Electronic States of the C_2 Radical

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Introduction

The investigation of the electronic properties for the carbon-carbon bond have generally been performed on the interactions between the π-electrons. For the precise study of charge distribution, hyperconjugation and so on, it is very desirable to take into consideration the mutual interactions between all the electrons, at least between all the valence electrons. Nevertheless, only a few investigations have been carried out in such a way, because of the complicated procedure required, in comparison with that for the π-electrons only. Moreover, it is very difficult to appraise the effect of the errors accompanying the calculation for the σ-electrons, since there are, in general, few experimental data except for the π-orbitals. From this point of view, the C_2 radical is one of the most suitable examples, because it is the simplest molecule and there are abundant experimental data on it.

The Swan bands and the Mulliken bands of the C_2 radical have been detected in flames, explosions and electric discharges of hydrocarbons, and recently also in flash photolysis; the other bands have also been observed by spectroscopic technique. On the other hand, theoretical investigations were qualitatively made by Mulliken[1], who predicted many unobserved states. A quantitative calculation was carried out by Araki, Tutihasi and Watari[2] using the AO method, but the results were not sufficiently satisfying to explain the observed electronic states. In the present work, therefore, the LCAO-SCF method was adopted and the interactions between all the electrons were included.

Outline of Calculation

The calculation was carried out by taking ten atomic orbitals c, s, σ, π_+, π_-, c', s', σ', π_+' and π_-' into consideration, which mean $1s$, $2s$, $2p\sigma$, $2p\pi_+$, $2p\pi_-$ orbitals of each carbon atom. The $1s$ AO's were regarded as the inner shells, since the overlap integrals between c or c' and the other AO's are fairly small in comparison with the others[3]. The internuclear distance was taken as 1.33 Å, nearly equal to the equilibrium internuclear distance of the observed lowest state $^3\Pi_u$, i. e., 1.31 Å[4].

The atomic orbitals used were the Hartree SCF AO's for the s^2p^2 configuration of carbon atom[5] as in the case of the CH radical[6], assuming that they satisfy the following Fock equations for the valence state $V_2(\sigma\pi)$ in the s^2p^2 configuration.

$$(I+2J_c-K_c+2J_s-K_s+J_\sigma-\frac{1}{2}K_\sigma+J_\pi-\frac{1}{2}K_\pi)s$$

$$=(I_s+2J_{cs}-K_{cs}+J_{ss}+J_{s\sigma}-\frac{1}{2}K_{s\sigma}+J_{s\pi}-\frac{1}{2}K_{s\pi})s, \tag{1}$$

$$(I+2J_c-K_c+2J_s-K_s+J_\pi-\frac{1}{2}K_\pi)\sigma$$

$$=(I_\sigma+2J_{c\sigma}-K_{c\sigma}+2J_{s\sigma}-K_{s\sigma}+J_{\sigma\pi}-\frac{1}{2}K_{\sigma\pi})\sigma, \tag{2}$$

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[1] R.S. Mulliken, *Phys. Rev.*, **41**, 751 (1932); **56**, 778 (1939).

[2] G. Araki, S. Tutihashi and W. Watari, *Prog. Theor. Phys.*, **6**. 135 (1951); G. Araki and W. Watari, *Prog. Theor. Phys.*, **6**, 945 (1951).

[3] $S_{cc'}=0.00005$, $S_{sc'}=0.05086$, $S_{\sigma c'}=0.08619$, while $S_{ss'}=0.45626$, $S_{s\sigma'}=0.44413$.

[4] G. Herzberg, "Molecular Spectra and Molecular Structure", D. Van Nostrand Company, Inc., New York (1950), Second Edition, Vol. 1, p. 518.

[5] C.C. Torrance, *Phys. Rev.*, **46**, 388 (1934). The Hartree-Fock SCF AO's for the V_2 $(\sigma\pi)$ have not yet been obtained, and therefore the Hartree SCF AO's were used.

[6] J. Higuchi, *J. Chem. Phys.*, **22**, 1339 (1954).

$$(I+2J_c-K_c+2J_s-K_s+J_\sigma-\frac{1}{2}K_\sigma)\pi_\pm$$
$$=(I_{\pi_\pm}+2J_{c\pi_\pm}-K_{c\pi_\pm}+2J_{s\pi_\pm}-K_{s\pi_\pm}+J_{\sigma\pi_\pm}$$
$$-\frac{1}{2}K_{\sigma\pi_\pm})\pi_\pm. \tag{3}$$

Here

$$I=-\frac{1}{2}\Delta_\nu-\frac{6}{r_{c\nu}}, \tag{4}$$

$$J_i{}^\nu\phi^\nu=\left(\int\bar{\phi}_i{}^\mu\frac{1}{r^{\mu\nu}}\phi_i{}^\mu d\tau^\mu\right)\phi^\nu, \tag{5}$$

$$K_i{}^\nu\phi^\nu=\left(\int\bar{\phi}_i{}^\mu\frac{1}{r^{\mu\nu}}\phi^\mu d\tau^\mu\right)\phi_i{}^\nu, \tag{6}$$

and

$$I_i=\int\bar{\phi}_i{}^\nu\left(-\frac{1}{2}\Delta_\nu-\frac{6}{r_{c\nu}}\right)\phi_i{}^\nu d\tau^\nu, \tag{7}$$

$$J_{ij}=\int\bar{\phi}_i{}^\mu\bar{\phi}_j{}^\nu\frac{1}{r^{\mu\nu}}\phi_i{}^\mu\phi_j{}^\nu d\tau^{\mu\nu}, \tag{8}$$

$$K_{ij}=\int\bar{\phi}_i{}^\mu\bar{\phi}_j{}^\nu\frac{1}{r^{\mu\nu}}\phi_j{}^\mu\phi_i{}^\nu d\tau^{\mu\nu}. \tag{9}$$

Consequently, one-center integrals calculated by Ufford[7] were used. It is very difficult, however, to calculate the majority of the two-center integrals and it is assumed that the use of the Slater AO's[8] instead of the SCF AO's gives good approximations of these integrals, and they were taken from the table by Kotani et al[9]. The core-field energies were obtained from the above Fock equations (1)–(3).

From the eight available AO's, the symmetry orbitals for the C_2 radical were obtained as follows:

$$\begin{aligned}
&\sigma_1=2^{-1/2}(s+s'), &&\sigma_2=2^{-1/2}(\sigma+\sigma')\\
&\sigma_3=2^{-1/2}(s-s'), &&\sigma_4=2^{-1/2}(\sigma-\sigma')\\
&\sigma_5=2^{-1/2}(\pi_++\pi_+'), &&\sigma_6=2^{-1/2}(\pi_-+\pi_-')\\
&\sigma_7=2^{-1/2}(\pi_+-\pi_+'), &&\sigma_8=2^{-1/2}(\pi_--\pi_-').
\end{aligned} \tag{10}$$

By taking linear combinations of these, a like number of MO's of the same symmetry was formed as follows:

$$\begin{aligned}
&K=c, &&K'=c'\\
&1\sigma_g=a_{11}\sigma_1+a_{12}\sigma_2, &&1\sigma_u=a_{33}\sigma_3+a_{34}\sigma_4\\
&2\sigma_g=a_{21}\sigma_1+a_{22}\sigma_2, &&2\sigma_u=a_{43}\sigma_3+a_{44}\sigma_4\\
&1\pi_g^+=a_{77}\sigma_7, &&1\pi_u^+=a_{55}\sigma_5\\
&1\pi_g^-=a_{88}\sigma_8, &&1\pi_u^-=a_{66}\sigma_6.
\end{aligned} \tag{11}$$

The prescripts 1, 2 are in the order of increasing energy within each symmetry. The coefficients of a_{ip}'s of the symmetry orbitals were chosen to satisfy the orthogonality conditions:

$$\int\bar{\phi}_i{}^\nu\phi_j{}^\nu d\tau^\nu=\sum_{p,q}\bar{a}_{ip}S_{pq}a_{jq}=\delta_{ij}, \tag{12}$$

where the overlap integrals S_{pq}'s are defined by

$$S_{pq}=\bar{S}_{qp}=\int\bar{\sigma}_p\sigma_q d\tau. \tag{13}$$

In the first place, the SCF calculation[10] was carried out for the lowest $^3\Sigma_g^-$ state $KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2(2\sigma_g)^2$, which has been considered to be close above the lowest $^3\Pi_u$ state or to be the ground state.

Next the SCF calculation was also carried out for the state $^1\Sigma_g^+$ $KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4$, which has been supposed to be the lowest singlet state. However, the energy for the lowest $^3\Pi_u$ state $KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^3(2\sigma_g)^1$, was not minimized, because the properties of the state can readily be inferred from the results of the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ states.

LCAO MO's

The LCAO MO's obtained by the SCF procedure are given in Table I, and the SCF solutions are given in Table II. The $^3\Sigma_g^-$

TABLE I

LCAO SCF MO's FOR $\begin{Bmatrix}^3\Sigma_g^-\\ ^1\Sigma_g^+\end{Bmatrix}$ STATE

$$\begin{aligned}
&K=c, \qquad\qquad K'=c'\\
&1\sigma_g=\begin{Bmatrix}0.628\\0.693\end{Bmatrix}\sigma_1+\begin{Bmatrix}0.395\\0.298\end{Bmatrix}\sigma_2\\
&2\sigma_g=\begin{Bmatrix}0.609\\0.534\end{Bmatrix}\sigma_1-\begin{Bmatrix}0.830\\0.870\end{Bmatrix}\sigma_2\\
&1\sigma_u=\begin{Bmatrix}1.089\\1.085\end{Bmatrix}\sigma_3-\begin{Bmatrix}0.303\\0.307\end{Bmatrix}\sigma_4\\
&2\sigma_u=\begin{Bmatrix}1.658\\1.660\end{Bmatrix}\sigma_3+\begin{Bmatrix}1.746\\1.745\end{Bmatrix}\sigma_4\\
&1\pi_u{}^\pm=0.888\,\sigma_{\substack{5\\6}},\quad 1\pi_g{}^\pm=1.193\,\sigma_{\substack{7\\8}}.
\end{aligned}$$

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[7] C.W. Ufford, *Phys. Rev.*, 53, 568 (1938).

[8] $c=(\delta'^3/\pi)^{1/2}\exp(-\delta' r)$, $s=(\delta^5/3\pi)^{1/2}r\exp(-\delta r)$, $\sigma=(\delta^5/\pi)^{1/2}r\exp(-\delta r)\cos\theta$, $\pi_\pm=(\delta^5/2\pi)^{1/2}r\exp(-\delta r)\sin\theta\exp(\pm i\varphi)$.

In the present calculation δ and δ' are chosen as 1.59 and 5.6875, respectively.

[9] M. Kotani, A. Amemiya, T. Shimose, *Proc. Phys-Math. Soc. Japan*, 20, Extra No. 1 (1938); M. Kotani, E. Ishiguro, K. Hijikata, T. Nakamura and A. Amemiya, *J. Phys. Soc. Japan*, 8, 463 (1953).

[10] In the present calculation, the following approximation was used

$$\int\bar{p}^\nu\left(-\frac{6}{r_{\nu c}}\right)q'^\nu d\tau^\nu+2(pq':cc)-(pc:cq')$$
$$\sim\int\bar{p}^\nu\left(-\frac{4}{r_{c\nu}}\right)q'^\nu d\tau^\nu,$$

where the c, p orbitals and the q' orbital belong to different atoms. In the calculation of $\int\frac{4}{r_{c\nu}}s^\nu q'^\nu d\tau^\nu$, the orthogonalized $2s$ function was used for s, because the error due to the nonorthogonal $2s$ function is very significant near the C nucleus.

TABLE II

SELF-CONSISTENT SOLUTIONS*

		state	$^3\Sigma_g^-$	$^1\Sigma_g^+$
$S_{\sigma_1\sigma_1}$	1.45626	$G_{\sigma_1\sigma_1}$	4.2347	4.3051
$S_{\sigma_1\sigma_2}$	0.44413	$G_{\sigma_1\sigma_2}$	1.7262	1.7115
$S_{\sigma_2\sigma_2}$	1.31869	$G_{\sigma_2\sigma_2}$	4.1287	4.5383
$S_{\sigma_3\sigma_3}$	0.54374	$G_{\sigma_3\sigma_3}$	1.4686	1.5006
$S_{\sigma_3\sigma_4}$	−0.44413	$G_{\sigma_3\sigma_4}$	−1.1376	−1.1632
$S_{\sigma_4\sigma_4}$	0.68131	$G_{\sigma_4\sigma_4}$	1.7847	1.8224
$S_{\sigma_5\sigma_5}$	1.28695	$G_{\sigma_5\sigma_5}$	3.6731	3.7450
$H'_{\sigma_1\sigma_1}$	−5.7954	$\varepsilon_{1\sigma_g}$	−1.1922	−1.1196
$H'_{\sigma_1\sigma_2}$	−2.5345	$\varepsilon_{2\sigma_g}$	−0.5395	−0.2044
$H'_{\sigma_2\sigma_2}$	−5.2574	$\varepsilon_{1\sigma_u}$	−0.6375	−0.5793
$H'_{\sigma_3\sigma_3}$	−1.8011	$\varepsilon_{2\sigma_u}$	+0.2559	+0.3103
$H'_{\sigma_3\sigma_4}$	+1.4718	$\varepsilon_{1\pi_u}$	−0.5448	−0.4851
$H'_{\sigma_4\sigma_4}$	−2.0356	$\varepsilon_{1\pi_g}$	+0.0699	+0.0854
$H'_{\sigma_5\sigma_5}$	−4.3742			

* S_{pq}'s are the overlap integrals, H'_{pq}'s the core-field energy matrix elements, G_{pq}'s the electronic interaction matrix elements, ε_i's the LCAO SCF orbital energies.

state MO's also satisfy the conditions which minimize the energy of the $^1\Delta_g$ state $KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2(2\sigma_g)^2$ and the $^1\Sigma_g^+$ state $KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2(2\sigma_g)^2$, because the energy differences between these states are only proportional to the energy $K_{1\pi_u{}^+1\pi_u{}^-}$ which is independent of the LCAO-SCF procedure. These LCAO MO'S are, therefore, also the $^1\Delta_g$ state MO's and the $^1\Sigma_g^+$ MO's as well as the $^3\Sigma_g^-$ state MO's.

The coefficients of the AO's in these LCAO MO's are in good agreement with those predicted by Mulliken, and the LCAO MO's for the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ states in Table I resemble each other. The special similarity for the weakly antibonding $1\sigma_u$ MO is due to the fact that the MO hardly effects the bonding property of the radical. In the strongly bonding $1\sigma_g$ MO, however, the coefficient of σ_1 for the $^1\Sigma_g^+$ state MO is rather large, but in the weakly bonding $2\sigma_g$ MO this relation is reversed, since the $2\sigma_g$ MO is vacant in the $^1\Sigma_g^+$ state while it is occupied in the $^3\Sigma_g^-$ state.

The coefficients of the AO's in the $^{1,3}\Pi_u$ MO's are generally considered to have the values between those of the $^3\Sigma_g^-$ state MO's and the $^1\Sigma_g^+$ stane MO's from the numbers of the occupied electrons in each MO's. In the total energies of the $^{1,3}\Pi_u$ states, however, the coefficients of the $K_{2\sigma_g 1\pi_u}$ are not the same and consequently the forms of the MO's will be somewhat different from each other. However, the $^3\Pi_u$ state MO's may be rather close to the $^3\Sigma_g^-$ state MO's (while the $^1\Pi_u$ state MO's may somewhat resemble to the $^1\Sigma_g^+$ state MO's), on account of the same coefficient of the $K_{2\sigma_g 1\pi_u}$. These MO's also rather resemble the N_2 ground state MO's by Scherr[11]. This is mainly due to the fact that the values of δR, R being the internuclear distance, are nearly equal and so the overlap integrals are very close in both cases.

In the $^3\Sigma_g^-$ state MO's, the orbital energy of $1\pi_u$ MO is very close to that of the $2\sigma_g$ MO. However, the result of the N_2 molecule by Scherr showed that the incomplete treatment gave the very close orbital energies for these MO's, while the $2\sigma_g$ MO energy is 0.96 eV. higher than the $1\pi_u$ MO enegy in the complete treatment. In consideration of these facts, the energy difference between these MO's will be increased by taking into account the inner-shell-outer-shell-mixing. The orbital energy of the $2\sigma_g$ MO in the $^1\Sigma_g^+$ state MO's is very high as compared with that in the $^3\Sigma_g^-$ state MO's, because the MO is vacant in the $^1\Sigma_g^+$ state and this value is the SCF orbital energy but not the orbital energy by Mulliken[12].

Electronic States

By using the LCAO MO's given in Table I, the energies of the lower electronic states were calculated without configuration interaction[13], and are shown in Fig. 1. The electronic configurations of these states are given in Table III. The energy levels calculated by both the LCAO MO's considerably resemble each other; therefore the energy levels which are to be obtained by the other state MO's than the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ state MO's will be very similar to those in Fig. 1, as in the case of the CH radical.

The calculated value (2.5 eV.) of the $^3\Pi_g$ (a)—$^3\Pi_u$ (a) transition and that (5.4–5.5 eV.) of the $^3\Pi_g$ (b)—$^3\Pi_u$ (a) transition are in good

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11) C.W. Scherr, *J. Chem. Phys.*, **23**, 569 (1955).

12) R.S. Mulliken, *J. chim. phys.*, **46**, 497 (1949).

13) The interactions between the wave functions arising from rotation operation were taken into consideration.

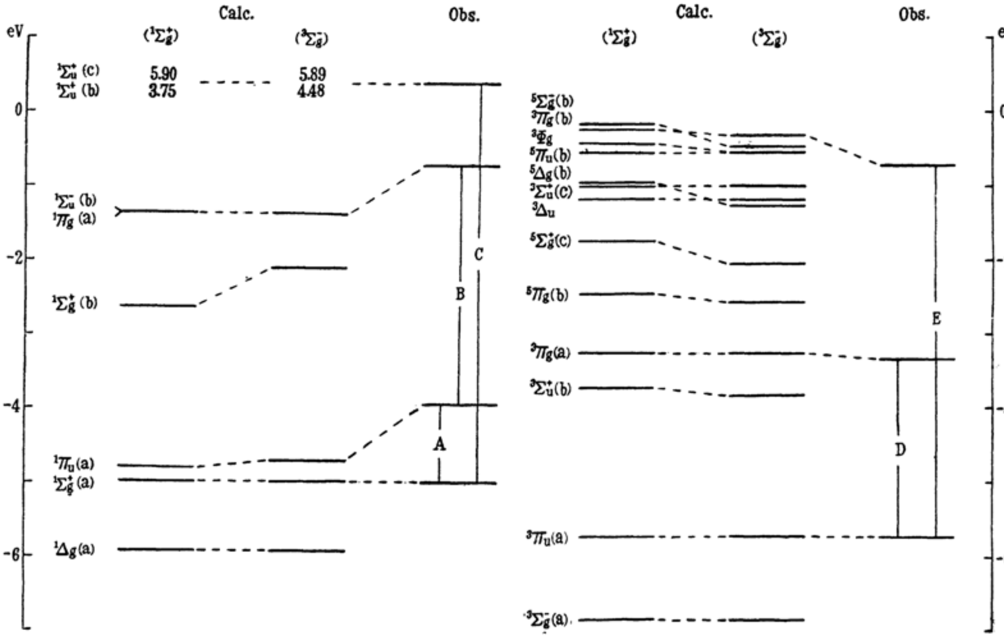

Fig. 1. Lower electronic states of the C_2 radical.
(A) The Phillips bands (B) The Deslandres-d'Azambuja bands (C) The Mulliken bands (D) The Swan bands (E) The Fox-Herzberg bands. The origin of energy is chosen to be $C(^3P)+C(^3P)$ without configuration interaction.

TABLE III

ELECTRON CONFIGURATIONS OF THE LOWER ELECTRONIC STATES

Configuration	State
$KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{\pm})^2(2\sigma_g)^2$	$^1\Delta_g$(a)
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{+})^1(1\pi_u^{-})^1(2\sigma_g)^2$	$^1\Sigma_g^+$(a), $^3\Sigma_g^-$(a)
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{\pm})^2(1\pi_u^{\mp})^1(2\sigma_g)^1$	$^{1,3}\Pi_u$(a)
〃 $(1\sigma_g)^2(1\sigma_u)^1(1\pi_u^{\pm})^2(1\pi_u^{\mp})^1(2\sigma_g)^2$	$^{1,3}\Pi_g$(a)
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{\pm})^2(1\pi_u^{\mp})^1(1\pi_g^{\mp})^1$	$^{1,3}\Sigma_u^+$(a), $^{1,3}\Sigma_u^-$(a)
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{\pm})^1(2\sigma_g)^2(1\pi_g^{\pm})^1$	$^{1,3}\Delta_u$
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{\pm})^2(2\sigma_g)^1(1\pi_g^{\pm})^1$	$^{1,3}\Phi_g$
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{+})^2(1\pi_u^{-})^2$	$^1\Sigma_g^+$(b)
〃 $(1\sigma_g)^2(1\sigma_u)^1(1\pi_u^{+})^2(1\pi_u^{-})^2(2\sigma_g)^1$	$^{1,3}\Sigma_u^+$(b)
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{\pm})^1(2\sigma_g)^2(1\pi_g^{\mp})^1$	$^{1,3}\Sigma_u^-$(b), $^{1,3}\Sigma_u^+$(c)
〃 $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u^{+})^1(1\pi_u^{-})^1(2\sigma_g)^1(1\pi_g^{\pm})^1$	$^{1,1,3,3,3,5}\Pi_g$(b)
〃 $(1\sigma_g)^2(1\sigma_u)^1(1\pi_u^{\pm})^2(1\pi_u^{\mp})^1(2\sigma_g)^1(1\pi_g^{\pm})^1$	$^{1,1,3,3,3,5}\Delta_g$(b)
〃 $(1\sigma_g)^2(1\sigma_u)^1(1\pi_u^{+})^1(1\pi_u^{-})^1(2\sigma_g)^2(1\pi_g^{\pm})^1$	$^{1,1,3,3,3,5}\Pi_u$(b)
〃 $(1\sigma_g)^2(1\sigma_u)^1(1\pi_u^{\pm})^2(1\pi_u^{\mp})^1(2\sigma_g)^1(1\pi_g^{\mp})^1$	$^{1,1,3,3,3,5}\Sigma_g^-$(b) $^{1,1,3,3,3,5}\Sigma_g^+$(c)

agreement with the observed value (5179 Å)[14] of the Swan bands and that (2495 Å) of the Fox-Herzberg bands, respectively. The $^1\Pi_g$ (a) —$^1\Pi_u$ (a) interval (3.4–3.5 eV.) in this calculation is also in good agreement with the observed value (3865 Å) of the Deslandres-d'Azambuja bands. The experimentally known Phillips bands and Mulliken bands

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[14] All the observed values are taken from reference (4).

correspond to the ${}^1\Pi_u$ (a)—${}^1\Sigma_g^+$ (a) (or ${}^1\Pi_u$ (a)—${}^1\Sigma_g^+$ (b)) and ${}^1\Sigma_u^+$ (c)—${}^1\Sigma_g^+$ (a) (or ${}^1\Sigma_u^+$ (b)—${}^1\Sigma_g{}^+$ (b)) transitions, respectively, but the calculated transition of the latter bands is considerably larger than the experimental one. This is mainly due to the facts that the present calculation ignores configuration interaction and that the SCF procedure is carried out for the ${}^3\Sigma_g^-$ (a) and ${}^1\Sigma_g^+$ (b) states only. The calculated ground state is the ${}^3\Sigma_g^-$, while the lowest state observed is the ${}^3\Pi_u$. As pointed out by Mulliken[1], the ground state of the C_2 radical has not yet been conclusively decided from the experiment. But the ${}^1\Sigma_g^+$ state is most unlikely from the standpoint of spin multiplicity. On the other hand, Norrish, Porter and Thrush[15] pointed out that the separation between the ${}^1\Sigma_g^+$ and ${}^3\Pi_u$ states of 0.69 eV., as predicted by Herzberg and Sutton[16], is quite possible. In the present calculation, this separation is 0.76 eV. in good agreement with their prediction. The ground state may, therefore, be likely to be the ${}^3\Sigma_g^-$. In the complete treatment with the inner-shell-outer-shell-mixing, however, the $1\pi_u$ MO energy is expected to be somewhat lowered as compared with the $2\sigma_g$ MO energy, as supposed from the result of N_2 by Scherr; then the ${}^3\Pi_u$ (a) state may be calculated as the ground state in accord with the experiment. In a similar way, the ${}^1\Sigma_g^+$ (b) state will be very close to the ${}^1\Sigma_g^+$ (a) state, consequently the Phillips bands will be satisfactorily explained, if consideration is made of the configuration interaction between the above two ${}^1\Sigma_g^+$ states.

The dissociation energy of C_2 has not definitely been known. Herzberg gave the value of 3.6 eV. from spectroscopic evidence. Gaydon[17], however, pointed out that an extrapolation of the vibrational levels leads to 4–7 eV. Brewer, Gilles and Jenkins[18] have measured the variation in intensity with temperature of the Swan bands and deduced 4.95±0.3 eV., which has been accepted by Gaydon. The value of about 6.2 eV.[19] has been suggested from the temperature dependence of the rate of evaporation of C_2 and graphite. Glockler[20] has given 5.9 eV. from bond energy-bond length relationships. In the present calculation, the dissociation energy obtained is 5.7 eV.[21] for the ${}^3\Pi_u$ state, which is rather close to the value by Gaydon, although the value will be decreased by the atomic configuration interaction.

Discussion

The results in the present calculation are qualitatively correct and also are semi-quantitatively satisfying. This is mainly due to the fact that the one-center integrals used are obtained by the SCF AO's. The two-center integrals are, however, still somewhat unsatisfying, because most of them are calculated by using the simple Slater AO's. In fact the errors due to the use of the simple *2s* AO are not small, but the strong influence near the nucleus is modified by the approximation given in reference (10). Further, the use of the Slater AO's reduces the electronic interaction, especially between the σ-electrons, and consequently the form of the LCAO MO's will be somewhat changed by use of the two-center integrals of the SCF AO's.

The use of the fixed internuclear distance of 1.33 Å is not completely satisfactory to explain the experiment, because the equilibrium distances of the various states do not generally coincide with the value of 1.33 Å; for example, the state such as the ${}^1\Sigma_g^+$(b) has a rather small internuclear distance. Moreover, the interpretation of multiple bond must include the change of bond distance. Considering these facts, it is desirable to carry out the calculations for various internuclear separations. The treatment with the inner-shell-outer-shell-mixing is also desirable in a precise discussion. But the approximations in the present calculation may be fairly useful for larger molecules, if the problem is restricted to the subjects such as the order of the orbital energies, the one-electron excitation levels and so on. In the light of these facts, it is very hopeful to investigate the electronic properties of hydrocarbons with considerable accuracy by means of such a treatment.

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[15] R. G. W. Norrish, G. Porter and B.A. Thrush, *Nature*, **169**, 582 (1952).

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[17] A.G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall Ltd., London (1953), Second Edition.

[18] L. Brewer, P.W. Gilles and F.A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

[19] T.L. Cottrell, "The Strength of Chemical Bonds", Butterworths Scientific Publications, London (1954), p. 199.

[20] G. Glockler, *J. Chem. Phys.*, **19**, 124 (1951).

[21] The zero-point energy is not included.

Summary

LCAO MO's and ionization energies have been calculated for the $^3\Sigma_g^-$ KK' $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2(2\sigma_g)^2$ and $^1\Sigma_g^+$ $KK'(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4$ states of the C_2 radical at the internuclear distance of 1.33 Å using the LCAO-SCF method. The interactions of all the electrons have been taken into consideration, but the orthogonality relationship between the 1*s* and the other orbitals was assumed. The LCAO MO's obtained are in good agreement with those predicted by Mulliken. Using these LCAO MO's, the lower electronic states have been investigated without configuration interaction. The calculated levels are generally in good agreement with the experimental. The ground state obtained is the $^3\Sigma_g^-$ state, while the observed is the $^3\Pi_u$, but the result is not conclusive because of the ignorance of the inner-shell-outer-shell-mixing.

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