

## The Electronic Emission Spectrum of $C^{13}O^{16}\dagger$

K. E. McCULLOH AND GEORGE GLOCKLER\*

*Department of Chemistry, State University of Iowa, Iowa City, Iowa*

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That part of the emission spectrum of  $C^{13}O^{16}$  occurring between 1900 and 6500A has been obtained in an uncondensed discharge under conditions of low current density. A rotational analysis of the 0-1, 0-2, 0-3, 0-4, 0-5, and 1-1 Angstrom bands has been made. The molecular constants derived therefrom agree closely with those calculated for  $C^{13}O^{16}$  from spectroscopic data pertaining to  $C^{12}O^{16}$ . The behavior, with respect to isotopic substitution, of the first vibrational quantum in the  $B\ ^1\Sigma^+$  electronic state suggests the possibility of rapid convergence of the levels. In the fourth positive group of  $C^{13}O^{16}$ , thirty-five band heads have been measured, involving nine  $v''$  progressions and twelve  $v'$  progressions, each including at least two measured bands. Band origins calculated from these data agree closely with those represented by term formulas herein proposed. Vibrational constants for the ground electronic states of the two isotopic species, consistent with the theory of the isotope effect and with existing experimental data are, in  $cm^{-1}$ ,

	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$
$C^{12}O^{16}$	2169.84	13.301	0.0123
$C^{13}O^{16}$	2121.47	12.715	0.0115

### INTRODUCTION

BECAUSE of the present availability of  $C^{13}$ , enriched in excess of 50 atom percent, it has become possible to observe spectra of isotopic modifications of carbon-containing molecules without resorting to extreme or unusual experimental methods. Investigation of such spectra is especially important in those cases where studies of the spectra of the ordinary isotopic species have failed to provide sufficient data for complete and unambiguous determination of structure or other molecular properties.

In this respect carbon monoxide is of interest because of a number of spectroscopic constants which remain to be determined, in spite of numerous investigations, the subject of which has been the  $C^{12}O^{16}$  spectrum. The present work is concerned with application of the results of an investigation of the electronic emission spectrum of  $C^{13}O^{16}$  to the problem of evaluating some of these constants. To be considered are the vibrational constants for the  $X\ ^1\Sigma^+$  state (ground electronic state and lower state of the fourth positive group) and for the  $B\ ^1\Sigma^+$  state (upper state of the Angstrom bands), as well as the constants  $T_e$  for the  $A\ ^1\Pi$  (lower state of the Angstrom bands and upper state of the fourth positive group) and  $B\ ^1\Sigma^+$  electronic states.

Existing reports of the spectrum of  $C^{13}O^{16}$  have been confined to absorption. Birge,<sup>1</sup> in 1929, reported observation of the main absorption progression in the fourth positive group of  $C^{13}O^{16}$ , but no wave numbers were published. More recently, the infrared fundamental<sup>2</sup>

and first overtone<sup>3</sup> have been observed. These infrared data, together with measurements of the fourth positive group herein reported, serve as experimental verification for vibrational constants to be proposed.

Of the vibrational formulas derived by a number of investigators for the ground electronic state of  $C^{12}O^{16}$ , three merit consideration in the light of the existing body of spectroscopic data. The first of these, obtained by Read<sup>4</sup> as a result of measurements of the fourth positive group, is most successful in expressing the relative positions of the higher vibrational levels. Inconsistency of this formula with the newer, more accurate infrared measurements<sup>2,3,5</sup> can apparently be traced to inaccuracies in data for vacuum ultraviolet fourth positive bands.

The second of these formulas was proposed by Rao<sup>6</sup> on the basis of an analysis of the Cameron bands. While this formula fits Rao's experimental values for the lowest few vibrational quanta very closely, it cannot be extended to represent the higher levels. The levels thus computed differ from the experimentally-determined term values in the vicinity of  $v=20$  by more than  $150\ cm^{-1}$ .

Recently, vibrational constants based on precise infrared measurements have been proposed by Plyler, Benedict, and Silverman.<sup>3</sup> When their formula is extrapolated in the direction of higher vibrational states, the difference between calculated and observed term value in no case exceeds  $10\ cm^{-1}$  where reliable data are available. In view of statements by these investigators concerning the sensitivity of the constants (especially  $\omega_e y_e$ ) to slight changes in the infrared data, it is believed that reasonable estimates of experimental uncertainty allow for minor alteration of the formula, in order to

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\* On leave of absence from the State University of Iowa during the academic year 1952-1953. Present address: Office of Army Ordnance Research, Box CM, Duke Station, Durham, North Carolina.

<sup>1</sup> R. T. Birge, *Phys. Rev.* **34**, 379 (1929).

<sup>2</sup> Lagemann, Nielsen, and Dickey, *Phys. Rev.* **72**, 284 (1947).

<sup>3</sup> Plyler, Benedict, and Silverman, *J. Chem. Phys.* **20**, 175 (1952).

<sup>4</sup> D. N. Read, *Phys. Rev.* **46**, 571 (1934).

<sup>5</sup> G. Herzberg and K. N. Rao, *J. Chem. Phys.* **17**, 1099 (1949).

<sup>6</sup> K. N. Rao, *Astrophys. J.* **110**, 304 (1949).

TABLE I. Angstrom bands of  $C^{13}O^{16}$ .

Band	$\nu_0$ (obs) $cm^{-1}$	$\nu_0$ (calc) $cm^{-1}$
0-1	20712.5	20712.4
0-2	19297.1	19296.5
0-3	17913.5	17913.6
0-4	16563.6	16563.7
0-5	15246.8	15246.8
1-1	22749.9	22749.7

bring it into agreement with term values for the higher levels obtained from measurements of the fourth positive group.

When the present authors examined the available data for the fourth positive<sup>7</sup> and infrared bands, it appeared that some of the vacuum ultraviolet measurements were subject to a systematic error of about  $2\text{ cm}^{-1}$ . This error, most apparent in the case of the two  $v'$  progressions with  $v''=0, 1$  in the fourth positive group, has the effect that Read's constant  $T_e=65074.3\text{ cm}^{-1}$  for the  $A\ ^1\Pi$  electronic state<sup>4</sup> is too low by about  $2.2\text{ cm}^{-1}$ . By making this correction, still retaining Read's vibrational constants for the  $A\ ^1\Pi$  state, but altering slightly the ground-state term formula given by Plyler, Benedict, and Silverman, a set of molecular constants, representing satisfactorily both the infrared and the fourth positive band systems, is obtained. The constants so derived appear in Table IV. It will be shown that this term formula, together with the ratio of reduced masses  $C^{12}O^{16}:C^{13}O^{16}=0.955913$  obtained from the isotope masses  $C^{12}=12.00382$ ,  $C^{13}=13.00751$ ,  $O^{16}=16$ ,<sup>8</sup> constitutes a satisfactory basis for calculating constants to represent the vibrational structure of the  $C^{13}O^{16}$  fourth positive group. These constants are also listed in Table IV.

For the  $B\ ^1\Sigma^+$  electronic state of  $C^{12}O^{16}$ , since only the first vibrational quantum is available from analysis of the Angstrom bands,<sup>9</sup>  $\omega_e$  and  $\omega_e x_e$  have not been known. In the present work approximate values for these constants have been obtained from a study of the isotope effect in the Angstrom bands.

#### EXPERIMENTAL DETAILS

The emission spectrum of  $C^{13}O^{16}$  was excited under conditions of low rotational temperature in the positive column of an end-on discharge tube of 1-cm internal

TABLE II. Rotational constants of  $C^{13}O^{16}$ .

Electronic state	$v$	$B$ (obs) $cm^{-1}$	$B$ (calc) $cm^{-1}$
$B$	0	1.861	1.862
$B$	1	1.836	1.837
$A$	1	1.509	1.509
$A$	2	1.489	1.488
$A$	3	1.468	1.467
$A$	4	1.446	1.445
$A$	5	1.424	1.423

<sup>7</sup> L. Gerö, Z. Physik **100**, 374 (1936).

<sup>8</sup> Hornyak, Lauritsen, Morrison, and Fowler, Revs. Modern Phys. **22**, 291 (1950).

<sup>9</sup> R. Schmid and L. Gerö, Z. Physik **93**, 656 (1935).

diameter, with aluminum electrodes in side arms spaced 30 cm apart. Power was supplied by a 60-cycle, 8000-volt, 25-milliampere luminous tube transformer. The tube was filled with carbon dioxide, 53 atom percent  $C^{13}$ , prepared by the method of Zwiebel, Turkevitch, and Miller<sup>10</sup> from enriched barium carbonate obtained from Eastman Kodak Company. Spectrograms were obtained with the discharge tube operating at pressures between 0.2 and 0.4 mm Hg. The spectrograph was a 3-meter grating instrument with a dispersion of 5.6A per mm in the first order. Spectra were photographed in the first order, using Eastman 103a-0 plates below 5000A, and Eastman 103-F3 above this wavelength. Exposures varied from five minutes to two hours.

All of the band systems of  $C^{13}O^{16}$ , analogous to those of  $C^{12}O^{16}$  occurring between 1900 and 6500A under similar conditions, were observed. These systems include the fourth positive group, the "3A" bands, the third positive group, the Herzberg bands, and the Angstrom bands. However, because of the limited dispersion employed, only the rotational fine structure of the Angstrom bands and the band heads of the fourth positive group were well enough resolved from  $C^{12}O^{16}$  bands to justify their measurement. For the remaining systems, the directions of degradation and of isotope shift were generally such that most of the  $C^{13}O^{16}$  band heads fell within the relatively close structures of their  $C^{12}O^{16}$  counterparts. Measurements were made against iron comparison spectra, except in the extreme ultraviolet region, where copper lines were taken as standards. A comparator of the type described by Glockler and Fullerton<sup>11</sup> was employed. Wave numbers were converted to vacuum with data from Kayser's *Tabelle der Schwingungszahlen*.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The rotational structures of the 0-1, 0-2, 0-3, 0-4, 0-5, and 1-1 Angstrom bands of  $C^{13}O^{16}$  have been analyzed insofar as rotational temperature, resolution, and overlapping  $C^{12}O^{16}$  bands permit. In all, 263 lines have been measured and assigned. Wave numbers of individual lines, together with discussion of perturbations affecting these bands, are available elsewhere.<sup>12</sup> In Table I, observed origins of these bands are listed and compared with values computed from molecular constants listed in Table IV. The absence of systematic discrepancies between observed and calculated origins in the  $v'=0$  progression is an indication of the reliability of these constants. It should be emphasized that the vibrational constants for the  $A\ ^1\Pi$  state of  $C^{13}O^{16}$  were not obtained directly from the spectrum, but rather from Read's<sup>4</sup> values for  $C^{12}O^{16}$  and the ratio of reduced masses.

For the  $B\ ^1\Sigma^+$  state, approximate values for the

<sup>10</sup> Zwiebel, Turkevitch, and Miller, J. Am. Chem. Soc. **71**, 376 (1949).

<sup>11</sup> G. Glockler and F. W. Fullerton, Rev. Sci. Instr. **4**, 530 (1939).

<sup>12</sup> K. E. McCulloh, Ph.D. dissertation, State University of Iowa, June, 1951 (unpublished).

vibrational constants were obtained from Schmid and Gerö's<sup>9</sup> first vibrational quantum for C<sup>12</sup>O<sup>16</sup>, together with the value for the corresponding quantum in C<sup>13</sup>O<sup>16</sup>, as determined in the present work. This quantity was evaluated by subtracting the wave number of the 0-1 Angstrom band origin from that of the 1-1 band. By neglecting  $\omega_e y_e$  and higher constants, and assuming that the ratio of corresponding constants for the two isotopic species is equal to the appropriate power of the inverse ratio of reduced masses, the values appearing in Table IV were obtained. The resulting constants would appear to suggest fairly rapid convergence of the vibrational levels, but an experimental test of this point is impossible because of the predissociation affecting all levels of this electronic state above  $v=1$ .

The rotational constants derived in the analysis of these bands are listed in Table II. Combination differences  $R(J) - P(J)$  were averaged for the  $v'=0$  progression. From these combination differences the constant  $B$  for the upper state was evaluated, taking the effect of centrifugal stretching into account. The remaining constants were determined from this value, together with data from  $Q$ -branches. Calculated constants appearing in Table II were obtained from Schmid and Gerö's<sup>9,13</sup> constants for C<sup>12</sup>O<sup>16</sup> and the ratio of reduced masses. Agreement between observed and calculated values is generally within  $\pm 0.001 \text{ cm}^{-1}$ , corresponding to the limits of experimental error.

In the vibrational analysis of the fourth positive group, measurements and assignments have been obtained for a total of thirty-five band heads appearing at wavelengths above 1900A. In order to determine wave numbers of the origins, C<sup>13</sup>O<sup>16</sup> rotational constants computed from Schmid and Gerö's<sup>13</sup> values for C<sup>12</sup>O<sup>16</sup> were used in the head-origin separation formula,

$$\nu_h - \nu_0 = (B' + B'')^2 / (4B'' - 4B')$$

These heads and origins are listed in Table III, together with their assignment and a comparison with corresponding wave numbers computed from the constants appearing in Table IV. The agreement between observed and calculated origins of the fourth positive bands of C<sup>13</sup>O<sup>16</sup> is within the limits of experimental error, approximately  $\pm 1 \text{ cm}^{-1}$  for accurately measured bands. This agreement offers additional confirmation of the reliability of the vibrational constants for the ground electronic state. Another test of these constants is provided by isotope shifts in the infrared bands. Calculated shifts, C<sup>12</sup>O<sup>16</sup>-C<sup>13</sup>O<sup>16</sup> for the 1-0 and 2-0 infrared band origins, 47.16 and 93.23  $\text{cm}^{-1}$ , respectively, compare favorably with the observed values, 47.11<sup>2</sup> and 93.27<sup>3</sup>  $\text{cm}^{-1}$ .

In general, the consistency of the isotope theory with the spectra of C<sup>12</sup>O<sup>16</sup> and C<sup>13</sup>O<sup>16</sup> has been demonstrated for the vibrational levels of the ground electronic state and the  $A \text{ } ^1\Pi$  state. With regard to rotational constants,

TABLE III. The fourth positive group of C<sup>13</sup>O<sup>16</sup>.<sup>a</sup>

Band	$\nu_h$ (obs) $\text{cm}^{-1}$	$\nu_0$ (obs) $\text{cm}^{-1}$	$\nu_0$ (calc) $\text{cm}^{-1}$
2-9	49674.5	49662.1	49661.7
2-10	47803	47790	47791.1
3-9	51056.7	51045.6	51044.6
3-10	49186.4	49174.5	49174.0
3-11	47340.4	47327.7	47328.1
4-10	50535.2	50524.6	50523.9
4-11	48689.5	48678.3	48678.0
4-12	46868.6	46856.5	46856.7
4-13	45073.2	45060.2	45060.0
4-14	43302.2	43288.1	43287.8
4-15	41555.9	41540.4	41540.0
5-11	50005.2	49995.1	49994.9
5-12	48184.2	48173.5	48173.6
5-13	46388.2	46376.8	46376.9
5-14	44616.7	44604.4	44604.7
5-15	42870.2	42856.8	42856.9
5-16	41148.0	41133.4	41133.5
6-12	49469.	49459	49457.6
6-13	47672.3	47662.1	47660.9
6-14	45900.0	45889.2	45888.7
6-15	44153.4	44141.8	44140.9
6-16	42431.3	42418.7	42417.5
6-17	40733.4	40719.7	40718.3
6-18	39058.8	39043.7	39042.4
7-14	47148.9	47139.2	47139.6
7-15	45402	45391	45391.8
8-16	44896.2	44886.5	44886.4
8-17	43197	43187	43187.2
8-19	39873.4	39861.3	39861.6
8-20	38247.3	38234.1	38234.9
9-18	42707	42697	42697.3
9-20	39431.4	39420.0	39419.9
10-19	42211	42202	42198.6
10-20	40586	40576	40571.9
10-21	38982	38972	38969.2

<sup>a</sup> Band heads listed to only five significant figures represent bands for which accurate measurement was impossible because of overlapping or perturbation.

experimental limitations do not permit a test of the theory within the accuracy to be expected thereof.

The vibrational constants herein proposed are believed to be more reliable than other values which have been published previously. The constants for the ground electronic state fit both the infrared vibration-rotation and fourth positive band systems of C<sup>12</sup>O<sup>16</sup>, as well as the spectrum of C<sup>13</sup>O<sup>16</sup>. The new vibrational formula for the  $B \text{ } ^1\Sigma^+$  electronic state, while going beyond previously available information, can be accepted only with reservation until further experimental work is possible. Most useful in this connection would be investigation of the spectrum of still another isotopic species of the carbon monoxide molecule.

TABLE IV. Molecular constants of carbon monoxide.

Electronic state	Isotopic species	$T_e$ $\text{cm}^{-1}$	$\omega_e$ $\text{cm}^{-1}$	$\omega_e x_e$ $\text{cm}^{-1}$	$\omega_e y_e$ $\text{cm}^{-1}$
X	C <sup>12</sup> O <sup>16</sup>	0	2169.84	13.301	0.0123
X	C <sup>13</sup> O <sup>16</sup>	0	2121.47	12.715	0.0115
A	C <sup>12</sup> O <sup>16</sup>	65076.5	1515.61 <sup>a</sup>	17.250 <sup>a</sup>	0
A	C <sup>13</sup> O <sup>16</sup>	65076.5	1481.82	16.490	0
B	C <sup>12</sup> O <sup>16</sup>	86927.6	2160.7	39.3	0 <sup>b</sup>
B	C <sup>13</sup> O <sup>16</sup>	86927.6	2112.2	37.6	0 <sup>b</sup>

<sup>a</sup> See reference 4.

<sup>b</sup> Assumed value.

<sup>13</sup> R. Schmid and L. Gerö, Z. Physik **101**, 343 (1936).