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Publication Date

1975-04-01

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Submitted to Journal of the American
Chemical Society

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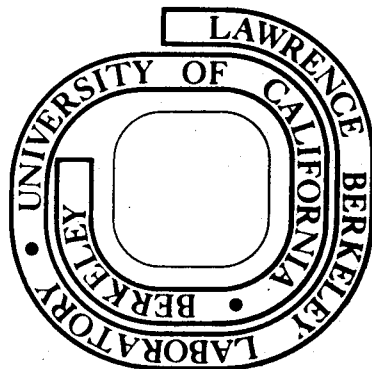
David R. Yarkony and Henry F. Schaefer III

April 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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MULTIPLY SPLITTINGS IN THE PHOTOELECTRON SPECTRA

OF ORGANIC RADICALS: TRIMETHYLENEMETHANE

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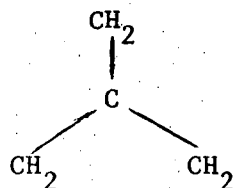
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ABSTRACT

Open shell self-consistent-field theory has been applied to systems arising from the photoionization of organic radicals. Specifically, the multiplet splittings of the $1a_2' 1e''^2$ electron configuration of $C(CH_2)_3^+$ have been investigated both analytically and numerically. These exchange splittings are found to be quite large and should definitely be considered in the interpretation of the photoelectron spectra of organic radicals.

In recent years photoelectron spectroscopy has become an increasingly important experimental tool in the study of the electronic structure of molecules. Present experimental techniques^{1,2} are capable of measuring the ionization potential (IP) of both core and valence electrons and this has stimulated considerable theoretical effort in an attempt to accurately determine these IP's.^{3,4} Of late experimental methods have been developed which permit the range of photoelectron spectra (pes) to be extended from stable, closed shell⁵ molecules to the more evanescent class of organic radicals.⁶ An important feature of the pes of these radicals should be the multiplet or exchange splittings arising from the open shell electron occupancies characteristic of these species. In fact this type of multiplet splitting has been observed in the core levels of a number of molecules, including some as large as di-t-butyl nitroxide.⁷ However valence level exchange splittings have yet to be identified in the pes of organic radicals.

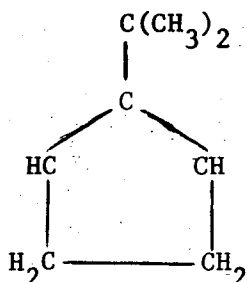
In this communication we report the results of a theoretical treatment of the trimethylenemethane radical (1)



(1)

which demonstrate that valence level multiplet splittings can be substantial, and must be considered in the interpretation of the

pes of organic radicals. Trimethylenemethane has been of particular interest since 1948, when Moffitt and Coulson⁸ showed that its central atom has the greatest π bond order attainable by a carbon atom. The relevance of $C(CH_2)_3$ to the question of exchange splittings comes from the fact that the pes of two related organic compounds have been determined. Dewar and Worley⁹ have reported eight ionization potentials for the iron carbonyl complex $C(CH_2)_3-Fe(CO)_3$ and Koenig¹⁰ has studied 2-isopropylidene cyclopent-1,3 diyl



(2)

Dewar and Worley attributed their second measured IP (at 9.15 eV) to trimethylenemethane and estimated that this IP would fall to 8.63 eV in the absence of the $Fe(CO)_3$ part of the complex. They also identify an IP at 11.07 eV with $C(CH_2)_3$ and note excellent agreement with their calculated semi-empirical π orbital energy. Dewar and Worley do not mention the possibility of multiplet splittings in the pes. Koenig's research, although not yet complete, yielded a pair of peaks, centered at 8.6 eV and split by 0.4 eV. Preliminary indications are that these two peaks should be attributed to the doubly degenerate ${}^2E''$ state (in D_{3h} symmetry), which has been perturbed by an unsymmetric environment.

The theoretical approach followed here is analogous to that used in our earlier study¹² of the $3A_2'$ ground state of the neutral radical. The ground electron configuration for $C(CH_2)_3$ is

$$1a_1'^2 1e'^4 2a_1'^2 3a_1'^2 2e'^4 4a_1'^2 3e'^4 1a_2'^2 4e'^4 1a_2''^2 1e''^2 \quad (3)$$

and the lowest two orbital occupancies for the positive ion are

$$\dots\dots 1a_2'^2 4e'^4 1a_2''^2 1e'' \quad (4)$$

and

$$\dots\dots 1a_2'^2 4e'^4 1a_2'' 1e''^2 \quad (5)$$

The ground state of the ion, resulting from (4) is a $2E''$ state, but the situation with respect to (5) is more complicated, with four different electronic states arising. The single configuration wavefunctions for these open-shell states may be written

$${}^4A_1'' : 1a_2'' \alpha 1e_x'' \alpha 1e_y'' \alpha \quad (6)$$

$${}^2A_1'' : \frac{2}{\sqrt{6}} 1a_2'' \beta 1e_x'' \alpha 1e_y'' \alpha - \frac{1}{\sqrt{6}} 1a_2'' \alpha 1e_x'' \alpha 1e_y'' \beta + \frac{1}{\sqrt{6}} 1a_2'' \alpha 1e_x'' \beta 1e_y'' \alpha \quad (7)$$

$${}^2E'', {}^2A_2'' : \frac{1}{\sqrt{2}} 1a_2'' \alpha 1e_x'' \alpha 1e_x'' \beta - \frac{1}{\sqrt{2}} 1a_2'' \alpha 1e_y'' \alpha 1e_y'' \beta \quad (8)$$

Reference to the Table shows our theoretical estimates of the lowest IP of trimethylenemethane are in good agreement with the available experimental values^{9,10} for related molecules. It is worth noting that simple arguments¹¹ suggest electron correlation should be perhaps 1 eV greater for $C(CH_2)_3$ than for its positive ion. However of particular interest here are the splittings between the four electronic states

arising from electron configuration (5). Assuming each state is adequately described by a single configuration wavefunction¹¹ constructed from a common set of molecular orbitals, one can readily obtain analytical expressions for the multiplet splittings:

$$\Delta E(^4A_1'' \rightarrow ^2A_1'') = \frac{7 + 2\sqrt{6}}{4} K_1 \quad (9)$$

$$\Delta E(^4A_1'' \rightarrow ^2E'') = K_1 + 2 K_2 \quad (10)$$

$$\Delta E(^2E'' \rightarrow ^2A_2'') = 2 K_2 \quad (11)$$

$$\Delta E(^2E'' \rightarrow ^2A_1'') = \frac{3 + 2\sqrt{6}}{4} K_1 - 2 K_2 \approx 2(K_1 - K_2) \quad (12)$$

where $K_1 = K(la_2'', le'')$, $K_2 = K(le_x'', le_y'')$ and the K's are the appropriate exchange integrals. Since $K(i,j) \geq 0$ ⁵ Eqs. (9)-(11) show that the $^4A_1''$ is the lowest lying state in the multiplet and that

$$E(^4A_1'') < E(^2E'') < E(^2A_2'')$$

However the exact location of the $^2A_1''$ state relative to the $^2E''$ and $^2A_2''$ states requires the numerical values of the above exchange integrals. Further as $K_1 \approx K_2$ (see below) the ordering of the $^2E''$ and $^2A_1''$ states is a delicate matter which cannot be finally resolved until the effects of electron correlation¹¹ are explicitly included in the wavefunctions.

As our common set of orbitals we selected those orbitals corresponding to the $^3A_2'$ ground state of the $C(CH_2)_3$ radical.¹³ The values of K_1 and K_2

which are 0.0652 and 0.0581 hartrees, respectively, are seen to be sizeable and of comparable magnitude, as mentioned earlier. We have also carried out direct SCF calculations on the five states arising from the electron occupancies (4) and (5). The results from both these methods, the direct SCF and frozen orbital approximation, are summarized in the Table. Note that the ordering of the ${}^2A_1''$ and ${}^2E''$ states corresponding to Eqs. (6) and (8) has been reversed by allowing the orbitals to relax. Also note that in neither method is the second ${}^2E''$ state a rigorous upper bound to the true ${}^2E''$ state, since in each case the wavefunctions corresponding to the second ${}^2E''$ state is connected to the lower ${}^2E''$ wavefunction through the Hamiltonian.

This research was supported by the Energy Research and Development Administration and by the National Science Foundation, Grant GP-41509X. Computations were performed on the Datacraft 6024/4 minicomputer, supported by the National Science Foundation, Grant GP-39317.

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TABLE. Theoretical predictions of the positions of the electronic states of $C(CH_2)_3^+$.

Energies are given in eV relative to the triplet ground state of the neutral radical.

<u>Electron Configuration</u>	<u>State</u>	<u>Frozen Orbital Approximation</u>	<u>Direct SCF Calculations</u>
..... $1a_2'^2 4e'^4 1a_2''^2 1e''$	$2E''$	8.74	8.03
..... $1a_2'^2 4e'^4 1a_2'' 1e''^2$	$4A_1''$	10.15	8.99
	$2A_1''$	15.42	12.75
	$2E''$	15.08	13.86
	$2A_2''$	18.24	16.62

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