ANALYSIS OF THE 1-2 BAND OF THE ÅNGSTRÖM ($B^1\Sigma^+ - A^1\Pi$) SYSTEM IN THE $^{14}C^{16}O$ MOLECULE*

R. KĘPA

Atomic and Molecular Physics Laboratory, Pedagogical University
35-310 Rzeszów, Poland

In the rare $^{14}C^{16}O$ isotopic molecule the so far unobserved 1-2 band belonging to the Ångström ($B^1\Sigma^+ - A^1\Pi$) system has been photographed under high resolution by conventional spectroscopy. After the rotational analysis of the band the rotational constants B_v and D_v of both combined levels and the ν_0 band origin have been calculated. A combined analysis of the bands belonging to the Ångström, Herzberg and $E^1\Pi - A^1\Pi$ systems made it possible to perform a precise relative spectroscopic characterization of the $v = 1$ level of the $B^1\Sigma^+$ state and the $v = 0$ levels in the $B^1\Sigma^+$, $C^1\Sigma^+$ and $E^1\Pi$ Rydberg states in the $^{14}C^{16}O$ molecule. Numerous rotational perturbations observed in $A^1\Pi$ state in this molecule have been identified.

Introduction

The investigations of isotopic molecules make it possible to obtain additional information about the most abundant natural molecule and to verify the data concerning this molecule and at the same time they enlarge the spectroscopic information about the spectrum and energetic structure of the isotopic molecule being investigated. In the case of the currently investigated carbon monoxide molecule, in addition to the $^{12}C^{16}O$ ordinary molecule the analyses have included the molecules created as a result of the combination of the ^{12}C, ^{13}C and ^{14}C with the ^{16}O, ^{17}O and ^{18}O isotopes. A number of carbon monoxide isotopic molecules have been identified in the solar spectrum [1,2] and in the spectra of different cosmic objects [3,4]. However, the basic information about the spectra and the energetic structure of CO isotopic molecules has been derived from the laboratory investigations. The spectroscopic studies of the $^{14}C^{16}O$ rare isotopic molecule originated in the microwave region of the spectrum and concerned exclusively the lowest molecular levels [5]. Subsequently, these studies have been extended to include the vibrational–rotational structure in the ground electronic state [6–8]. The initial investigations including the excited electronic states were preliminary and fragmentary [9,10]. Further and more complete studies of the spectra and energetic structure included the following $E^1\Pi - A^1\Pi$ [11], Herzberg ($C^1\Sigma^+ - A^1\Pi$) [12], $c^3\Pi - a^3\Pi$ [13], $E^1\Pi - B^1\Sigma^+$ and

---

$C^1\Sigma^+ - B^1\Sigma^+$ [14] as well as the Ångström ($B^1\Sigma^+ - A^1\Pi$) [15] band systems. The fundamental investigations of the Ångström system in $^{14}C^{16}O$ performed by Domin et al [15], have included the most intense bands belonging to the $0 - v''$ (where $v'' = 0 - 5$) and $1 - v''$ ($v'' = 0, 1, 5$ and 6) progressions. The objective of the present work, which extends the previous observations of the Ångström system, is the so far unobserved 1–2 band, belonging to the weaker bands of this system. On the basis of the results derived from the analysis of this band and on the basis of the complex analysis of the bands of the Ångström, Herzberg and $E - A$ systems, new and more precise information has been obtained about the structure of the excited rovibronic levels of the $^{14}C^{16}O$ molecule.

Experimental details

The source of the 1–2 band lines of the Ångström system was a water-cooled Geissler-type tube, the same as in the earlier investigations of this system [15]. The tube was filled with gaseous carbon monoxide enriched with radiocarbon ^{14}C of 59.3 mCi/mmol activity. The pressure in the lamp was about 0.3 kPa. The lamp was supplied by a 5 kV A.C. generator, the mean current was about 25 mA. The spectrum was photographed in the 5-th order of the 2-meter plane-grating Ebert spectrograph PGS-2, equipped with a 651 grooves/mm grating (total number of grooves was 45600) blazed at 1.0 μm. The theoretical resolving power was about 225 000 and reciprocal linear dispersion was about 0.085 nm/mm. The exposure time on ORWO WO1 plate was 2 h. As a calibration spectrum the Th standard lines [16] obtained from several overlapped orders of spectrum and emitted from a hollow-cathode type tube were employed. The relative positions of the lines were measured repeatedly with an accuracy of about 0.5–1.0 μm by using an Abbé-type comparator. The standard deviation of the least-squares fit, by fourth order polynomials, for about 20 calibration lines was $3.5 \cdot 10^{-3}$ cm^{-1}. The precision of the wavenumbers of molecular lines is, however, considerably smaller and is estimated to be $0.010 - 0.020$ cm^{-1}, excluding lines marked by an asterisk. Table I presents the observed wavenumbers of lines of the 1–2 band and their rotational assignments.

Calculation and results

A. Rotational analysis and constants

The rotational analysis of the band and the identification of lines were performed by using the earlier information about the upper $B^1\Sigma^+(v = 1)$ level [15] and the lower $A^1\Pi(v = 2)$ level [11,12,15] of this transition and by using traditional spectroscopic methods.

The B_v and D_v constants for both levels have been determined by means of the combinational method $-\Delta_2 F(J)$ rotational term differences. By making use of the procedure discussed previously in detail [17], the constants listed in

Table I

Observed wavenumbers (in cm^{-1}) and
rotational assignments of the 1–2 band lines
of the Ångström system of $^{14}C^{16}O$

J	$R(J)$	$Q(J)$	$P(J)$
1		21345.103*	
2	21357.083*	346.550	
3	362.522	348.522	21338.053*
4	368.860	351.183	337.141
5	375.539	354.561	336.904*
6	383.306	358.552	337.358
7	391.548*	363.294	338.470
8	21400.350	368.392	340.304
9	409.862	374.529	342.767
10	420.070	381.229	345.937
11	430.995	388.564	349.777
12	442.524	396.599*	354.247
13	454.724	21405.261	359.446
14	467.556	414.617	365.266
15	481.132*	424.669	371.786
16	495.361	435.353	378.966*
17	21510.243*	446.734	386.837
18		458.758	395.363
19		471.545	
20		484.975*	

* Denotes blended line not used in the evaluation
of molecular constants

Table II

Rotational constants (in cm^{-1}) of the $B^1\Sigma^+(v=1)$
and $A^1\Pi(v=2)$ levels in $^{14}C^{16}O$ molecule[a]

		This work	Earlier results
$B^1\Sigma^+$	B_1	1.76708(30)	1.76698(39)[b]
	$D_1 \cdot 10^6$	6.81(67)	7.337(67)[b]
$A^1\Pi$	B_2	1.43328(26)	1.43102(62)[b] 1.43336(30)[c] 1.43313(25)[d]
	$D_2 \cdot 10^6$	7.43(46)	3.59(80)[b] 8.64(61)[c] 8.15(42)[d]

[a] Values in parentheses denote one standard deviation
in units of the last quoted digit
[b] After Domin et al [15]
[c] After Kępa and Rzeszut [11]
[d] After Kępa [12]

Table II have been determined. By combining the lines of the currently found 1–2

Table III

Molecular constants (in cm^{-1}) of the $B^1\Sigma^+(v=1)$ level
relative to the $B^1\Sigma^+(v=0)$, $C^1\Sigma^+(v=0)$ and $E^1\Pi(v=0)$ levels
in the $^{14}C^{16}O$ molecule[a]

	$x = B^1\Sigma^+(v=0)$ [15]	$x = C^1\Sigma^+(v=0)$ [12]	$x = E^1\Pi(v=0)$ [11]
	$-1998.037(12)$		
$G^x(0) - G^B(1)$		$3003.632(10)$	$4016.152(13)$
	$-1998.038(12)^b$		
	$23.28(15)$		$36.794(95)^c$
$(B_0^x - B_1^B) \cdot 10^{13}$		$19.46(13)$	
	$22.92(75)^b$		$26.43(19)^d$
			$-1.13(28)^c$
$(D_0^x - D_1^B) \cdot 10^6$	$-0.933(35)$	$-0.211(32)$	
			$-2.30(60)^d$

[a] Values in parentheses denote one standard deviation in units of the last quoted digit
[b] After Domin et al [15]
[c] For the e, Λ-component
[d] For the f, Λ-component

band with corresponding lines of the 0–2 bands belonging to the Ångström [15], Herzberg [12] and $E^1\Pi - A^1\Pi$ [11] systems, according to the formulas introduced by Jenkins and McKellar [18] the precise values of differences of parameters of the rovibronic structure of the $B^1\Sigma^+(v=1)$ and $B^1\Sigma^+(v=0)$, $C^1\Sigma^+(v=0)$ as well as $E^1\Pi(v=0)$ levels in the $^{14}C^{16}O$ molecule have been derived and listed in Table III.

B. Band origin and isotope shifts

The band origin of the 1–2 band has been calculated by means of $g_Q(J)$, $g_{PR}(J)$ and $g_{\overline{PR}}(J)$ Kovács's functions [19]. By using this method already described in detail in our earlier work [12], the following value has been calculated:

$$\nu_0(1-2) = 21343.078 \pm 0.025 \ cm^{-1}.$$

By making use of the above constant and of the analogous value of the 1–2 band origin for the $^{12}C^{16}O$ molecule [20], we have calculated the isotope shift of the 1–2 band origin:

$$\Delta\nu_0(1-2) = \nu_0(^{14}C^{16}O) - \nu_0(^{12}C^{16}O),$$

$$\Delta\nu_0(1-2) = 22.118 \pm 0.033 \ cm^{-1}.$$

By means of a similar procedure, and on the basis of the currently determined value of the $\Delta G_{1/2}$ vibrational quantum in the $B^1\Sigma^+$ state and by using analogous value for the $^{12}C^{16}O$ molecule [20], an isotope shift of the $\Delta(\Delta G_{1/2})$ vibrational quantum

listed in Table IV has been calculated. The predicted isotope shifts of the band origin and the vibrational quantum can be calculated by means of the Dunham isotope relations [18] and vibrational constants for both combined states. The confrontation of the observed and calculated isotope shifts derived from different vibrational constants is presented also in Table IV. The comparison of the determined values also allows to appreciate the quality of the already known vibrational constants of the $B^1\Sigma^+$ [20–22] and $A^1\Pi$ [23–25] states and to estimate their electronic isotope effect [26].

Table IV
Observed and calculated isotope shifts (in cm^{-1}) for the
vibrational quantum $\Delta G_{\frac{1}{2}}$ in the $B^1\Sigma^+$ state and 1–2
band origin of the Ångström system in $C^{14}O^{16}$ [a]

	Observed	Calculated	
$\Delta(\Delta G^B_{\frac{1}{2}})$	$84.135(26)$ [b]	84.182(55)	After [20]
		83.716	After [22]
		85.693	After [21]
$\Delta\nu_0(1-2)$	$22.118(33)$ [c]	21.058	B state after [20] and A after [25]
		20.990	B state after [20] and A after [24]
		21.337	B state after [22] and A after [24]

[a] Values in parentheses denote one standard deviation in units of the last quoted digit
[b] From this work, Domin et al [15] and Kępa and Rytel [20] results
[c] From this work and Kępa and Rytel [20] results

C. Perturbations of the $A^1\Pi$ state

The numerous and extensive perturbations of the $A^1\Pi$ state in the $^{12}C^{16}O$ molecule have already been repeatedly described and analysed [24–29]. The most comprehensive and the most exhaustive analysis of the A state perturbations has been performed for the $v = 0$ level [30].

Much less information is available for the isotope CO molecules. However, there has been no information so far concerning the perturbations for the A state in the $^{14}C^{16}O$ molecule.

The analyses of perturbations in the isotope molecules can be a source of additional information about the nearby electronic states interacting with the A state and at the same time they allow to verify the already known perturbations and quality of the molecular constants of all interacting states in the $^{12}C^{16}O$ molecule. The present analysis of perturbations of the $A^1\Pi$ state in the $^{14}C^{16}O$ molecule has been performed in the aspect of the confrontation of the perturbations observed and predicted on the basis of the previous analyses of the A state in the $^{12}C^{16}O$ molecule. The analysis of perturbations observed in $^{14}C^{16}O$ has been performed by using our current results and all the observations made so far, including the bands of the Ångström [15], Herzberg [12] and $E^1\Pi - A^1\Pi$ [11] systems performed in our laboratory.

Table V

Observed and calculated perturbations of the $A^1\Pi$ state
of the $^{14}C^{16}O$ molecule

| $A^1\Pi(v)$ | Maximum perturbation (J) of the Λ-doubling component: | | | | Perturbing state | |
| | f | | e | | | |
	obs.	cal.	obs.	cal.	triplet component	vibrational level
			5–6	5	F(1)	
	8–9	8			F(2)	$e^3\Sigma^-(v=1)$
			10–11	11	F(3)	
		14		14	F(1)	
0		18		18	F(2)	$d^3\Delta(v=4)$
		22		22	F(3)	
		25			F(1)	
				28	F(2)	$a'^3\Sigma^+(v=9)$
		31			F(3)	

Remarks: The e-parity sublevels resulting from P and R lines were observed from the $B-A$ system bands up to $J=19$ and from the $C-A$ system up to $J=20$; whereas f-parity (from Q lines) were observed from the $B-A$ bands up to $J=18$ and from the $C-A$ bands up to $J=20$.

$A^1\Pi(v)$	f obs.	f cal.	e obs.	e cal.	triplet component	vibrational level
		31		31		$D^1\Delta(v=1)$
	35–36					$I^1\Sigma^-(v=2)$
1				41	F(1)	
		44			F(2)	$e^3\Sigma^-(v=3)$
				47	F(3)	

Remarks: The e-levels were observed from the $B-A$ bands up to $J=18$, from the $C-A$ bands up to $J=29$ and from the $E-A$ bands up to $J=18$; whereas f-levels, from the $B-A$ bands up to $J=19$, from the $C-A$ bands up to $J=27$ and from the $E-A$ bands up to $J=18$ were observed.

$A^1\Pi(v)$	f obs.	f cal.	e obs.	e cal.	triplet component	vibrational level
	8–9	9				$I^1\Sigma^-(v=3)$
			24–25	25	F(1)	
	29–30	28			F(2)	$e^3\Sigma^-(v=4)$
				31	F(3)	
		30–31		30–31	F(1)	
2		34–35		34–35	F(2)	$d^3\Delta(v=7)$
		38–39		38–39	F(3)	
		32			F(1)	
				35	F(2)	$a'^3\Sigma^+(v=12)$
		38			F(3)	

Remarks: The e-levels were observed from the $B-A$ bands up to $J=29$, from the $C-A$ bands up to $J=31$ and from the $E-A$ bands up to $J=20$; whereas the f-levels, from the $B-A$ bands up to $J=23$, from the $C-A$ bands up to $J=27$ and from the $E-A$ bands up to $J=18$ were observed.

Table V(continued)

$A^1\Pi(v)$	Maximum perturbation (J) of the Λ-doubling component:				Perturbing state	
	f		e		triplet component	vibrational level
	obs.	cal.	obs.	cal.		
		6		6	F(1)	
		10		10	F(2)	$d^3\Delta(v=8)$
		14		14	F(3)	
3	10–11	10			F(1)	
			13–14	13	F(2)	$a'^3\Sigma^+(v=13)$
	16–17	16			F(3)	
		37		37		$D^1\Delta(v=4)$
		42				$I^1\Sigma^-(v=5)$

Remarks: The e-levels were observed from the $B-A$ bands up to $J=23$, from the $C-A$ bands up to $J=33$, whereas the f-levels from the $B-A$ bands up to $J=22$ and from the $C-A$ bands up to $J=31$ were observed.

$A^1\Pi(v)$	f obs.	f cal.	e obs.	e cal.	triplet component	vibrational level
	4–5	12	4–5	12		$D^1\Delta(v=5)$
	24	24				$I^1\Sigma^-(v=6)$
		31–32		31–32	F(1)	
		35–36		35–36	F(2)	$d^3\Delta(v=10)$
		39–40		39–40	F(3)	
4				34	F(1)	
		37			F(2)	$e^3\Sigma^-(v=7)$
				40	F(3)	
		35			F(1)	
				38	F(2)	$a'^3\Sigma^+(v=15)$
		41			F(3)	

Remarks: The e-levels were observed from the $B-A$ bands up to $J=23$, and from the $C-A$ bands up to $J=31$, whereas the f-levels from the $B-A$ bands up to $J=23$ and from the $C-A$ bands up to $J=31$ were observed.

$A^1\Pi(v)$	f obs.	f cal.	e obs.	e cal.	triplet component	vibrational level
				13	F(1)	
		16			F(2)	$e^3\Sigma^-(v=8)$
				19	F(3)	
	18–19	17–18			F(1)	
5			21–22	20–21	F(2)	$a'^3\Sigma^+(v=16)$
		23–24			F(3)	
	22–23		22–23		F(1)	
	26–27		26–27		F(2)	$d^3\Delta(v=11)$
	30–31		30–31		F(3)	
	40–41		40–41			$D^1\Delta(v=7)$

Remarks: The e-levels were observed from the $B-A$ bands up to $J=24$, and from the $C-A$ bands up to $J=26$, whereas the f-levels from the $B-A$ bands up to $J=25$ and from the $C-A$ bands up to $J=26$ were observed.

Table V(continued)

$A^1\Pi(v)$	Maximum perturbation (J) of the Λ-doubling component:				Perturbing state	
	f		e		triplet	vibrational
	obs.	cal.	obs.	cal.	component	level
		21–22		21–22		$D^1\Delta(v=8)$
		31				$I^1\Sigma^-(v=9)$
6		37			F(1)	
				40	F(2)	$a'^3\Sigma^+(v=18)$
		43			F(3)	
				40	F(1)	
		43			F(2)	$e^3\Sigma^-(v=10)$
				46	F(3)	

Remarks: The e- and f-levels were observed only from the $B-A$ bands both up to $J=18$.

$A^1\Pi(v)$	obs.	cal.	obs.	cal.	component	level
		22			F(1)	
				25	F(2)	$a'^3\Sigma^+(v=19)$
		28			F(3)	
7				26	F(1)	
		29			F(2)	$e^3\Sigma^-(v=11)$
				32	F(3)	
		31–32		31–32	F(1)	
		35–36		35–36	F(2)	$d^3\Delta(v=14)$
		39–40		39–40	F(3)	

Remarks: No observations of the rotational structure at this vibrational level.

The identification and classification of the observed perturbations have been performed by employing the $f_x(J)$ and $g_x(J)$, where $x = Q, PR$ and $\overline{PR}$ functions introduced by Kovács [19]. The analysis of the course of these functions calculated by using the lines of the respective branches and bands allows to localize (J) and identify the perturbing state. The predicted perturbations of the $A^1\Pi$ state by nearby $I^1\Sigma^-$, $D^1\Delta$, $e^3\Sigma^-$, $d^3\Delta$ and $a'^3\Sigma^+$ electronic states in the $^{14}C^{16}O$ molecule have been calculated by means of the rovibronic term-crossing method. The respective calculations were performed for the A state in the range of $v = 0-7$ and $J = 1-45$ levels by using the rovibronic structure constants for the A, I, e, d and a' states calculated by Field [24] and by means of the constants for the D state calculated by Kittrell and Garetz [31] and recalculated from the $^{12}C^{16}O$ molecule for the $^{14}C^{16}O$ molecule by means of standard isotope relations. Table V presents the comparison of the perturbations observed and predicted for both Λ-doubling components of the $A^1\Pi$ state in the $^{14}C^{16}O$ molecule.

Acknowledgement

References

1. D. N. B. Hall, Astrophys. J., *182*, 977, 1973.
2. R. Farrenq, G. Guelachvili, A. J. Sauval, N. Grevesse and C. B. Farmer, J. Mol. Spectrosc., *149*, 375, 1991.
3. J. P. Maillard, Highlights of Astronomy, ed. G. Contopoulos, D. Reidel, Dordrecht, 1974.
4. M. A. Frerking, W. D. Langer and R. W. Wilson, Astrophys. J., *262*, 590, 1982.
5. B. Rosenblum, A. H. Nethercot and C. H. Townes, Phys. Rev., *109*, 400, 1958.
6. J. Mink, A. Ayoub, G. Kemeny, R. Kremo and F. Kling, Spectrochim. Acta, *36A*, 151, 1980.
7. J. Mink, A. Ayoub, G. Kemeny and F. Kling, J. Mol. Spectrosc., *86*, 258, 1981.
8. C. Amiot, J. Verges and C. R. Vidal, J. Mol. Spectrosc., *103*, 364, 1984.
9. J. Domin, U. Domin and M. Rytel, Acta Phys. Hung., *43*, 197, 1977.
10. R. K. Dhumwad, A. B. Patwardhan and V. T. Kulkarni, J. Mol. Spectrosc., *78*, 341, 1979.
11. R. Kępa and Z. Rzeszut, Acta Phys. Hung., *50*, 237, 1981.
12. R. Kępa, Acta Phys. Polon., *A62*, 467, 1982.
13. T. Siwiec-Rytel, J. Mol. Spectrosc., *97*, 234, 1983.
14. C. Amiot, J.-Y. Roncin and J. Verges, J. Phys., *B19*, L19, 1986.
15. J. Domin, U. Domin, Z. Malak and M. Rytel, Acta Phys. Hung., *55*, 165, 1984.
16. B. A. Palmer and R. Engleman, Atlas of Thorium, Los Alamos National Laboratory, unpublished.
17. R. Kępa, Canad. J. Phys., *66*, 1012, 1988.
18. G. Herzberg, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules, D. Van Nostrand, New York, 1950.
19. I. Kovács, Rotational Structure in the Spectra of Diatomic Molecules, Akadémiai Kiadó, Budapest and A. Hilger, London, 1969.
20. R. Kępa and M. Rytel, J. Phys., *B26*, 3355, 1993.
21. S. G. Tilford and J. T. Vanderslice, J. Mol. Spectrosc., *26*, 419, 1968.
22. M. Eidelsberg, J.-Y. Roncin, A. Le Floch, F. Launay, C. Letzelter and J. Rostas, J. Mol. Spectrosc., *121*, 309, 1987.
23. S. G. Tilford and J. D. Simmons, J. Phys. Chem. Ref. Data, Vol. 1, No.1, 1971.
24. R. W. Field, Ph. D. Thesis, Harvard University, Cambridge, USA, 1971.
25. R. Kępa, J. Mol. Spectrosc., *135*, 119, 1989.
26. R. Kępa, to be published.
27. J. D. Simmons, A. M. Bass and S. G. Tilford, Astrophys. J. *155*, 345, 1969.
28. R. W. Field, B. G. Wicke, J. D. Simmons and S. G. Tilford, J. Mol. Spectrosc., *44*, 383, 1972.
29. A. C. Le Floch, Ph. D.(etate), Thesis, Paris-Sud University, Centre d'Orsay, 1989.
30. A. C. Le Floch, F. Launay, J. Rostas, R. W. Field, C. M. Brown and K. Yoshino, J. Mol. Spectrosc., *121*, 337, 1987.
31. C. Kittrell and B. A. Garetz, Spectrochim. Acta, *45A*, 31, 1989.