

Note on Electronic States of Diatomic Carbon, and the Carbon-Carbon Bond

ROBERT S. MULLIKEN

University of Chicago, Chicago, Illinois

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It is shown that the $\lambda 2300$ carbon band analyzed by Landsverk belongs very probably to the transition $\sigma_g^2\sigma_u\pi_u^4\sigma_g$, ${}^1\Sigma_u^+ \rightarrow \sigma_g^2\sigma_u^2\pi_u^4$, ${}^1\Sigma_g^+$. The ${}^1\Sigma_g^+$ state should lie not far above the normal state of C_2 , or possibly be the normal state. Approximate energies and internuclear distances (r_0) are predicted and tabulated for all low-energy states of C_2 and C_2^+ ; an equation for predicting r_0 's is given. Carbon-carbon bond distances in polyatomic carbon compounds are compared with those in C_2 . Apparently bonding to other atoms helps to shorten C-C and C=C bonds in polyatomic compounds as compared with C_2 . The same effect is noted in nitrogen compounds.

I. ELECTRONIC STATES OF DIATOMIC CARBON, AND INTERPRETATION OF THE $\lambda 2300$ CARBON BAND

LANDSVERK'S analysis of the $\lambda 2313$ band of the carbon arc shows definitely¹ that this "band" is the zero sequence of a $\Sigma \rightarrow \Sigma$ transition² of the C_2 molecule. From the absence of any indication of fine structure in the band lines, and from the excitation conditions, ${}^2\Sigma \rightarrow {}^2\Sigma$ of C_2^+ and ${}^3\Sigma \rightarrow {}^3\Sigma$ of C_2 are very unlikely, and ${}^1\Sigma \rightarrow {}^1\Sigma$ of neutral C_2 is altogether probable.²

Assuming ${}^1\Sigma^+ \rightarrow {}^1\Sigma^+$, Landsverk's analysis still leaves ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ and ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ as possibilities, with evidence from intensities perhaps favoring the latter. The present paper attempts to decide between these alternatives and to determine the electron configurations and approximate energies of the two Σ states.

The low energy states of the C_2 molecule have been discussed in a previous article.³ These and others of C_2 and C_2^+ are listed in Table I, together with rough estimates of their energies and of the internuclear separations r_0 for their respective lowest states of vibration.

Table I is obtained in the following way. For energies up to at least 10 ev above the normal state of C_2 or C_2^+ , we can be sure that, besides the four K electrons, there are always two electrons in the $z\sigma_g$ MO (molecular orbital). This MO is a strongly bonding hybrid of $\sigma_g 2s$ and $\sigma_g 2p$, with $\sigma_g 2s$ somewhat preponderating in the

mixture. There remain six electrons (or five in C_2^+) to be distributed among MO's of higher energy. The MO's $y\sigma_u$, $w\pi_u$, $x\sigma_g$, and $v\pi_g$, with energy increasing in the order named, here come into consideration. Of these four MO's the weakly antibonding $y\sigma_u$, a hybrid of $\sigma_u 2s$ and $\sigma_u 2p$ with the former somewhat preponderating, is definitely the most stable, as is known from a study of the N_2^+ spectrum.^{2, 3} Next in order are the strongly bonding degenerate MO $w\pi_u \equiv \pi_u 2p$ and the weakly bonding $x\sigma_g$, the latter a hybrid of $\sigma_g 2s$ and $\sigma_g 2p$ with the latter somewhat preponderating. Highest in energy is the strongly antibonding degenerate $v\pi_g \equiv \pi_g 2p$. (There is also the very strongly antibonding $u\sigma_u$, a hybrid of $\sigma_u 2s$ and $\sigma_u 2p$ with the latter preponderating, but its energy is higher than that of $\pi_g 2p$, and we need not consider it.)

As a rough approximation, we may assume $y\sigma_u$ to lie 3 ev deeper than $w\pi_u$ and $x\sigma_g$, and 9 ev deeper than $v\pi_g$, for internuclear distances in the neighborhood of 1.25A. These figures are justified by what is known of the energy levels of C_2 , N_2 and N_2^+ , and CN. For simplicity it may be assumed that $w\pi_u$ and $x\sigma_g$ lie equally deep for internuclear distances corresponding to the most stable states, as seems to be indicated to be approximately true by data for nitrogen.³ The mean energies for various low energy electron configurations, relative to the lowest-energy configuration taken as zero, are then as given in Table I. In case there is more than one electronic state for a given configuration, the energies of the several states may be expected to be distributed about the tabulated mean value.

Next we need a system for estimating r_0

¹ O. G. Landsverk, Phys. Rev. 56, 769 (1939).

² This identification was made tentatively some time ago by Dieke and by Mulliken (cf. R. S. Mulliken, Zeits. f. Elektrochemie 36, 605 (1930)).

³ R. S. Mulliken, Rev. Mod. Phys. 4, 66, 81 (1932).

TABLE I. Approximate energy and r_0 values for low energy electron configurations of C_2 and C_2^+ .

$y\sigma_u$	$w\pi_u$	$x\sigma_g$	$v\pi_g$	EST. MEAN ENERGY* (EV)	STATES	NO. OF C-C BONDS	r_0 VALUES (A)	
							CALC.	OBS.
2	4			0	$1\Sigma_g^+$	2	1.24	1.243
2	3	1		0	$3\Pi_u, 1\Pi_u$	2	1.32	1.313, 1.318
2	2	2		0	$3\Sigma_g^-, 1\Delta_g, 1\Sigma_g^+$	2	1.40	
1	4	1		3	$3\Sigma_u^+, 1\Sigma_u^+$	3	1.18	1.240
1	3	2		3	$3\Pi_g, 1\Pi_g$	3	1.26	1.266, 1.257
2	3	0	1	6	$3, 1\Sigma_u^+, 3, 1\Delta_u, 3, 1\Sigma_u^-$	1	1.46	
2	2	1	1	6	$3, 1\Phi_g, 5, 3, 3, 3, 1, 1, 1\Pi_g$	1	1.54	1.541
2	1	2	1	6	$3, 1\Sigma_u^+, 3, 1\Delta_u, 3, 1\Sigma_u^-$	1	1.62	
0	4	2		6	$1\Sigma_g^+$	4	1.12	
0	4	2			$C\equiv C$	4	1.12	
(1)	4	(1)			$-C\equiv C-$	3	1.18	1.20
(1)	2+(1)	(1)	(1)		$>C=C<$	2	1.40	1.34
(1)	(2)	(1)	(2)		$\geq C-C\leq$	1	1.62	1.54
2	3			0	$2\Pi_u$	$1\frac{1}{2}$	1.35	
2	2	1		0	$4, 2\Sigma_g^-, 2\Delta_g, 2\Sigma_g^+$	$1\frac{1}{2}$	1.43	
2	1	2		0	$2\Pi_u$	$1\frac{1}{2}$	1.51	
1	4			3	$2\Sigma_u^+$	$2\frac{1}{2}$	1.21	
1	3	1		3	$4, 2, 2\Pi_g$	$2\frac{1}{2}$	1.29	
1	2	2		3	$4, 2\Sigma_u^-, 2\Delta_u, 2\Sigma_u^+$	$2\frac{1}{2}$	1.37	
2	2	0	1	6	$2\Phi_g, 4, 2, 2, 2\Pi_g$	$1\frac{1}{2}$	1.57	
2	1	1	1	6	$4, 2, 2(\Sigma_u^-, \Delta_u, \Sigma_u^+)$	$1\frac{1}{2}$	1.65	
2	0	2	1	6	$2\Pi_g$	$1\frac{1}{2}$	1.73	
0	4	1		6	$2\Sigma_g^+$	$3\frac{1}{2}$	1.15	
0	3	2		6	$2\Pi_u$	$3\frac{1}{2}$	1.23	

* The energy values are rough estimates made for internuclear distances near 1.25A. If r_0 differs much from 1.25A, the energy at r_0 is considerably lowered, as can be seen by drawing $U(r)$ curves. The above estimated energy values are based on the observed energy intervals of 2.39 eV ($3\Pi_g-3\Pi_u$) and 3.20 eV ($1\Pi_g-1\Pi_u$) between states of the configurations $\sigma_u^2\pi_u^3\sigma_g$ and $\sigma_u\pi_u^3\sigma_g^2$, and of 4.91 eV between $\sigma_u^2\pi_u^3\sigma_g$, $3\Pi_u$ and $\sigma_u^2\pi_u^3\sigma_g\pi_g$, $3\Pi_g$ (the latter found and identified by Fox and Herzberg, reference 4). The observed energy intervals just mentioned are those between the *minima* of potential curves; the required correction to constant r increases them, especially that for the Fox-Herzberg bands.

values. The simplest possibility is that the following equation is valid:

$$r_0 = P + yN_y - wN_w - xN_x + vN_v, \quad (1)$$

where N_y , N_w , N_x , and N_v are the numbers of electrons in the respective MO's $y\sigma_u$, $w\pi_u$, $x\sigma_g$, and $v\pi_g$, and P , y , w , x , v are adjustable positive constants. Bonding electrons then make negative, antibonding electrons positive contributions to r_0 in Eq. (1). The several constants in Eq. (1) must be determined so as to give correctly the r_0 values of known states of C_2 . Known states^{1, 3, 4} are the $3\Pi_u$ and $1\Pi_u$ of $z\sigma^2y\sigma^2w\pi^3x\sigma$ with $r_0=1.3135A$ and $1.318A$, respectively (average $1.316A$), the $3\Pi_g$ and $1\Pi_g$ states of $z\sigma^2y\sigma w\pi^3x\sigma^2$ with $r_0=1.26A$ and $1.25A$, respectively (average r_0 $1.261A$), and the $3\Pi_g$ state⁴ of $z\sigma^2y\sigma^2w\pi^2x\sigma v\pi$ ($r_0=1.54A$); also the two probable $1\Sigma^+$ states, with $r_0=1.243A$ for the lower and $1.240A$ for the upper. From the data on the Π states, we get $x+y=0.058A$ and $w+v=0.224A$. Making

the assumptions $x=y$ and $v=w$, which seem on the whole to be indicated as roughly true by available r_0 data⁵ on N_2 , N_2^+ , and O_2 , we then get $x=y=0.03$, $w=v=0.11$, and $P=1.62$. Hence, in A,

$$r_0 = 1.62 + 0.03(N_y - N_x) - 0.11(N_w - N_v). \quad (2)$$

Eq. (2) has been used to obtain the "calculated" r_0 values in Table I.

Examination of r_0 data on various states of N_2 and O_2 indicates that such an equation as Eq. (2) is likely to hold fairly well only over a moderate range of r_0 values, but to give too small values when r_0 is unusually small or unusually large.

If, in the manner first proposed by Herzberg, we count the number of bonds between two atoms in a diatomic molecule as equal to half the number of bonding electrons minus half the number of antibonding electrons, the numbers of bonds for the various low-energy states of

⁴ J. G. Fox and G. Herzberg, Phys. Rev. 52, 638 (1937).

⁵ Cf. H. Sponer, *Molekülspektren*, Vols. I, II (J. Springer, Berlin, 1935-36).

C_2 and C_2^+ are as given in the seventh column of Table I. It will be noted that for a given number of bonds, the r_0 values vary considerably. This is, of course, because different bonding (and antibonding) MO's differ considerably in their bonding (or antibonding) power.

Turning to the identification of the electronic states of the $\lambda 2300$ band, we note that r_0 has the values 1.240A and 1.243A for the upper and lower states, respectively. Referring to Table I one finds only one $\Sigma \rightarrow \Sigma$ transition between low energy C_2 states both with predicted r_0 values near 1.24A. This is $\sigma_u \pi_u^4 \sigma_g$, ${}^1\Sigma_u^+$ (predicted $r_0 = 1.18A$) $\rightarrow \sigma_u^2 \pi_u^4$, ${}^1\Sigma_g^+$ (predicted $r_0 = 1.24A$). For the lower state the predicted and observed r_0 's agree, for the upper there is a disagreement of 0.06A. For the energy change, the predicted value is 3 ev plus an amount equal to half the ${}^1\Sigma_u^+ - {}^3\Sigma_u^+$ interval for $\sigma_u \pi_u^4 \sigma_g$,—or say roughly about 4 ev. The observed value is 5.34 ev. Although there is a greater disagreement between observation and prediction than one can easily explain, every other $\Sigma \rightarrow \Sigma$ transition of C_2 or C_2^+ (including those between higher states than are listed in Table I) gives much worse agreement.⁶

By way of explaining the discrepancies between observed and predicted features, the following may perhaps help. In Table I two additional ${}^1\Sigma_u^+$ states, with r_0 values of 1.46A and 1.62A, are predicted to lie near 6 ev. It seems likely that the $U(r)$ curve of the lower of these, rising steeply near 1.24A since its minimum is near 1.5A, intersects that of the predicted $\sigma_u \pi_u^4 \sigma_g$, ${}^1\Sigma_u^+$ not far from the latter's minimum near 1.2A. Interaction of the two curves might give rise to two new curves of which one (the upper) could have the characteristics of the upper level of the $\lambda 2300$ band. It may here be noted also that a low ${}^1\Sigma_g^+$ state with r_0 about 1.40A is predicted which should lie near the $\sigma_u^2 \pi_u^4$, ${}^1\Sigma_g^+$ state identified as the lower state of the $\lambda 2300$ band; these two states may interact to some extent.

Accepting the foregoing interpretation of the $\lambda 2300$ band as correct, we may ask, what is the

⁶ The transition $\pi_u^4 \sigma_g$, ${}^2\Sigma_g^+ \rightarrow \sigma_u \pi_u^4$, ${}^2\Sigma_u^+$ is the most likely C_2^+ possibility, but the predicted r_0 's are 1.15 and 1.21A and the predicted energy change only 3 ev; and the lines should be narrow doublets.

lowest electronic level (normal state) of C_2 ? If the assumption made in Table I of equal energy for the configurations $\sigma_g^2 \sigma_u^2 \pi_u^4$, $\sigma_g^2 \sigma_u^2 \pi_u^3 \sigma_g$, and $\sigma_g^2 \sigma_u^2 \pi_u^2 \sigma_g^2$ is correct, then ${}^3\Pi_u$ of $\sigma^2 \sigma^2 \pi^3 \sigma$ (lower state of the Swan bands) is probably lowest (as is now generally assumed), with ${}^3\Sigma_g^-$ of $\sigma^2 \sigma^2 \pi^2 \sigma^2$ a close second, and with ${}^1\Sigma_g^+$ of $\sigma^2 \sigma^2 \pi^4$ and ${}^1\Delta_g$ of $\sigma^2 \sigma^2 \pi^2 \sigma^2$ not very much higher.⁷ If, however, the configuration $\sigma^2 \sigma^2 \pi^2 \sigma^2$ is lowest of the three, the normal state of C_2 may be ${}^3\Sigma_g^-$ instead of ${}^3\Pi_u$. On the other hand, if $\sigma^2 \sigma^2 \pi^4$ is the lowest-energy configuration and is sufficiently low,⁷ ${}^1\Sigma_g^+$ could be the normal state instead of ${}^3\Pi_u$. On the basis of present knowledge, none of the foregoing possibilities can be excluded, although ${}^3\Pi_u$ appears still to be the best guess for normal state. In any case, all the states mentioned may be expected to play a role for astrophysical problems where C_2 spectra are involved.

II. CARBON-CARBON BOND DISTANCES IN CARBON COMPOUNDS

In connection with Table I, it seemed of interest to attempt to use Eq. (2) to calculate carbon to carbon bond distances for single and multiple C—C bonds in carbon compounds. This can be done if we assume that the bonds formed with other atoms make use of C_2 MO's in the manner indicated by the assignments in parentheses in the middle section of the table.⁸ In all cases a pair of $z\sigma_g$ electrons not given in the table is supposed to be present and to form one C—C bond. The calculated values are seen to agree roughly with average observed values as given by Pauling.⁹ In the cases of double and single bonds the observed values are smaller than the calculated, suggesting that the C—C bonds are here strengthened by the process of sharing carbon electrons with other atoms instead of just between two carbons. However,

⁷ These statements are based on estimated energies (relative to the mean energy for the given electron configuration) of -0.5 , 0.0 , and $+0.5$ ev for ${}^3\Sigma_g^-$, ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ of $\sigma^2 \sigma^2 \pi^2 \sigma^2$, -0.8 and $+0.8$ ev for ${}^3\Pi_u$ and ${}^1\Pi_u$ of $\sigma^2 \sigma^2 \pi^3 \sigma$, and 0.0 for ${}^1\Sigma_g^+$ of $\sigma^2 \sigma^2 \pi^4$. These represent revisions of estimates given previously (reference 3).

⁸ Cf. R. S. Mulliken, J. Chem. Phys. **3**, 517 (1935) for a description of the way in which the C_2 MO's are used to form bonds to other atoms.

⁹ Cf. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), p. 154.

the orbitals, particularly $z\sigma_g$, should be considerably modified (especially as regards extent of $s-p$ mixing) by the clustering of other atoms around the carbons, so that r_0 values calculated on the basis of a diatomic carbon molecule are no longer entirely appropriate.

When a table similar to Table I and an

equation similar to Eq. (2) are written down for N_2 and N_2^+ , one finds relations similar to those for carbon: bonding to other atoms seems to shorten the $N=N$ and $N-N$ bond distances as compared with those for N_2 itself. The equation for N_2 and N_2^+ is

$$r_0 = 1.49 + 0.03(N_y - N_x) - 0.10(N_w - N_v). \quad (3)$$

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The Infra-Red Spectrum and Molecular Constants of Nitric Oxide

ALVIN H. NIELSEN* AND WALTER GORDY**

Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

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The infra-red spectrum of nitric oxide has been re-measured under high dispersion with the result that the fundamental at 5.3μ has been almost completely resolved. The absorption in this region comprises two superposed bands arising from a ${}^2\Pi_{1/2, 3/2}$ electronic ground state. In the P , and R branches a great many of the lines split up into doublets, the components of which belong to these two bands, respectively. The lines were found to fit the following two empirical formulas:

$$\begin{aligned} \nu_{\Omega=1/2} &= 1877.36 + 3.34 J - 0.019 J^2 \text{ cm}^{-1} \\ &\text{where } J=0, \pm 3/2, 5/2, \dots, \\ \nu_{\Omega=3/2} &= 1877.00 + 3.42 J - 0.019 J^2 \text{ cm}^{-1} \\ &\text{where } J=0, \pm 5/2, 7/2, \dots \end{aligned}$$

An experimental curve in percent absorption against frequency in cm^{-1} is compared with a theoretical intensity plot of the bands. From the new data some of the constants have been re-calculated, and compared with the results of the electronic band spectra. $I_0 = 1.63 \times 10^{-30} \text{ g cm}^2$, $r_0 = 1.15 \times 10^{-8} \text{ cm}$, $\nu_0 = 1891.3 \text{ cm}^{-1}$.

I. INTRODUCTION

AMONG the diatomic molecules having infra-red spectra nitric oxide is of special interest. Because of its electronic configuration, which gives it a ground state of ${}^2\Pi_{1/2, 3/2}$, the molecule has resultant angular momentum of $(1/2)\hbar$ and $(3/2)\hbar$ around its nuclear axis. It becomes, therefore, the only one of the diatomic molecules to exhibit a Q branch in the infra-red.

Warburg and Leithauser¹ in 1908, the first to investigate the spectrum, succeeded in showing that the contour of the fundamental at 5.3μ was a doublet. Later, in 1929–1930, Snow, Rawlins, and Rideal² resolved both the fundamental at 5.3μ and the first harmonic at 2.7μ into rotational structure by means of a grating spectrometer.

This spectrum has been re-investigated using an instrument of somewhat better resolving power. Several details of interest were observed and are reported here. Some of the constants are calculated from our data and compared with values given in the earlier work, and with those determined from the electronic band spectrum.³

II. APPARATUS

The nitric oxide was prepared according to the method outlined by Snow, Rawlins, and Rideal.² A large spherical bulb was filled to atmospheric pressure by passing gas through the bulb until all the air had been displaced by the gas. The nitric oxide was allowed to generate and flow until the colorlessness of the gas in the storage tank attested to its purity. For the 5.3μ region a cell 2 cm long fitted with rocksalt windows was used; for the 2.7μ region the cells used were from 10–30 cm long. Each cell was

* Department of Physics, University of Tennessee, Knoxville, Tennessee.

** Mary Hardin Baylor College, Belton, Texas.

¹ Warburg and Leithauser, *Ber. D. Chem. Ges.* **1**, 145 (1908).

² C. P. Snow, F. I. G. Rawlins and E. K. Rideal, *Proc. Roy. Soc.* **124**, 453 (1929); C. P. Snow, F. I. G. Rawlins and E. K. Rideal, *Proc. Roy. Soc.* **126**, 355 (1929).

³ M. Guillery, *Zeits. f. Physik* **42**, 121 (1927); F. A. Jenkins, H. A. Barton and R. S. Mulliken, *Phys. Rev.* **30**, 150 (1927); R. S. Mulliken, *Phys. Rev.* **32**, 186 (1928).