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TRANSITION PROBABILITIES FOR LOW LYING
ELECTRONIC STATES IN C_2

Enrico Clementi

March 25, 1960

ABSTRACT

The probabilities for nine electronic transitions among the low lying excited states in the C_2 molecule are calculated by the dipole moment operator method and are given in the form of oscillator strength (or f values).

The amount of hybridization in the $2\sigma_u$ and $3\sigma_u$ molecular orbitals are calculated with a semi-empirical method closely related to the Mulliken "magic formula". The agreement between the coefficient of hybridization thus obtained and those obtained with more refined calculations is satisfactory for the $^1\Sigma_g^+(a)$ ground state (the only state that could be compared). The f values for the Swan, Deslandres-d'Azambua, Mulliken, Fox-Herzberg, Phillips, and Ballik-Ramsay transitions are calculated as $f = 0.048$ (experimental 0.034), $f = 0.0650$, $f = 0.1025$, $f = 0.8184$, $f = 0.0027$ and $f = 0.0066$, respectively.

The f values for three additional yet unknown transitions between low lying states are also reported.

I. INTRODUCTION

Recent experimental studies on the C_2 molecule have settled the problem of the assignment for the ground state (Ballik and Ramsay 1959), have determined with sufficient precision the value of the dissociation energy for the ground state¹ and have located a new low-lying excited state

¹L. Brewer, W. T. Hicks, and O. H. Krikorian, paper to be submitted for publication.

(Ballik and Ramsay (1958).

On the theoretical side the location of the low-lying excited states has been reinvestigated (Clementi and Pitzer 1960) substantially confirming some old (Mulliken 1932, 1939) and more recent predictions (Pitzer and Clementi 1959).

There is still disagreement between the theoretical and experimental determination of the oscillator strength (or f value or f number) for the Swan transition. The experimental value for this transition is $f = 0.034$ (Hicks 1957) within a factor of two due to about 5 kcal of uncertainty in the determination of the heat of formation of C_2 . The calculated value for the Swan transition is $f = 0.027$ (Lyddane, Rogers and Roach 1941) if no hybridization is taken into account; a limiting value of $f = 0.13$ was proposed (Shull 1950) if hybridization is allowed to take place between the $2p_\sigma$ and $2s$ atomic orbitals.

It seems appropriate at this time to reinvestigate the calculation of the f number in the C_2 molecule. In addition to the oscillator strength of the Swan transition, we shall consider several transitions from the three lowest electronic states to excited states lying below the dissociation energies of the ground state.

Let us start by giving the molecular orbitals and the electronic configurations for the states hereafter considered. The molecular orbitals in order of increasing energy (Mulliken 1939) are as follows:

$$1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 1\pi_u, 3\sigma_g, 1\pi_g, 3\sigma_u, \dots \quad (1)$$

Here we have adopted a contracted notation in which the possibility of a substantial amount of hybridization in the $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, and $3\sigma_u$ is not explicitly indicated.

Following Mulliken we could indicate the molecular orbitals $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$ with the notation $(\sigma_g \text{hy}_s)$, $(\sigma_u \text{hy}_s)$, $(\sigma_g \text{hy}_p)$, $(\sigma_u \text{hy}_p)$, respectively. The subscript s or p indicates that the hybrid molecular orbital has predominant s or p character. In this paper we shall use the notation in equation (1) because it is shorter, but we shall interpret it as it would be for the previous expanded notation.

The twelve electrons of the molecule fill all the orbitals up to the $3\sigma_g$ for the ground state so that its symmetry is $1\Sigma_g^+$. The electronic configurations and the corresponding states (in which we shall be interested) are given below:

(a)	$2\sigma_u^2 1\pi_u^4$	$1\Sigma_g^+(a)$
(b)	$2\sigma_u^2 1\pi_u^3 3\sigma_g$	$3\Pi_u(b), 1\Pi_u(b)$
(c)	$2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	$3\Sigma_g^-(c), 1\Delta_g(c), 1\Sigma_g^+(c)$
(d)	$2\sigma_u 1\pi_u^3 3\sigma_g^2$	$3\Pi_g(d), 1\Pi_g(d)$
(e)	$2\sigma_u^2 1\pi_u^2 3\sigma_g 1\pi_g$	$3\Pi_g(e)$
(f)	$2\sigma_u 1\pi_u^4 3\sigma_g$	$1\Sigma_u^+(f)$
(g)	$2\sigma_u 1\pi_u^3 1\pi_g$	$1\Sigma_u^+(g)$

In these electronic configurations we have omitted the six electrons in the $1\sigma_g, 1\sigma_u, 2\sigma_g$ molecular orbitals to avoid unnecessary repetitions. We have indicated the electronic states by their symmetry and configuration so to avoid the Herzberg notation (Herzberg 1950) for the C_2 case which is now inconsistent with the Jenkins notation (Jenkins 1953) because of the new assignment of the ground state (Ballik and Ramsay 1958).

If we consider only one-electron transitions (obtained by allowing one electron at a time to jump from a given molecular orbital to a different one) the corresponding oscillator strength is given by

$$f = \frac{4\pi^2 m c v_{1,2}}{3n} \left| \int \phi_1^* M \phi_2 d\tau \right|^2 \quad (2)$$

where M is the electric dipole moment operator, ϕ_1 and ϕ_2 are the initial and final molecular orbitals, and $v_{1,2}$ is the observed frequency for the transition $\phi_2 \rightarrow \phi_1$. Here we have used the dipole moment matrix elements (to obtain the

f numbers of the transitions) instead of the momentum matrix element (see, for example, Chandrasekhar 1945) because it is easier. The dipole moment needed for equation (2) and the corresponding transitions are indicated as follows:

$$\begin{array}{ll}
 {}^1\Pi_u(b) \longrightarrow {}^1\Sigma_g^+(a) & \langle 1\pi_u | X + Y | 3\sigma_g \rangle \\
 {}^1\Sigma_u^+(f) \longrightarrow {}^1\Sigma_g^+(a) & \langle 2\sigma_u | Z | 3\sigma_g \rangle \\
 {}^1\Sigma_u^+(g) \longrightarrow {}^1\Sigma_g^+(a) & \langle 1\pi_u | Z | 1\pi_g \rangle \\
 {}^3\Sigma_g^-(c) \longrightarrow {}^3\Pi_u(b) & \langle 1\pi_u | X + Y | 3\sigma_g \rangle \\
 {}^3\Pi_g(d) \longrightarrow {}^3\Pi_u(b) & \langle 2\sigma_u | Z | 3\sigma_g \rangle \\
 {}^3\Pi_g(e) \longrightarrow {}^3\Pi_u(b) & \langle 1\pi_u | Z | 1\pi_g \rangle \\
 {}^1\Delta_g(o) \longrightarrow {}^1\Pi_u(b) & \langle 1\pi_u | X + Y | 3\sigma_g \rangle \\
 {}^1\Sigma_g^+(o) \longrightarrow {}^1\Pi_u(b) & \langle 1\pi_u | X + Y | 3\sigma_g \rangle \\
 {}^1\Pi_g(d) \longrightarrow {}^1\Pi_u(b) & \langle 2\sigma_u | Z | 3\sigma_g \rangle
 \end{array}$$

All the known low lying transitions are here included. Since we are primarily interested in the Swan transition, and in those transitions which are of interest in the calculation of the f number for the intercombination ${}^3\Pi_u(b) \longrightarrow {}^1\Sigma_g^+(a)$ (this will be discussed in a following paper), the Freymark transition (Freymark 1951) is not included. We remember that this transition involves an excited state substantially above the dissociation products of the ground states.

In the calculation of equation (2) the assumption is made that the orbitals not directly involved in the transition are unchanged by the transition (Mulliken and Rieke 1941).

II. HYBRIDIZATION OF THE $2\sigma_u$ AND $3\sigma_g$ MOLECULAR ORBITALS

We assume that the variation of the equilibrium internuclear distances for state wave functions belonging to different electronic configurations are proportional to the bonding power of the molecular orbitals of the configurations. It follows that, if two state wave functions, which belong to configurations differing only by one molecular orbital, namely ϕ_1 and ϕ_2 respectively, have equilibrium internuclear distances r_1 and r_2 respectively, then the quantity $\Delta r = r_1 - r_2$ is dependent on the difference in bonding power of ϕ_1 and ϕ_2 . In addition, if Δr is positive, then ϕ_1 is less bonding than ϕ_2 , and conversely if Δr is negative, ϕ_1 is more bonding than ϕ_2 . We might indicate this by means of the symbolic notation $\Delta r(\phi_1 \rightarrow \phi_2)$, which says that the difference in bonding energy which follows the promotion of one electron from the molecular orbital ϕ_1 to the molecular orbital ϕ_2 is responsible for the variation Δr in the bond length. We note that $\Delta r(\phi_1 \rightarrow \phi_2) = -\Delta r(\phi_2 \rightarrow \phi_1)$.

Let us consider the following states: $^3\Pi_u(b)$, $^3\Sigma_g^-(c)$, $^1\Pi_u(b)$, $^3\Pi_g(d)$, $^1\Pi_g(d)$ and $^3\Pi_g(e)$. By comparing the internuclear distances of the $^3\Pi_u(b)$ with those of the $^3\Sigma_g^-(c)$, $^3\Pi_g(d)$ and $^3\Pi_g(e)$ we obtain $\Delta r(1\pi_u \rightarrow 3\sigma_g) = -0.0576 \text{ \AA}$, $\Delta r(1\pi_u \rightarrow 1\pi_g) = -0.2233 \text{ \AA}$, $\Delta r(2\sigma_u \rightarrow 3\sigma_g) = 0.0457 \text{ \AA}$. From these quantities we obtain the dependent relations $\Delta r(1\pi_u \rightarrow 2\sigma_u) = \Delta r(1\pi_u \rightarrow \sigma_g) + \Delta r(3\sigma_g \rightarrow 2\sigma_u) = -0.1033 \text{ \AA}$, $\Delta r(1\pi_g \rightarrow 3\sigma_g) =$

$$\Delta r(1\pi_g \rightarrow 1\pi_u) + \Delta r(1\pi_u \rightarrow 3\sigma_g) = 0.1687 \text{ \AA} \text{ and } \Delta r(1\pi_g \rightarrow 2\sigma_u) = \\ \Delta r(1\pi_g \rightarrow 1\pi_u) + \Delta r(1\pi_u \rightarrow 3\sigma_g) + \Delta r(3\sigma_g \rightarrow 2\sigma_u) = 0.1200 \text{ \AA}.$$

These relations are valid for the states of configuration (b), (c), (d), and (e) listed previously. The differences in internuclear distance of 0.0063 Å between the $^3\Pi_u(b)$ and $^1\Pi_u(b)$ and of 0.0070 Å between the $^3\Pi_g(d)$ and $^1\Pi_g(d)$ are interpreted as due mainly to difference in the electronic correlation between triplet and singlet states.

Since hybridization modifies the bonding power of a molecular orbital we take these observations as an indication that these electronic states of the configurations (b), (c), (d), and (e) all have the same amount of hybridization in the $2\sigma_u$ and $3\sigma_g$ molecular orbitals.

The $\Delta r(\phi_1 \rightarrow \phi_2)$ relation just obtained does not apply for the state of the configuration (a), (f) and (g) and we take this as an indication that for these states the amount of hybridization for the $2\sigma_u$ and $3\sigma_g$ is different. For the ground state the amount of hybridization is obtained from the calculation of Ransil (Ransil 1953). We will return later to this point. For the $^1\Sigma_g^+(c)$, $^1\Delta_g(c)$ and $^1\Sigma_u^+(g)$ we shall assume an equilibrium internuclear distance of 1.380 Å, 1.375 Å, and 1.430 Å, respectively (Clementi 1960). The internuclear distances for known states are those given by Herzberg (Herzberg 1950). The value of 1.3693 Å for the $^3\Sigma_g^-(c)$ state was obtained from private communication with Professor D. A. Ramsay. The internuclear distances at equilibrium are here

summarized (r_e in Å units):

$^1\Sigma_g^+(a)$	1.2422	$^3\Pi_g(d)$	1.2660
$^3\Pi_u(b)$	1.3117	$^1\Pi_g(d)$	1.2730
$^1\Pi_u(b)$	1.3180	$^3\Pi_g(e)$	1.5350
$^3\Sigma_g^-(c)$	1.3693	$^1\Sigma_u^+(f)$	1.2378
$^1\Delta_g(c) \sim$	1.375	$^1\Sigma_u^+(g) \sim$	1.490
$^1\Sigma_g^+(c) \sim$	1.380		

The hybridization in the $2\sigma_u$ and in the $3\sigma_g$ may be such as to increase or decrease the bonding character of the original nonhybridized $2\sigma_u$ and $3\sigma_g$ molecular orbitals (Mulliken 1953). The amount of hybridization is calculated with a method suggested by R. S. Mulliken (1953) and making use of the semi-empirical constants obtained by the use of Mulliken's "magic formula". (Mulliken 1953). It is shown that the dissociation energy of a given state may be expressed by the equation

$$E = - \sum_i \frac{\beta_i}{1 + S_i} + \sum_j \frac{\mu_j \beta_j}{1 - S_j} \quad (3)$$

$$= + \sum_i \frac{K_i S_i}{1 + S_i} - \sum_j \frac{\mu_j K_j S_j}{1 - S_j} \quad (4)$$

where β_i and β_j are the bond integrals for bonding and anti-bonding orbitals respectively. The β integrals are taken proportional to the overlap integral and in particular

$\beta_{\sigma} = - 8.0 S_{\sigma}$ and $\beta_{\pi} = - 10.5 S_{\pi}$. These values are obtained following Mulliken's work (1953).

The constant μ_j has the effect of decreasing the bonding power of the antibonding orbitals and it is given by the semi-empirical relation (Mulliken 1950)

$$\mu_j = \frac{1 + S_j}{1 - S_j} + 1.4 S_j (1 - S_j) \quad (5)$$

where the value $1.4 = 2 \nu$ is again obtained from Mulliken's work (1953). In the following the assumption is made that the core energy (i.e. the contribution to the total energy due to the core electrons and nuclei) is the same for different electronic states at the same internuclear distance. This core energy is here indicated with E_0 . Then a given state energy is given by the core energy plus an expression of the form of equation (4) for the valency electrons

$$E = E_0 + \sum_i \frac{K_i S_i}{1 + S_i} - \sum_j \frac{K_j \mu_j S_j}{1 - S_j} \quad (6)$$

where now the summations are only on valency electrons, that is for the electrons in the $2\sigma_u$, $1\pi_u$, $1\pi_g$, and $3\sigma_g$ molecular orbitals. If hybridization is present in some of the valency molecular orbitals then S_i or S_j is replaced by S_i^h or S_j^h where the superscript h indicates that the overlap integral must be computed by using hybrid molecular orbitals. The hybrid orbitals for $3\sigma_g$ and $2\sigma_u$ are

$$\psi(3\sigma_g) = [2(1 + s_g^h)]^{-1/2} [a_1(z_A) + a_1(z_B) + b_1(2s_A) + b_2(2s_B)] \quad (7)$$

where

$$s_g^h = a_1^2 \int (z_A)(z_B) d\tau + b_1^2 \int (2s_A)(2s_B) d\tau + 2a_1b_1 \int (2s_A)(z_B) d\tau \quad (7')$$

and

$$\psi(2\sigma_u) = [2(1 - s_u^h)]^{-1/2} [a_2(2s_A) - a_2(2s_B) + b_2(z_A) - b_2(z_B)] \quad (8)$$

where

$$s_u^h = a_2^2 \int (2s_A)(2s_B) d\tau + b_2^2 \int (z_A)(z_B) d\tau + 2a_2b_2 \int (2s_A)(z_B) d\tau \quad (8')$$

The $2p_g$ atomic orbitals are chosen so that the positive lobe points toward the other atom. The coefficients a and b are related by the equation $a_1^2 + b_1^2 = a_2^2 + b_2^2 = 1$. Let us indicate with $100 \times b_1^2$ and $100 \times b_2^2$ the per cent of hybridization in the $3\sigma_g$ and $2\sigma_u$ molecular orbitals, respectively.

By making a system of equation (6) for the ${}^3\Pi_u(b)$ state and the ${}^3\Pi_g(d)$ state at the internuclear distance of $1.3117 \text{ \AA}$ and by solving for the unknown a_1 and b_1 we obtain 0.5 per cent of hybridization for the $2\sigma_g$ molecular orbital, and we find that a_1 and b_1 are opposite in sign. By making a system of

equation (6) for the ${}^3\Pi_u(b)$ state and the ${}^3\Sigma_g^-(c)$ state, we obtain 1.0 per cent of hybridization for the $2\sigma_u$ molecular orbital and a_2 and b_2 are opposite in sign.

Proceeding in an analogous way we can solve for the per cent of hybridization of the other states. From the ${}^1\Sigma_g^+(a)$ and ${}^1\Pi_u(b)$ states we obtain 6.5 per cent of hybridization for the $2\sigma_u$ molecular orbital in the ${}^1\Sigma_g^+(a)$ state. The sign of the coefficient b_2 is opposite to the sign of the coefficient a_2 . Finally, from the ${}^1\Sigma_g^+(a)$ and the ${}^1\Sigma_u^-(f)$ states we obtain 0.5 per cent of hybridization for the $3\sigma_g$ in the ${}^1\Sigma_u^-(f)$ state. This last value is obtained by assuming that the hybridization of the $2\sigma_u$ molecular orbital in the ${}^1\Sigma_u^-(f)$ state is the same as the hybridization of the $2\sigma_u$ in the ${}^1\Sigma_g^+(a)$ state. This last assumption, if incorrect, will effect the resulting f value only for the case of the Mulliken transition.

Let us comment briefly on the results here obtained. The sign of the coefficient of hybridization is in agreement with what one would expect by considering the internuclear distances for the various states. The amount of hybridization is somewhat smaller than that previously suggested by H. Shull (1950) for the case of the ${}^3\Pi_u(b)$ and ${}^3\Pi_g(d)$ states and ${}^1\Pi_u(b)$ and ${}^1\Pi_g(d)$ states.

We have the possibility to check the reliability of the coefficient of hybridization for the case of the ${}^1\Sigma_g^+(a)$ state. Ransil (1959) calculated that for this state the coefficient of hybridization is 6.5 per cent using Slater LCAO-MO wave functions. This value remains practically unchanged if, instead

of Slater LCAO-MO wave functions, the Best-Atom LCAO-MO wave functions are used, but is lowered to about 4 per cent if Best-Limited LCAO-MO wave functions are used. Since in our calculation we have adopted the Slater screening constant, we must compare our 6.5 per cent of the hybridization with Ransil's value of 6.5 per cent of hybridization for the $1\sigma_g^+(a)$. Since the agreement is satisfactory, we think that our hybridization coefficients for the other states are not far from the correct ones.

III. RESULTS OF THE CALCULATIONS FOR THE f NUMBERS

Slater's type of functions were used in the construction of the molecular orbitals, and an effective Z value of 3.25 was used.

For the computation of the integrals, the usual transformation into cofocal elliptic coordinates λ , μ , ϕ is made. The problem is then reduced to the evaluation of integrals of the form

$$A_n(\alpha) = \int_1^{\infty} \lambda^n \exp(-\alpha\lambda) d\lambda \quad (9)$$

$$B_n(\beta) = \int_{-1}^{+1} \mu^n \exp(-\beta\mu) d\mu \quad (10)$$

The arguments α and β of these functions are given in terms of the Z effective and the internuclear distances. The integrals $A_n(\alpha)$ and $B_n(\beta)$ are available in tabulated form (Kotani, Smeyliya, Ishiguro and Kimura 1955; Miller, Gerhauser and Matsen 1959).

The resulting f values for the different transitions are reported in Table 1 together with the value of $\nu_{1,2}$ (see equation (2)). The last three reported f values of

Table 1

Table 1 belong to yet unknown transitions. The value for $\nu_{1,2}$ of these transitions is obtained from the previous calculations (Clementi and Pitzer 1960) and estimate (Mulliken 1939) and is enclosed in brackets in Table I.

The implications of these results on the molecular abundance of C_2 in the solar reversing layer shall be analyzed in a forthcoming paper.

In the course of this work several values for the Z effective were taken into consideration. We have attempted to devise an empirical relation such that the Z_{eff} for the bonding orbitals would result higher than the Z_{eff} for the antibonding orbitals for the cases where Slater's rule gives the same value for both bonding and antibonding orbitals. The relation we have used is such to insure that at infinite and zero distances the molecular Z effective goes over the Slater's Z effective of the infinitely separated or united atoms respectively. The relation has the form

$$Z_{(A+A)} = \exp(-r_{A+A}/\langle r_A^{n\ell} \rangle)(Z_{AA} - Z_A) + Z_A$$

$r_{(A+A)}$ and $\langle r_A^{n\ell} \rangle$ are the internuclear distance for the molecule and the mean radius for the electron with quantum numbers n and ℓ in the atom A .

Table 1
OSCILLATOR STRENGTH FOR TRANSITIONS IN C_2

Transition	$\nu_{1,2}$ (cm^{-1})	Calculated f	Experimental f
$^3\Pi_g(d) - ^3\Pi_u(b)$ Swan	19,306.26	0.0485	0.034*
$^1\Pi_g(d) - ^1\Pi_u(b)$ Deslandres-d'Arambuja	25,870.24	0.0650	-
$^1\Sigma_u^+(f) - ^1\Sigma_g^+(a)$ Mulliken	43,240.23	0.1025†	-
$^3\Pi_g(e) - ^3\Pi_u(b)$ Fox-Herzberg	40,080.41	0.8184	-
$^1\Pi_u(b) - ^1\Sigma_g^+(a)$ Phillips	8,391.66	0.0027	0.0038‡
$^3\Sigma_g^-(c) - ^3\Pi_u(b)$ Ballik-Ramsay	5,656.	0.0066	-
$^1\Sigma_g^+(a) \rightarrow ^1\Sigma_u^+(g)$	(40,341)	0.7520	-
$^1\Pi_u(b) \rightarrow ^1\Sigma_g^+(c)$	(8,875)	0.0101	-
$^1\Pi_u(b) \rightarrow ^1\Delta_g(c)$	(1,614)	0.0018	-

* Experimental error may be as large as a factor of two.

† Calculated using 8.5 per cent of hybridization in the $2\sigma_u$. If a value of 6.5 per cent of hybridization is used then $f = 0.0999$, if 4 per cent of hybridization is used then $f = 0.0875$.

‡ Experimental error may be as large as a factor of three (the reported value is for the (2-0) band.)

For the case of H_2 the screening constant obtained with the last equation is 1.175 which may be compared with the Weinbaum's $Z = 1.193$ (Weinbaum 1933) or the Wang's $Z = 1.166$ (Wang 1928). The use of this equation introduces a variation of 15% at most in the calculated f values of C_2 . Since the above equation is not proven valid in general, and since the variation in f value is not pronounced, the standard value for C of 3.25 was finally adopted.

This work was performed under the auspices of the U. S. Atomic Energy Commission. It is my pleasure to thank Professor R. S. Mulliken for suggesting to use Rensil's data (as a check for the obtained hybridization coefficients for the $^1\Sigma_g^+$ (a) state) and for correspondence on some points concerning the best notation for molecular orbitals. It is my pleasure also to thank Professor L. Brewer, Professor J. G. Phillips, and Professor K. S. Pitzer for their interest in this work.

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