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TRANSITION PROBABILITIES FOR ELECTRONIC SPECTRA OF C_2

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ABSTRACT

The probabilities for nine electronic transitions among low excited states in the C_2 molecule are calculated. The results are given in form of the oscillator strength, or f values. Particular emphasis is given to the computation of the amount of hybridization in the $\sigma_u(2s)$ and $\sigma_g(2p_u)$ molecular orbitals.

For the Swan transition an f value of 0.048 is calculated, which may be compared with the experimental values of 0.037 reported in literature.

INTRODUCTION

Recent experimental studies on the C_2 molecule have settled the problem of the assignment for the ground state,¹ have determined with sufficient precision the value of the dissociation energy for the ground state² and have located a new low-lying excited state.³

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1. E. A. Ballik and D. A. Ramsey, J. Chem. Phys. 31, 1128 (1959).
 2. L. Brewer, W. T. Hicks, and O. N. Krikorian (to be submitted for publication).
 3. A. Ballik and D. A. Ramsey, J. Chem. Phys. 29, 1418 (1958).

On the theoretical side the location of the low-lying excited states has been reinvestigated⁴ substantially confirming some old⁵ and more recent predictions.⁶

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4. E. Clementi and K. S. Pitzer, J. Chem. Phys. (In press).
 5. R. S. Mulliken, Phys. Rev. 56, 778 (1939); Rev. Mod. Phys. 4, 66 (1932).
 6. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. 81, 4477 (1959).

There is still some 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 $f = 0.034$ ⁷ within a factor of two due to about 5 kcal

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7. W. T. Hicks, Spectroscopy of High Temperature Systems (thesis) UCRL-3696, Feb., 1957.
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of uncertainty in the determination of the heat of formation of C_2 . The calculated value for the Swan transition is $f = 0.027^8$ if no

8. Lyddane, Rogers and Roach, Phys. Rev. 60, 281 (1941).

hybridization is taken into account; a limiting value of $f = 0.13$ was proposed⁹ if hybridization is allowed to take place in the $\sigma_g(2p_0)$

9. H. Shull, J. Astrophys. 112, 532 (1950).

and $\sigma_u(2s)$ molecular orbitals.

It seems appropriate at this time to reinvestigate the calculations of the f number in the C_2 molecule. In addition to the oscillator strength for the Swan transition, we will consider all the possible f values for allowed transitions among the low-lying electronic states.

2. Allowed transitions for the low-lying electronic states in C_2 .

The molecular orbitals for the C_2 molecule are here given in order of increasing energy (see Ref. (6) for more details)

$$K K \sigma_g(2s) \sigma_u(2s) \pi_u(2p_x) \sigma_g(2p_z) \pi_g(2p_x) \sigma_u(2p_z) \dots \quad (1)$$

The twelve electrons of the molecule fill all the orbitals up to the $\sigma_u(2p_z)$ for the ground state so that its symmetry is $1 \sum_g^+$. 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 oscillator strength is given by

$$f = \frac{8\pi^2 m c \nu_{1,2}}{3h} \left| \int \Psi_1^* M \Psi_2 d\tau \right|^2 \quad (2)$$

where M is the electric dipole moment operator, Ψ_1 and Ψ_2 are the initial and final molecular orbitals, $\nu_{1,2}$ is the observed frequency for the transition. In Table I, we tabulate the transitions which will be considered in this paper. The dipole moment matrix elements are given in the last column and are obtained by applying Eq. (2) to the configuration indicated for each state.

Table I

Transitions for the Low Lying Electronic States in C_2

Configuration and Initial State	Configuration and Final State	Transition	Dipole Moment
$\dots \sigma_u^2 \pi_u^4 \quad 1\Sigma_g^+$	$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 1\Pi_u$	Phillips	$\langle \pi_u X+Y \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^4 \quad 1\Sigma_g^+$	$\dots \sigma_u \pi_u^4 \sigma_g \quad 1\Sigma_u^+$	Mulliken	$\langle \sigma_u Z \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^4 \quad 1\Sigma_g^+$	$\dots \sigma_u^2 \pi_u^3 \pi_g \quad 1\Sigma_u^+(1)$		$\langle \pi_u Z \pi_g \rangle$
$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 1\Pi_u$	$\dots \sigma_u \pi_u^3 \sigma_g^2 \quad 1\Pi_g$	Deslandres d'Azambuja	$\langle \sigma_u Z \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 1\Pi_u$	$\dots \sigma_u^2 \pi_u^2 \sigma_g^2 \quad 1\Sigma_g^+(1)$		$\langle \pi_u X+Y \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 1\Pi_u$	$\dots \sigma_u^2 \pi_u^2 \sigma_g^2 \quad 1\Delta_g$		$\langle \pi_u X+Y \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 3\Pi_u$	$\dots \sigma_u^2 \pi_u^2 \sigma_g^2 \quad 3\Sigma_g^-$	Ballik- Ramsey	$\langle \pi_u X+Y \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 3\Pi_u$	$\dots \sigma_u \pi_u^3 \sigma_g^2 \quad 3\Pi_g(1)$	Swan	$\langle \sigma_u Z \sigma_g \rangle$
$\dots \sigma_u^2 \pi_u^3 \sigma_g \quad 3\Pi_u$	$\dots \sigma_u^2 \pi_u^2 \sigma_g \pi_g \quad 3\Pi_g(2)$	Fox-Hernberg	$\langle \pi_u Z \pi_g \rangle$

In the following the assumption is made that the orbitals not directly involved in the transition are unchanged by the transition.¹⁰

10. R. S. Mulliken and C. A. Rieke, Phys. Soc. Rep. Prog. Phys. 6, 231 (1941).

3. Hybridization of the $\sigma_u(2s)$ and $\sigma_g(2p_\sigma)$ molecular orbitals. We assume that the variations 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 electronic configuration.

It follows that two state wave functions which belong to configurations differing only by one molecular orbital, namely, ψ_1 and ψ_2 respectively, have equilibrium internuclear distances r_1 and r_2 . The quantity $\Delta r = (r_1 - r_2)$ tells us the difference in bonding power of ψ_1 and ψ_2 . If Δr is positive, then ψ_1 is less bonding than ψ_2 , and conversely if Δr is negative, ψ_1 is more bonding than ψ_2 .

If we consider the triplet states and the ${}^1\Pi_u$ and ${}^1\Pi_g$ states of Table II we note that a promotion of a single electron from a $\Pi_u(2p_\pi)$ to a $\sigma_g(2p_\sigma)$ molecular orbital induces a contraction of 0.052 Å in the bond length (here taken as the equilibrium internuclear distance).

We indicate this fact with the notation $\Delta r [\Pi_u(2p_\pi) \rightarrow \sigma_g(2p_\sigma)] = 0.052 \text{ Å}$ or $\Delta r [\Pi_u(2p_\pi) \leftarrow \sigma_g(2p_\sigma)] = -0.052 \text{ Å}$. From Table II it is easy to derive the following relations for the above-mentioned states.

Table II

Internuclear Distances for the Low Lying Electronic States in C_2

Configuration	State	r_e	Configuration	State	r_e
$\dots \sigma_u^2 \pi_u^3 \sigma_g$	$^3\Pi_u$	1.317	$\dots \sigma_u^2 \pi_u^4$	$^1\Sigma_g^+$	1.245
$\dots \sigma_u \pi_u^3 \sigma_g^2$	$^3\Pi_g(1)$	1.269	$\dots \sigma_u^2 \pi_u^3 \sigma_g$	$^1\Pi_u$	1.322
$\dots \sigma_u^2 \pi_u^2 \sigma_g s$	$^3\Pi_g(2)$	1.543	$\dots \sigma_u \pi_u^3 \sigma_g^2$	$^1\Pi_g$	1.278
$\dots \sigma_u^2 \pi_u^2 \sigma_g^2$	$^3\Sigma_g^-$	1.369	$\dots \sigma_u \pi_u^4 \sigma_g$	$^1\Sigma_u^+$	1.241

$\Delta r [\sigma_u(2s) \rightarrow \sigma_g(2p_o)] = 0.048 \text{ \AA}, \Delta r [\pi_g(2p_x) \rightarrow \sigma_u(2s)] = 0.126 \text{ \AA},$
 $\Delta r [\pi_g(2p_y) \rightarrow \pi_u(2p_x)] = 0.226 \text{ \AA}.$ These values are internally consistent
 and additive so that (for example) $\Delta r [\pi_u(2p_x) \rightarrow \sigma_u(2s)] = \Delta r [\pi_u(2p_x) \rightarrow$
 $\sigma_g(2p_o)] + \Delta r [\sigma_g(2p_o) \rightarrow \sigma_u(2s)] = 0.052 + 0.048 = 0.100 \text{ \AA}$ (This
 may be verified by comparing the internuclear distances of the ${}^3\Pi_g(1)$ state
 and ${}^3\Sigma_g^-$ state).

Since hybridization modifies the bonding power of a molecular orbital,
 we take the above observations as indications that the triplet states
 and the ${}^1\Pi_u$ state and the ${}^1\Pi_g$ state have the same degree of hybridization
 for the same molecular orbitals. By the same reasoning, we conclude that
 the ${}^1\Sigma_g^+$ and the ${}^1\Sigma_u^+$ state have a degree of hybridization different from
 that of the triplet states, since the Δr 's for those states are different
 from the corresponding Δr 's of the triplet states.

The very small difference in r_e for the pairs of states ${}^3\Pi_u, {}^1\Pi_u$ and
 ${}^3\Pi_g$ and ${}^1\Pi_g(1)$ are interpreted as due to difference in electronic
 correlation between triplets and singlets. If instead those differences
 in r_e should be interpreted as due to a difference in hybridization, it
 is clear that such a difference is very small, and consequently the
 approximation of the same hybridization in the triplets and in the ${}^1\Pi_u$
 and ${}^1\Pi_g(1)$ is still valid.

We will assume in addition (see Ref. (9)) that there is no hybridization
 in the $\sigma_g(2s)$ molecular orbital.

The hybridization in the $\sigma_u(2s)$ and in the $\sigma_g(2p_o)$ may be such
 as to increase or decrease the bonding character of the original non-

hybridized $\sigma_u(2s)$ and $\sigma_g(2p_g)$ molecular orbitals.¹¹ The amount of

11. R. S. Mulliken, J. Phys. Chem. 56, 295 (1953).

hybridization is calculated with a method suggested by R. S. Mulliken¹¹ and making use of semiempirical constants obtained by the use of Mulliken's "magic formula."¹¹ It is shown¹¹ 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 antibonding orbitals respectively. The β integrals are taken proportional to the overlap integral and in particular $\beta_\sigma = -8.05_\sigma$ and $\beta_\pi = -10.5_\pi$. These values are obtained following Mulliken's work.¹¹

The constant μ_j has the effect of decreasing the bonding power of the antibonding orbitals and it is given by the semiempirical relation (see Ref. (11)):

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

where the value 1.4 = 2 γ is again obtained from Mulliken's work.¹¹ 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 Eq. (4) for the valency electrons:

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

where now the summations are only on valency electrons. Hereafter the electrons of the $\sigma_g(2s)$, $\sigma_u(2s)$, $\pi_u(2p)$, $\pi_g(2p)$, $\sigma_g(2p)$ are considered as valency electrons. 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 $\sigma_g(2p)$ and $\sigma_u(2s)$ are

$$\Psi_{\sigma_g(2p)} = [2(1 + S_g^h)]^{-1/2} [a_1(z_A) + a_1(z_B) + b_1(2s_A) + b_1(2s_B)] \quad (7)$$

where

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

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

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

Here the $2p_g$ atomic orbitals are chosen so that the positive lobe points toward the other atom. The coefficient 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 percent of hybridization in the $\sigma_g(2p_g)$ and $\sigma_u(2s)$ molecular orbitals. By making a system of Eq. (6) for the $^3\Pi_u$ and $^3\Pi_g(1)$ states (at $r = 1.317$) we obtain 0.5 percent of hybridization for the $\sigma_g(2p_g)$ molecular orbital and we find that a_1 and b_1 are opposite in sign. Analogously from the use of Eq. (6) for the $^3\Pi_u$ state and the $^3\Sigma_g^-$ state we obtain 1.0 percent hybridization for the $\sigma_u(2s)$ molecular orbital and again a_2 and b_2 are opposite in sign.

Proceeding in analogous way from the $^1\Sigma_g^+$ and $^1\Pi_u$ states we obtain 8.5 percent of hybridization for the $\sigma_u(2s)$ molecular orbital in the $^1\Sigma_g^+$ state. The sign of the coefficient b_2 is opposite to that of a_2 . Finally from the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states we obtain 0.5 percent of hybridization for the $\sigma_g(2p_g)$ molecular orbital of the $^1\Sigma_u^+$ state. The last value is obtained by assuming that the hybridization of the $\sigma_u(2s)$ molecular orbital in the $^1\Sigma_u^+$ state is that of the $^1\Sigma_g^+$ state.

This last assumption is somewhat arbitrary and, if incorrect, it will affect the resulting f values 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 at equilibrium for the various states. The amount of the hybridization is somewhat smaller than that previously suggested by H. Shull. The higher hybridization of

$\sigma_u(2s)$ with respect to $\sigma_g(2p_g)$ is in accordance with H. Shull findings. For the different hybridization in ${}^1\Sigma_g^+$ we may note that if that state would have the same hybridization as the triplets and ${}^1\Pi_u$ and ${}^1\Pi_g$ states then one would expect for the ${}^1\Sigma_g^+$ an internuclear equilibrium distance (starting for example from ${}^1\Pi_u$) of $1.322 - .052 = 1.270$ A. The experimental fact that for the ${}^1\Sigma_g^+$ state the internuclear distance is 1.245 may be explained by the above results where an additional contraction is expected as a result of a less antibonding character of the $\sigma_u(2s)$ molecular orbitals in the ${}^1\Sigma_g^+$ state as compared with the ${}^1\Pi_u$ state.

4. 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. (Additional discussion on the effective Z value is given in the Appendix I.)

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

$$A_n(\alpha) = \int_0^\infty \lambda^n e^{-\alpha\lambda} d\lambda$$

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

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.^{12,13}

12. M. Kotani, M. Suenamiya, E. Ishiguro, T. Kimura, Table of Molecular Integrals, Marusen Co., Ltd., 1955.

13. J. Miller, J. M. Gerhauser, F. A. Matsen, Quantum Chemistry, Integrals and Tables, University of Texas Press, 1959.

The resulting f values for the different transitions are reported in Table III together with the value of $\sqrt{12}$ (see Eq. (2)).

Table III

Oscillator Strength for Transitions in C_2

Transition	ν_{12} (cm^{-1})	Calculated f	Experimental f
Swan	19,306.26	0.0485	0.034*
Deslandres-d'Aranbujá	25,870.24	0.0650	-
Mulliken	43,240.23	0.1025	-
Fox-Herzberg	40,080.41	0.8184	-
Phillips	8,391.66	0.0027	0.0038**
Ballick-Ramsey	5,656.	0.00661	-
$^1\Sigma_g^+ \longrightarrow ^1\Sigma_u^+ (2)$ (40,341)		0.7520	-
$^1\Pi_u \longrightarrow ^1\Sigma_g^+ (1)$ (8,875)		0.0101 0.0021	-
$^1\Pi_u \longrightarrow ^1\Delta_g$ (1,614)		0.0018 0.0002	-

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

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

The last three reported f values of Table III belong to yet unknown transitions. The value for 12 of these transitions is obtained from the above-mentioned previous calculations⁴ and estimate.⁵

From the above results it appears that the abundance of C_2 molecules in the solar reversal layer should not be very different from what Lyddane⁸ computed by using a value of 0.027 for the oscillator strength of the Swan transition. This problem will be analyzed in more detail in future work.

Appendix I

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 ensure that at infinite and zero distances the molecular Z effective goes over the Slater's Z effective of the infinitely separated or united atoms. The relation has the form

$$Z_{(A+A)}^{eff} = (Z_{AA}^{eff} - Z_A^{eff}) \exp \left[-r_{(A+A)} / r_A^{nl} \right] + Z_A^{eff},$$

where $Z_{(A+A)}^{eff}$, Z_{AA}^{eff} and Z_A^{eff} are the Z effective for the molecule (A+A), for the united atom (AA) and for the infinitely separated atoms, where

$r_{(A+A)}$ and $r_{\frac{ne}{A}}$ are the internuclear distance for the molecule and the mean radius for the electron with quantum numbers n and ℓ in the atom A .

For the case of H_2 the screening constant obtained with the above equation is 1.175 which may be compared with the Weinbaum's $Z = 1.193$ ¹⁴

14. E. Weinbaum, J. Chem. Phys. 1, 593 (1933).

or the Wang's $Z = 1.166$.¹⁵

15. S. C. Wang, Phys. Rev. 31, 579 (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.

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