, Q_{12ef}, P_{11ee}, and P_{12ff}, where the definition of e/f parity of each level is defined by Brown *et al.*[23] Additionally, the pairs of branches, P_{11}/Q_{12}, Q_{11}/R_{12}, P_{21}/Q_{22}, and Q_{21}/R_{22} often overlapped with each other in terms of small value of spin-rotation interaction constant of the lower level. Adopting the effective Hamiltonian of Brown *et al.*,[24] the matrix elements given by Amiot *et al.*,[25] are used in the present work

$$H(X^2\Sigma^+) = T_v + B_v x(x \mp 1) - D_v x^2 (x \mp 1)^2 \pm 0.5\gamma_v (x \mp 1), \quad (1)$$

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$$\begin{aligned}&\left\langle {}^2\Pi_{1/2},J,v,e/f\right|H_{\rm eff}\left|{}^2\Pi_{1/2},J,v,e/f\right\rangle\\ &= T_v-0.5A_v-0.5A_{Dv}(x^2+1)+B_v(x^2+1)\\ &\quad -D_vx^2(x^2+3)\mp(q_v+0.5p_v)x, \qquad (2)\\ &\left\langle {}^2\Pi_{3/2},J,v,e/f\right|H_{\rm eff}\left|{}^2\Pi_{3/2},J,v,e/f\right\rangle\\ &= T_v+0.5A_v+0.5A_{Dv}(x^2-1)+B_v(x^2-1)\\ &\quad -D_vx^2(x^2-1), \qquad (3)\end{aligned}$$

and

$$\begin{aligned}&\left\langle {}^2\Pi_{1/2},J,v,e/f\right|H_{\rm eff}\left|{}^2\Pi_{3/2},J,v,e/f\right\rangle\\ &= -[B_v-2D_vx^2\mp0.5q_vx](x^2-1)^{1/2}, \qquad (4)\end{aligned}$$

where T_v is the vibrational energy, B_v and D_v are the rotational constants, γ_v is the spin-rotation constant, A_v and A_{Dv} are the spin-orbit coupling constants, p_v and q_v are the lambda-doubling constants, and $x=J+0.5$. The upper and lower signs $(\pm)$ or $(\mp)$ refer to the e/f levels, respectively.

3. Results and analysis

In the present work, the spectral lines were obtained via different experimental techniques. Some of the lines were observed by emission grating spectroscopy, while the others were observed by laser absorption spectroscopy. Hence, they should give different resultant molecular constants due to their different accuracies. In order to evaluate these different contributions, the weight of each band is given in the analysis, and normally, $w=1/\delta^2$, where δ is the experimental uncertainty. Kępa *et al.*[22] declared that their experimental uncertainty was about 0.005 cm^{-1}. However, we do not believe that the grating spectrum can reach such a high accuracy due to the calibration and the resolution. On the other hand, the root-mean-square deviation σ is nearly half of the experimental uncertainty in a correct fitting, which further confirms that their declared accuracy was over-estimated. Therefore, the weight of each band is set to $w=1/\sigma^2$ instead in the present analysis, where σ is the fitting error in the previous publications. In detail, as to the bands of Kępa *et al.*,[22] σ is set to 0.0123 cm^{-1}, 0.0199 cm^{-1}, 0.0184 cm^{-1}, 0.0198 cm^{-1}, 0.0309 cm^{-1}, and 0.0194 cm^{-1} for the (0, 2), (4, 2), (6, 0), (7, 0), (7, 1), and (8, 1) bands, respectively. σ of the bands of Haridass *et al.*[8] are all set to 0.016 cm^{-1},[8] and the σ of the bands of Yang and his coworker[12–17] are all set to 0.0036 cm^{-1}.

To obtain a precise set of molecular constants, we perform a global nonlinear least-squares analysis of all the available spectral lines involving the 14 vibrational levels with $v'=0$–4 and 6–8, and with $v''=0$–4 and 6. The molecular constants obtained are listed in Tables 1 and 2, and those of Haridass *et al.*,[7,8] Yang *et al.*,[13] Zhang *et al.*,[14] Shao *et al.*,[16] and Kępa *et al.*[22] are listed for comparison. Generally, the present results are in good agreement with previous ones within 3σ errors. Furthermore, most of the constants are improved, and especially, as listed in Table 1, the molecular constants of the levels in the $A^2\Pi_i$ state are improved by one order in precision.

Table 1. Rotational structure constants (in cm^{-1}) of the $A^2\Pi_i$ state of $^{12}C^{16}O^+$ molecule.

v	B_v	$D_v\times10^6$	$-A_v$	$-A_{Dv}\times10^4$	$p_v\times10^2$	$-q_v\times10^4$
0	1.57959664(18)	6.60671(24)	122.057371(43)	1.7172(13)	1.42153(25)	2.5039(15)
	1.5796211(84)[a]	6.735(11)[a]	122.0513(18)[a]	2.179(55)[a]	1.549(14)[a]	2.619(75)[a]
1	1.560082641(95)	6.51873(20)	121.979398(14)	1.50096(68)	1.31901(13)	2.4707(12)
	1.5600731(30)[b]	6.4784(44)[b]	121.98095(48)[b]	1.439(23)[b]	1.3105(50)[b]	2.505(39)[b]
2	1.54073492(25)	6.64298(53)	121.891653(41)	1.4202(23)	1.26108(42)	2.5083(41)
	1.5407359(93)[c]	6.631(12)[c]	121.89440(46)[c]	1.391(22)[c]	1.2344(53)[c]	2.395(34)[c]
3	1.52132978(35)	6.68086(76)	121.834042(50)	1.0187(27)	1.11370(52)	2.6614(53)
	1.5213257(67)[d]	6.666(14)[d]	121.83585(26)[d]	1.009(15)[d]	1.1452(34)[d]	2.770(32)[d]
4	1.50201878(17)	6.78899(27)	121.866431(19)	1.1870(26)	0.926282(34)	3.2809(52)
	1.5019307(81)[d]	6.534(21)[d]	121.86195(34)[d]	2.583(47)[d]	0.8673(84)[d]	1.38(15)[d]
6	1.4632143(61)	6.8024(95)	120.3621(11)	6.337(41)	2.560(10)	0.848(71)
	1.463182(31)[c]	6.737(47)[c]	120.3656(53)[c]	6.31(20)[c]	2.532(50)[c]	0.75(34)[c]
7	1.4435651(10)	6.4568(16)	120.62058(21)	0.5399(80)	0.6017(18)	6.840(14)
	1.443841(42)[c]	6.882(69)[c]	120.4136(77)[c]	2.76(29)[c]	0.721(64)[c]	9.01(48)[c]
8	1.424105(17)	7.153(67)	120.4206(16)	0.48(21)	1.053(41)	0.66(67)
	1.42367(12)[c]	6.23(58)[c]	120.4130(82)[c]	0.6(12)[c]	0.11(25)[c]	16.7(45)[c]

*Numbers in parentheses denote the differences between the observed and calculated values in units of the last quoted digits.
[a] Results taken from Ref. [8].
[b] Results taken from Ref. [14].
[c] Results taken from Ref. [22].
[d] Results taken from Ref. [16].

Table 2. Rotational structure constants (in cm^{-1}) of the $X^2\Sigma^+$ state of $^{12}C^{16}O^+$ molecule.

v	B_v	$D_v\times10^6$	$\gamma_v\times10^3$
0	1.96746314(25)	6.31707(28)	8.9039(28)
	1.967462265(60)[a]	6.3170(18)[a]	9.10556(50)[a]
1	1.94846951(29)	6.38956(39)	9.1662(28)
	1.94843818(64)[a]	6.3674(47)[a]	9.0495(34)[a]
2	1.929313634(52)	6.29054(6)	8.87221(57)
	1.92935252(90)[a]	6.4278(81)[a]	8.9729(38)[a]
3	1.9102375(11)	6.3856(16)	8.7436(80)
	1.9102425(60)[b]	6.4618(97)[b]	8.724(24)[b]
4	1.8909462(25)	6.3394(62)	8.830(13)
	1.8909388(29)[c]	6.3390(78)[c]	8.832(15)[c]
5	1.871699(20)[d]	6.402(22)[d]	[8.5825][d]
	1.87170(2)[e]	6.424(10)[e]	10.70(12)[e]
6	1.8524084(26)	6.5368(71)	8.146(17)
	1.8524041(23)[f]	6.491(6)[f]	8.222(12)[f]

* Numbers in parentheses denote the differences of the observed and calculated in units of the last quoted digits. Value in the square bracket was fixed.

[a] Result taken from Ref. [8].
[b] Result taken from Ref. [14].
[c] Result taken from Ref. [13].
[d] Result taken from Ref. [22].
[e] Result taken from Ref. [7].
[f] Result taken from Ref. [16].

The equilibrium molecular constants B_e, α_e, and γ_e of the A and X states are fitted according to the standard spectroscopic relation

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \delta_e\left(v+\frac{1}{2}\right)^3 \cdots . \quad (5)$$

Simultaneously, the T_e, ω_e, $\omega_e x_e$, and $\omega_e y_e$ are fitted according to the relation

$$T_v = T_e + \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 + \cdots . \quad (6)$$

Therefore, the equilibrium molecular constants for both the A and X states, listed in Table 3, can be determined using the least-squares fitting method based on the above obtained molecular constants. Note that the weight of each constant is also given according to their fitting errors in this procedure. Undoubtedly, the results are in good agreement with those obtained by Kępa *et al.*[22] and Haridass *et al.*[8] In principle, the resultant equilibrium molecular constants of the *A* state should be more accurate. Actually, one might find that the obtained equilibrium constants are almost at the same precision as those of Kępa *et al.*[22] and Haridass *et al.*,[8] as listed in Table 3. This might result from the ro-vibrational perturbation, which will be discussed later. Our results are closer to those of Haridass *et al.*[8] However, adopting the molecular constants given by Haridass *et al.*,[8] we cannot obtain such precise equilibrium constant B_e of the X state as that listed in Ref. [8]. We do not know how they realized that.

Table 3. Equilibrium constants (in cm^{-1}) of the A and X states of the $^{12}C^{16}O^+$ molecule.

		This work	Ref. [22]	Ref. [8]
$A^2\Pi_i$	T_e	20731.507(34)	20732.037(19)	20731.528(64)[a]
	ω_e	1562.880(34)	1561.806(20)	1562.79(18)
	$\omega_e x_e$	13.832(34)	13.4785(51)	13.926(89)
	$\omega_e y_e\times10^2$	3.64(19)	0.865(37)	65(12)
	B_e	1.589185(92)	1.589392(21)	1.589482(20)
	$\alpha_e\times10^2$	1.9339(50)	1.9494(12)	1.9806(36)
	$\gamma_e\times10^4$	–0.093(54)	–0.117(15)	1.66(18)
$X^2\Sigma^+$	ω_e	2214.10(29)	2214.127(35)	2214.15(15)
	$\omega_e x_e$	15.07(10)	15.094(21)	15.150(25)
	$\omega_e y_e\times10^2$	–1.20(9)	–1.17(34)	–
	B_e	1.977011(43)	1.976841(39)	1.97695082(80)
	$\alpha_e\times10^2$	1.9000(29)	1.8943(34)	1.89615(19)
	$\gamma_e\times10^4$	–0.264(40)	–0.344(62)	–3.018(70)

*Numbers in parentheses denote the differences between the observed and calculated values in units of the last quoted digits.

[a] Value conversed from Ref. [8].

Table 4. Franck–Condon factor (FC) and band origin (BO in cm^{-1}) of the bands in the comet-tail system of $^{12}C^{16}O^+$.

v'' \ v'		0	1	2	3	4	5	6	7	8
0	FC	0.0424	0.1135	0.1673	0.1802	0.1589	0.1221	0.0848	0.0547	0.0332
	BO	20406.2097	21941.4872	23449.2260	24930.3482	26384.7206	27812.0499	29212.8262	30587.5785	31935.6116
1	FC	0.1518	0.1929	0.0985	0.0138	0.0047	0.0421	0.0799	0.0960	0.0911
	BO	18222.2854	19757.5642	21265.3060	22746.4210	24200.7933	25628.1228	27028.899	28403.6514	29751.6845
2	FC	0.2503	0.0810	0.0029	0.0730	0.0961	0.0493	0.0063	0.0037	0.0285
	BO	16068.5102	17603.7876	19111.5265	20592.6487	22047.0210	23474.3505	24875.1267	26249.8790	27597.9121
3	FC	0.2521	0.0005	0.1078	0.0701	0.0009	0.0311	0.0705	0.0581	0.0213
	BO	13945.3592	15480.6366	16988.3751	18469.4977	19923.8700	21351.1995	22751.9757	24126.7280	25474.7611
4	FC	0.1734	0.0919	0.0853	0.0037	0.0769	0.0576	0.0037	0.0146	0.0501
	BO	11852.3544	13387.6318	14895.3707	16376.4929	17830.8652	19258.1946	20658.9709	22033.7232	23381.7563
5	FC	0.0863	0.1913	0.0004	0.0972	0.0367	0.0082	0.0624	0.0479	0.0054
	BO	9789.8343	11325.1118	12832.8506	14313.9728	15768.3451	17195.6746	18596.4508	19971.2031	21319.2362
6	FC	0.0321	0.1764	0.0723	0.0630	0.0190	0.0790	0.0147	0.0122	0.0531
	BO	7757.7402	9293.0176	10800.7565	12281.8786	13736.2510	15163.5804	16564.3566	17939.1090	19287.1421

The new obtained equilibrium constants are employed to compute the RKR potential curves with vibrational energy levels of both the A and X states of the $^{12}C^{16}O^{+}$, plotted in Fig. 1, using the program RKR of Le Roy.[26] The vibrational perturbations can clearly be found in Fig. 1. Additionally, the precise RKR curves are used to calculate the band origin and Franck–Condon factor, listed in Table 4, of each band in the $A^2\Pi_i - X^2\Sigma^+$ system using the program Level 7.1 of Le Roy.[27]

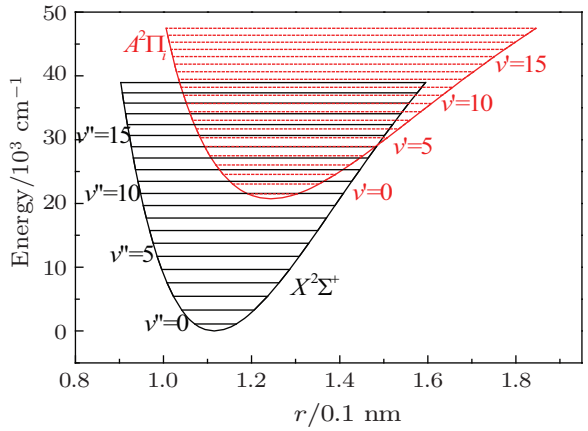


Fig. 1. (color online) Accurate RKR potential curves of the comet-tail system of $^{12}C^{16}O^{+}$.

4. Conclusion

In conclusion, a global rotational analysis of 19 bands of the comet-tail ($A^2\Pi_i - X^2\Sigma^+$) system of the $^{12}C^{16}O^{+}$ cation is carried out. Precise molecular constants of the involved vibrational levels are obtained by a weighted nonlinear least-squares fitting procedure. In addition, the resultant equilibrium molecular constants are used to compute accurate RKR potential curves, and thus band origins and Franck–Condon factors in the comet-tail system of $^{12}C^{16}O^{+}$ are calculated as well.

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