

ON THE ÅNGSTRÖM BANDS OF $^{12}\text{C}^{16}\text{O}$

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The photographs of the Ångström system in the emission spectrum of the $^{12}\text{C}^{16}\text{O}$ —molecule have been made with the dispersion ranging from 0.6 to 1.1 Å/mm. The analysis yielded the following values of the constants for the $B^1\Sigma^+$ —state:

$$\begin{aligned} G(1) - G(0) &= (2082.171 \pm 0.004) \text{ cm}^{-1}, \\ B_0 &= (1.94805_9 \pm 0.00002_5) \text{ cm}^{-1}, \quad D_0 = (6.70_0 \pm 0.01_5) \cdot 10^{-6} \text{ cm}^{-1}, \\ B_1 &= (1.92164 \pm 0.00004) \text{ cm}^{-1}, \\ D_1 &= (6.6 \pm 0.6) \cdot 10^{-6} \text{ cm}^{-1}; \text{ and for the } A^1\pi \text{ state:} \\ B_2 &= 1.558 \text{ cm}^{-1}, \quad B_3 = 1.5344 \text{ cm}^{-1}, \quad B_4 = 1.511 \text{ cm}^{-1}, \\ B_5 &= 1.488 \text{ cm}^{-1}, \quad D = (8 \pm 1) \cdot 10^{-6} \text{ cm}^{-1}, \\ \sigma_{00} &= 22171.34 \text{ cm}^{-1}, \quad \omega_e = (1518.36_9 \pm 0.02) \text{ cm}^{-1}, \\ \omega_e x_e &= (17.662_4 \pm 0.007) \text{ cm}^{-1}, \quad \omega_e y_e = (0.0140_8 \pm 0.001) \text{ cm}^{-1}. \end{aligned}$$

It was found that as a result of rotational perturbations the rotationless vibrational levels of the A —state with $v = 1$ and $v = 4$ are shifted upwards by 5.24 cm^{-1} and 0.60 cm^{-1} , respectively. The $v = 5$ level is probably shifted by about 0.2 cm^{-1} downwards, while the levels with $v = 0$, $v = 2$ and $v = 3$ show no significant shift within the limits of experimental error.

Introduction

As a part of preliminary work carried out for the preparation of investigations of Ångström system in the spectra of isotopic carbon monoxide molecules the authors have made the photographs of a number of bands of this system for the $^{12}\text{C}^{16}\text{O}$ molecule with a comparatively high dispersion. This system has been already measured and analysed by many authors, the most precise measurements being the results of Schmid and Gerö [1] and Coster and Brons [2].

It seems that our present results are more accurate than those mentioned above. The reasons for this are both a good resolution of the apparatus and the possibility of using better wavelength standards.

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Experimental

The light source used for obtaining the spectra was a standard discharge tube 25 cm long, 0.6 cm in diameter, with electrodes located at the sides and windows at the ends. The tube was supplied from a high voltage transformer, the current ranging from 0.1 to 0.2 Å. It was filled with carbon dioxide under the pressure of about 0.5 cm Hg. The spectra were obtained by means of a 2m plane grating PGS 2 spectrograph (manufactured by VEB C. Zeiss, Jena) in the 3^d, 4th and 5th order of the grating (651 lines per millimeter). The dispersion obtained varied from 0.6 to 1.1 Å/mm. The temperature of the room, in which the spectrograph was installed, was controlled by means of a thermostat. The photographic plates were highly sensitive NP 27 plates. The exposition times varied from 3 to 10 minutes. The measurements were made by means of an Abbé-type comparator (manufactured by VEB C. Zeiss, Jena). The calibrating spectrum was the spectrum of an arc between iron electrodes whose wavelengths were taken according to the tables of Zaidel *et al.* [3]. The tables of Kayser [4] with the corrections introduced by Edlén [5] were used to express the wavelengths in terms of wave numbers.

Calculations and results

All stronger Ångström bands have been analysed, *i.e.* six bands of the progression 0- v'' (from 0-0 to 0-5) and two bands of the progression 1- v'' (1-0 and 1-1). The rotational temperature was rather high: a good measurement of the lines up to the predissociation limit was possible in all bands. It is well known that the higher state of this system, $B^1\Sigma^+$, undergoes predissociation from $J = 38$ for $v' = 0$ and from $J = 18$ for $v' = 1$, and the behaviour of its terms is completely regular, whereas the lower state $A^1\pi$ is subject to turbation in different ways. rotational per

According to our estimation the relative errors of the wave numbers of the lines do not exceed 0.02 cm^{-1} and the absolute values of the errors 0.05 cm^{-1} . In the bands measured by Schmid and Gerö [1], *i.e.*, 0-0, 0-1, 1-0 and 1-1 we have found systematic deviations up to 0.15 cm^{-1} while in the bands measured by Coster and Brons [2] the deviations reached 0.4 cm^{-1} .¹

Rotational analysis

In order to determine the rotational constants B_v two basic methods were used.

The first consisted in the calculation of the second differences of the terms $\Delta_2 F(J) = F(J+1) - F(J-1)$ which can be presented by means of the formula

$$\Delta_2 F(J) = (4B_v - 6D_v) \left(J + \frac{1}{2} \right) - 8D_v \left(J + \frac{1}{2} \right)^3 \quad (1)$$

¹ We do not present the tables of wave numbers as they are too long. We shall really make them available when requested.

and in the use of the least squares method for the determination of the constants and their standard errors (The denotations used throughout the paper are those commonly accepted in literature [7, 8], only the wave number of the line is denoted by σ).

The second method, which has been proposed by Jenkins and McKellar [6], leads to the calculation of the vibrational quantum and the difference between the constants B_v corresponding to the same electronic state and is based on the relations:

$$\left. \begin{aligned} R_{v'v_1''}(J) - R_{v'v_2''}(J) \\ Q_{v'v_1''}(J) - Q_{v'v_2''}(J) \\ P_{v'v_1''}(J) - P_{v'v_2''}(J) \end{aligned} \right\} = G''(v_2'') - G''(v_1'') - (B_{v_1''} - B_{v_2''})J(J+1) \quad (2a)$$

$$\left. \begin{aligned} R_{v_2'v''}(J-1) - R_{v_1'v''}(J-1) \\ Q_{v_2'v''}(J)Q_{v_1'v''}(J) \\ P_{v_2'v''}(J+1) - P_{v_1'v''}(J+1) \end{aligned} \right\} = G'(v_2') - G'(v_1') - (B_{v_1'} - B_{v_2'})J(J+1). \quad (2b)$$

Obviously in perturbed bands the formulas (1) and (2) are valid only in their regular parts.

The $\Delta_2 F'_0(J)$ values for the $B^1\Sigma^+$ state were calculated by means of the relationship

$$\Delta_2 F'(J) = R(J) - P(J) \quad (3)$$

from the six bands of the progression $0-v''$ for $v' = 0$, and then their mean values were calculated. The values of B'_0 and D'_0 given in Table I were obtained on the basis of Eq. (1) with the use of the least squares method.

TABLE I

List of constants for the $B^1\Sigma^+$ -state

$B_0 = (1.94805_9 \pm 0.00002_5) \text{ cm}^{-1}$;	$B_1 = (1.92164 \pm 0.00004) \text{ cm}^{-1}$;
$D_0 = (6.70_0 \pm 0.01_5) \times 10^{-6} \text{ cm}^{-1}$;	$D_1 = (6.6 \pm 0.6) \times 10^{-6} \text{ cm}^{-1}$;
$G(1) - G(0) = (2082.171 \pm 0.004) \text{ cm}^{-1}$	

The values of B'_1 and D'_1 were calculated from the mean values of $\Delta_2 F'_1(J)$ computed from the bands 1-0 and 1-1. They amount to:

$$B'_1 = (1.9216 \pm 0.0002) \text{ cm}^{-1} \quad \text{and} \quad D'_1 = (6.6 \pm 0.6) \cdot 10^{-6} \text{ cm}^{-1}.$$

The accuracy is here lower than in the case of $v' = 0$, which is the result of a smaller number of points (the bands are shortened by predissociation) and a smaller number of bands.

Forming the differences of the corresponding lines of the bands 1-0 and 0-0, as well as 1-1 and 0-1 according to the formula (2b) and then averaging over all branches of both bands and using the least squares method we have obtained $\Delta G'_{1/2} = G'(1) - G'(0) = (2082.171 \pm 0.004) \text{ cm}^{-1}$ and $B'_0 - B'_1 = (0.02642 \pm 0.00003) \text{ cm}^{-1}$ (the value of $\Delta G'$ can be also subject to systematic errors). From the difference $B'_0 - B'_1$ and the value of B'_0 obtained earlier it was possible to obtain $B'_1 = (1.92164 \pm 0.00004) \text{ cm}^{-1}$ which is in agreement with the value obtained before, but with a much better precision.

The calculation of the constants for the lower $A^{1}\pi$ -state were considerably hindered by the irregularities resulting from perturbations. When studying a particular vibrational level we have calculated the differences $\Delta_2 F''(J)$ of two kinds (for two A -components):

$$\Delta_2 F''_d(J) = R(J-1) - P(J+1) \quad (4a)$$

$$\Delta_2 F''_c(J) = R(J) - Q(J+1) + Q(J-1) - P(J). \quad (4b)$$

The data obtained were, however, insufficient for the establishment of any information about the A -doubling. They only allowed us to notice a difference in the behaviour of the two components with respect to perturbations. No attempt was made of a closer study of the perturbations (except those influencing the positions of the bands, which was necessary in vibrational analysis). There are, however, the papers of Gerö and Schmid which deal with perturbations in the A state basing on both the studies of the Ångström system and the studies of the fourth positive system [9–14].

After finding the values of $\Delta_2 F''(J)$ we plotted the dependence of $\Delta_2 F''(J)/J + \frac{1}{2}$ on $(J + \frac{1}{2})^2$. The graph obtained should be a straight line in those J -ranges in which the behaviour of the rotational terms is regular. From the slope of this line it is possible to find the value of the constant D_v , while the intercept with the vertical axis defines the value of the constant B_v . This graphical method was used for calculating the D_v'' values and those values of B_v'' for which a more accurate procedure could not be used because of perturbation.

In those cases where the perturbation were smaller we have used in the regular J -ranges both methods of the determination of both B_v'' and $\Delta B_v''$ described above and based on the least squares method (in case of the second method we have also obtained the vibrational quanta). An exceptionally wide regular range and an undisturbed beginning of the band has the 0–3 band. In the case of this band it was possible to determine B_3'' with a particularly good accuracy. A regular beginning is also shown by the 0–2 band where we could also use more accurate methods. In case of the 0–4 and 0–5 bands we have applied the graphical method and for the 0–1 and 0–0 bands the rotational constants have not been determined. We have thus obtained two sets of B_v'' values: one obtained directly from $\Delta_2 F''(J)$ (together with the values of D_v'') and the other calculated from $\Delta B_v''$ assuming $B_3'' = 1.5344 \text{ cm}^{-1}$. A list of these values is given in Table II. The table also contains the mean values of B_v''

TABLE II

The constants B_v for the $A^{1}\pi$ -state in cm^{-1}

v	The values obtained by other authors		Present results		
	[9]	[15]	obtained directly	obtained from the differences between B_v''	mean
2	1.5550	1.5561	1.558 ₂	1.557 ₆	1.558
3	1.5324	1.5329	1.5344	1.5344*	1.5344
4	1.5099	1.5089	1.511 ₆	1.510 ₈	1.511
5		1.4861	1.488 ₄	1.487 ₁	1.488

* assumed value.

which can be regarded as accurate up to unity on the last decimal place. In addition the table contains the B_v'' values obtained by Gerö from the analysis of the Ångström system [9] and those obtained by Schmid and Gerö from the fourth positive system [15]. Our values are systematically higher than those obtained so far, the difference being certainly greater than the possible errors.

The obtained values of $D_v \cdot 10^6$ for $v = 2-5$ were 9.1, 7.4, and 8.9. It seems that it is possible to accept a common value $D'' = 8 \pm 1 \cdot 10^{-6} \text{ cm}^{-1}$.

Vibrational analysis

The plots of the dependence $A_2 F''(J)/J + \frac{1}{2}$ on $(J + \frac{1}{2})^2$ were clearly showing those regions where perturbations occur. A particularly characteristic pattern had those perturbations which appeared at the beginning of the band since their influence was still visible in a regular way on the distance of even more than the values of J .

The plots of the quantities appearing on the left hand side of Eqs (2a) vs. $J(J+1)$, which in the regular parts of the two bands under consideration should be straight lines with the slope $\Delta B''$, look similar. The intercept with the vertical axis gives in each case the vibrational quantum. In case when one of the bands is perturbed at the beginning, the plot deviates from a straight line and its intercept with the vertical axis gives the real value of the vibrational quantum whereas the intercept of the extrapolated straight line gives the value of the vibrational quantum such as it would be like if there were no perturbations.

The analysis of such plots leaves no doubt which of the bands of the system are shifted. It follows from our analysis that the bands shifted are above all those with $v'' = 1$ (i.e. 0-1 and 1-1) and the 0-4 band, in accordance with the suggestion of Johnson and Asundi [15] made already a long time ago (although later authors have often assumed a different situation). A very small shift also appears in the 0-5 band. The 0-3 and 0-2 bands exhibit no perturbations at the beginning while the 0-0 band, though being highly perturbed in general, has probably a regular beginning, a fact which we have assumed in our vibrational analysis.

The real values of the beginning of the bands have been found by interpolation of the branches P and R as well as from Q . They have been given together with the estimated values of their errors in the first column of Table III. In addition, the values of extrapolated unperturbed vibrational quanta have been found in those cases where such a procedure was possible.

From the values of these quanta and from the unperturbed beginnings of the 0-0, 1-0, 0-2 and 0-3 bands we have obtained six differences between unperturbed beginnings of the bands from which three constants ω_e'' , $\omega_e'' x_e''$ and $\omega_e'' y_e''$ have been determined and their errors estimated. These constants and the beginnings of the bands permitted the determination of σ_{00} .

The following values have been obtained:

$$\begin{aligned} \sigma_{00} &= 22171.34 \text{ cm}^{-1}; & \omega_e'' &= (1518.36_9 \pm 0.02) \text{ cm}^{-1} \\ \omega_e'' x_e'' &= (17.662_4 \pm 0.007) \text{ cm}^{-1}; & \omega_e'' y_e'' &= (0.0140_8 \pm 0.001) \text{ cm}^{-1} \end{aligned}$$

TABLE III

The beginnings of the Ångström bands and their shifts resulting from perturbations

Band	Observed	Calculated	Shift
0-0	22171.35±0.05	22171.34	—
0-1	20683.01±0.02	20688.25	-5.24
0-2	19240.36±0.01	19240.36	—
0-3	17827.58±0.01	17827.58	—
0-4	16449.23±0.02	16449.83	-0.60
0-5	15107.26±0.20	15107.03	(+0.23)
1-0	24253.50±0.05	24253.51	—
1-1	22765.17±0.02	22770.42	-5.25

The unperturbed beginnings of the bands calculated with these constants are listed in the second column of Table III.

The values of the shift are given in the last column of Table III. It can be stated on their basis that in the $A^1\pi$ state the following (nonexisting) rotationless levels are shifted: the $v = 1$ level upwards by about 0.60 cm^{-1} and the $v = 5$ level downwards by about 0.2 cm^{-1} (unfortunately the band head of the 0-5 band reached the spectral sensitivity limit of the photographic plates and thus the accuracy in this region was poor). A check of the constants and shifts of the bands corresponding to the fourth positive system was, however, impossible owing to the low accuracy of the data existing in literature.

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