

In a more important way it has tried to show that linear models can be successfully applied to quantum mechanical results just as they are to empirical results. This greatly improves the chemical utility of the results since the known errors can be gradually eliminated and quantities produced which relate more directly to experimental measurements.

The paper also demonstrates that, once a sufficiently consistent collection of results is available, quantum calculations are susceptible to chemical explanation and interpretation. This appears to be a most fruitful starting point for the further investigation of many concepts that had seemed to disappear under the sheer mass of numbers produced by the computer.

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References and Notes

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Ab Initio Calculations on Large Molecules Using Molecular Fragments. Unrestricted Hartree-Fock Calculations on the Low-Lying States of Formaldehyde and Its Radical Ions¹

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Abstract: This paper describes the extension of the *ab initio* molecular fragment procedure to open-shell systems using the unrestricted Hartree-Fock (UHF) approach. A method of obtaining initial charge density and bond order matrices is also presented. Calculations are performed for the $^3A_1(\text{GS})$, $^1,^3A_2(n \rightarrow \pi^*)$ and $^3A_1(\pi \rightarrow \pi^*)$ states of formaldehyde, for the $^2B_1(\text{GS})$ and $^2B_2(n \rightarrow \pi^*)$ states of the anion, and for the $^2B_2(\text{GS})$ and $^2B_2(\pi \rightarrow n)$ states of the cation. A number of properties of these states are presented and analyzed, including the dependence of the total energy on the out-of-plane bending angle, Franck-Condon transitions, molecular orbital structure, and several other molecular properties. Except for the $^3A_1(\pi \rightarrow \pi^*)$ state, where a very shallow potential curve makes definitive conclusions difficult, the geometric predictions are excellent, with predicted equilibrium angles within a few per cent of other calculated or measured values. For all states examined, where comparisons were possible, the correct ordering of states was obtained. For cases where quantitative agreement was not obtained, analysis of the charge distribution and other properties allows assessment of the basis set adequacies and deficiencies and indicates how improvements can be made.

Over the past several years a large number of closed-shell molecular systems have been investigated by the *ab initio* molecular fragment procedure.⁷ This procedure, based on the Hall-Roothaan equations,³ has been found to be applicable to a wide range of problems concerning small molecules such as cumulenes⁴ and larger molecules such as acetylcholine⁵ and glycine polypeptides.⁶ The procedure is currently being extended to handle molecules containing second-row atoms.⁸ Based on the success of the closed-shell studies, it seemed appropriate to examine the suitability of the molecular fragment procedure for the study of open-shell systems. An extension of the method to open-shell states of large molecules would provide another source of new chemical and spectroscopic information which would be quite useful in understanding the chemistry of various neutral and charged species as well as various excited states. The current paucity of information of this nature for large molecular systems underscores further the need for such techniques.

The single determinantal unrestricted Hartree-Fock (UHF) model⁹ used in the current studies has already been applied using the molecular fragment procedure in a preliminary investigation.¹⁰ This paper deals with the applica-

tion of the molecular fragment procedure to an examination of the ground and excited states of formaldehyde and its cation and anion radicals (H_2CO , H_2CO^+ , H_2CO^-). In order to study the usefulness of this procedure, a number of molecular properties were calculated, such as transition energies, excited state geometries, barriers to inversion, molecular orbital (MO) orderings, charge distributions, dipole moments, and Hellmann-Feynman field strengths at the nuclei. A comparison of the computed values and the available experimental data for the wide range of properties listed above provides valuable information concerning the suitability of the method for describing certain properties of open-shell systems and also suggests possible changes to the procedure which would improve the calculation of these properties. Since the UHF wave function is usually not an eigenfunction of the spin-squared operator (S^2), the effect of annihilating the spin component of next higher multiplicity on the various computed properties is also examined.

I. Method and Analysis

The basis set consists of normalized, nonorthogonal, floating spherical Gaussian orbitals (FSGO) defined as follows

$$G_i^\sigma(\gamma) = (2/\pi\rho_i^2)^{3/4} \exp\{-(\mathbf{r} - \mathbf{R}_i)^2/\rho_i^2\} \quad (1)$$

where ρ_i is the orbital radius, and \mathbf{R}_i is the location of the FSGO relative to some arbitrary origin. The π -type orbitals are represented by a fixed linear combination of two FSGO's placed symmetrically on a line passing through the given atom and perpendicular to the π plane, *i.e.*

$$G_i^\pi(\gamma) = [2(1 - \Delta_{ud})]^{-1/2}(G_u^\sigma - G_d^\sigma) \quad (2)$$

where G_u^σ and G_d^σ are FSGO's placed above and below the atom, respectively. Δ_{ud} is the overlap integral between G_u^σ and G_d^σ .

The position and size of each FSGO is determined *via* energy minimization calculations on molecular fragments chosen to mimic various anticipated bonding environments.^{11,12} The orbitals so obtained are then used as basis functions for a UHF-MO calculation on a particular large molecule.

The UHF wave function which describes a system of p α -spin and q β -spin electrons¹³ is of the following single determinantal form

$$\Psi_{\text{UHF}} = [(p+q)!]^{-1/2} \det\{\phi_1^\alpha(1)\alpha(1) \dots \phi_p^\alpha(p)\alpha(p)\phi_1^\beta(p+1)\beta(p+1) \dots \phi_q^\beta(p+q)\beta(p+q)\} \quad (3)$$

where the $\{\phi_i^\alpha\}$ and $\{\phi_i^\beta\}$ sets of MO's are not constrained to be the same. Each MO is taken as a linear combination of FSGO's of the general form

$$\phi_i^\eta = \sum_r C_{ri}^\eta \chi_r \quad (4)$$

$$\eta = \alpha \text{ or } \beta; i = 1, 2, \dots, p \text{ or } q$$

where χ_r is represented by FSGO's of the form G_i^σ or G_i^π given in eq 1 and 2. The linear expansion coefficients, C_{ri}^η , are obtained by solving the nonlinear, coupled UHF equations

$$\mathbf{F}^\eta \mathbf{C}_i^\eta = \Delta \mathbf{C}_i^\eta \epsilon_i^\eta \quad (5)$$

where

$$F_{rs}^\eta = H_{rs} + J_{rs} - K_{rs}^\eta \quad (6)$$

$$\Delta_{rs} = \langle \chi_r | \chi_s \rangle \quad (7)$$

$$H_{rs} = \left\langle \chi_r \left| \left(-\frac{1}{2} \nabla^2 - \sum_\alpha \frac{Z_\alpha}{r_\alpha} \right) \right| \chi_s \right\rangle \quad (8)$$

$$J_{rs} = \sum_{t,u} P_{tu} \left(\chi_r(1)\chi_s(1) \left| \frac{1}{r_{12}} \right| \chi_t(2)\chi_u(2) \right) \quad (9)$$

$$K_{rs}^\eta = \sum_{t,u} P_{tu}^\eta \left(\chi_r(1)\chi_u(1) \left| \frac{1}{r_{12}} \right| \chi_t(2)\chi_s(2) \right) \quad (10)$$

until self-consistency is obtained. \mathbf{C}_i^η is a column vector which represents the MO coefficients of the i th α - or β -spin MO and ϵ_i^η is its corresponding orbital energy. The charge and bond-order matrices \mathbf{P}^α and \mathbf{P}^β for α - and β -spin electrons, respectively, are defined as

$$P_{rs}^\eta = \sum_i C_{ri}^\eta C_{si}^\eta \quad (11)$$

and the total charge and bond-order matrix is defined as

$$\mathbf{P} = \mathbf{P}^\alpha + \mathbf{P}^\beta \quad (12)$$

while the spin-density matrix is given by

$$\mathbf{P}^{\text{SD}} = \mathbf{P}^\alpha - \mathbf{P}^\beta \quad (13)$$

It is important to note that single determinantal UHF wave functions are usually not eigenfunctions of S^2 , although they are eigenfunctions of S_z , *i.e.*

$$S_z \Psi_{\text{UHF}} = s' \Psi_{\text{UHF}} \quad (14)$$

with $s' = 1/2(p - q)$. As shown by Amos and Hall,¹⁴ the expectation value of S^2 is given by

$$S^2 = A - \text{tr}(\mathbf{P}^\alpha \mathbf{P}^\beta) \quad (15)$$

where

$$A = s'(s' + 1) + q \quad (16)$$

To examine the effect of the spin contamination, the UHF wave function can be expanded as a linear combination of states of definite spin multiplicity,¹⁴⁻¹⁷ *i.e.*

$$\Psi_{\text{UHF}} = \sum_{n=0}^q C_{s'+n} \Psi_{s'+n} \quad (17)$$

such that

$$S^2 \Psi_{s'+n} = (s' + n) \{(s' + n) + 1\} \Psi_{s'+n} \quad (18)$$

Using eq 17 the expectation value of a general operator, Λ , with respect to Ψ_{UHF} , is given by

$$\langle \Lambda \rangle = \langle \Psi_{\text{UHF}} | \Lambda | \Psi_{\text{UHF}} \rangle = \sum_{n=0}^q |C_{s'+n}|^2 \langle \Psi_{s'+n} | \Lambda | \Psi_{s'+n} \rangle \quad (19)$$

where $|C_{s'+n}|^2$ represents the relative contribution of the $s' + n$ spin component to the total expectation value. In the current work we are concerned primarily with the Hamiltonian and spin-squared operators. As has been discussed by several authors^{14,17} $|C_{s'+n}|^2 \geq |C_{s'+1}|^2 \gg |C_{s'+2}|^2 \gg \dots \gg |C_{s'+q}|^2$, so that eq 21 can usually be written, to a good approximation, as

$$\langle \Lambda \rangle \cong |C_{s'+n}|^2 \langle \Psi_{s'} | \Lambda | \Psi_{s'} \rangle + |C_{s'+1}|^2 \langle \Psi_{s'+1} | \Lambda | \Psi_{s'+1} \rangle \quad (20)$$

As discussed initially by Amos and Hall¹⁴ and in more detail by Amos and Snyder,¹⁵ the component of next highest spin multiplicity can be annihilated from Ψ_{UHF} , *i.e.*

$$A_{s'+1} \Psi_{\text{UHF}} \cong \Psi_{s'} \quad (21)$$

where the annihilation operator is given by

$$A_{s'+1} = S^2 - (s' + 1)(s' + 2) \quad (22)$$

The resulting (renormalized) wave function, Ψ_{UHF} , should be close to being an eigenfunction of S^2 , and thus $\langle \Psi_{\text{UHF}} | S^2 | \Psi_{\text{UHF}} \rangle$ should be close to the value obtained for a state of pure spin symmetry.¹⁸ Amos and Snyder¹⁵ have developed the appropriate formalism for obtaining the charge and bond-order matrices of a given UHF wave function after single annihilation. The singly annihilated charge and bond-order matrices can then be used to evaluate spin-independent first-order electronic properties and the total energy.

The UHF wave function can also be examined in a different fashion which lends itself more naturally to a discussion of electron correlation effects. As discussed by Amos and Hall,¹⁴ the $\{\phi_i^\alpha\}$ and $\{\phi_i^\beta\}$ sets of MO's can be unitarily transformed into a set of orbitals, related to the natural orbitals, which leave the wave function invariant to within a phase factor. Expansion of the transformed wave function in terms of its natural orbitals¹⁹ leads to an expression of the form^{16,20,21}

$$\Psi_{\text{UHF}} = C_s{}^{\text{rf}}\Psi_s{}^{\text{rf}} + C_s{}^{\text{se}}\Psi_s{}^{\text{se}} + C_{s'+1}{}^{\text{se}}\Psi_{s'+1}{}^{\text{se}} + \dots + C_s{}^{\text{de}}\Psi_s{}^{\text{de}} + C_{s'+1}{}^{\text{de}}\Psi_{s'+1}{}^{\text{de}} + \dots \quad (23)$$

where $\Psi_s{}^{\text{rf}}$ is closely related to the corresponding open-shell restricted Hartree-Fock (RHF) wave function^{15,20-22} and the superscripts se, de, ... refer to configurations formed from single, double, ... excitations between the natural orbitals. Hence, the second and higher terms in the series of eq 23 represent a *limited* configuration interaction (CI).

For geometries reasonably close to the equilibrium geometry, the UHF wave function for a closed-shell ground state is identical with that obtained using RHF theory, and hence no correlation energy is recovered. However, it is clear from the above discussion that open-shell excited states treated by the UHF method will account for some amount of correlation energy. This should reduce the calculated transition energies, although such an interpretation is strictly valid only when *complete* basis sets are used. In the current investigation limited basis sets were utilized, so care must be exercised in this respect.

Finally, it should be recalled that only the lowest energy state associated with each distinct combination of spatial and spin symmetry is capable of being examined by the UHF procedure. Hence, it may not be possible to examine all the important excited states of a molecule, such as the singlet $\pi \rightarrow \pi^*$ state of formaldehyde. However, a reasonable number of states can be examined for most molecules of intermediate symmetry. One aspect on the practical side of this problem is examined in the next section.

II. Initial Charge and Bond-Order Matrices (P Matrices)

Prior to starting the iterative sequence used to solve the above UHF equations, it is necessary to obtain an initial guess of the charge and bond-order matrices, \mathbf{P}^n . For closed-shell states of some molecules, experience has shown that the initial \mathbf{P} matrix must be sufficiently close to the final \mathbf{P} matrix to ensure that the iterative SCF procedure will indeed converge.²³ In addition, it has been observed for open-shell states that the initial \mathbf{P} matrices must be chosen properly and subsequently monitored to ensure that the converged wave function will have the desired symmetry. Development of the procedure for the construction of initial \mathbf{P} matrices of closed-shell ground states is given in detail elsewhere.²³ Only points pertinent to open-shell states are presented below.

The localized, nonorthogonal FSGO basis is related to a symmetrically orthonormalized²⁴ basis by

$$\lambda = \chi \Delta^{-1/2} \quad (24)$$

where λ and χ are row vectors, and Δ is the overlap matrix defined by eq 7. The $\{\lambda_i\}$ constitute the set of orthonormal functions which are closest, in a least-squares sense, to the original nonorthogonal basis functions.²⁵ Hence, the $\{\lambda_i\}$ will tend to be localized in the same regions of space as the original localized FSGO's. The \mathbf{P} matrices for the two bases are related by

$$\mathbf{P}(\chi) = \Delta^{-1/2} \mathbf{P}(\lambda) \Delta^{-1/2} \quad (25)$$

As illustrated for closed-shell systems,²³ the bond orders and charge distributions over the $\{\lambda_i\}$ can easily be estimated in the molecular fragment approach using chemical intuition, since the $\{\lambda_i\}$ can be readily identified as primary contributors to inner-shell, lone-pair, or bonding orbitals. $\mathbf{P}(\chi)$ can then be formed using eq 25.

The technique of constructing initial \mathbf{P} matrices of excited states will be illustrated for the ${}^3A_2(n \rightarrow \pi^*)$ state of

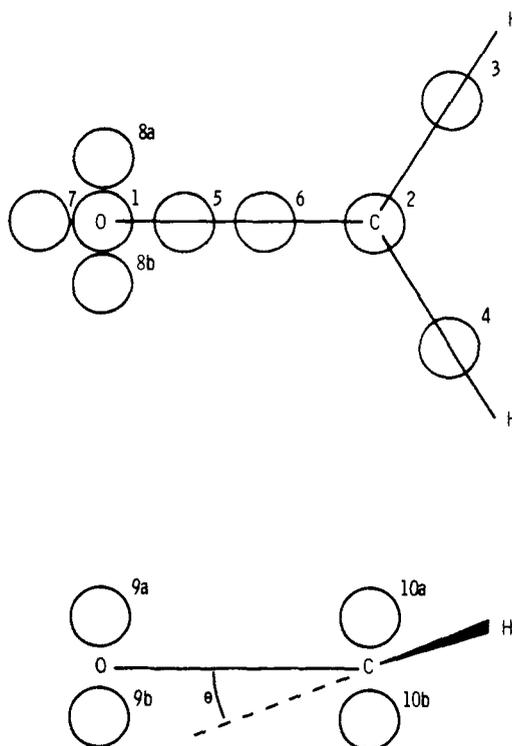


Figure 1. Approximate FSGO positions in formaldehyde. Orbitals 8, 9, and 10 are p-type orbitals, each of which is a linear combination of two FSGO's. The positions are only approximate and the radii of the circles are not related to the orbital radii. For exact values, see Table I. In the lower drawing the second hydrogen atom (behind the one depicted) has been deleted for clarity.

formaldehyde. There are nine α -spin and seven β -spin electrons in the description of this state. Figure 1 shows the approximate positions of the FSGO's in the formaldehyde molecule. It is emphasized that each λ_i closely resembles the associated localized χ_i and that it is the $\mathbf{P}(\lambda)$ which are being constructed. Thus, $\mathbf{P}^\alpha(\lambda)$ and $\mathbf{P}^\beta(\lambda)$ are given respectively as

$$\mathbf{P}^\alpha(\lambda) = \begin{bmatrix} \text{O}(\text{IS}) & \text{C}(\text{IS}) & \text{CH}_1(\sigma) & \text{CH}_2(\sigma) & \text{CO}(\sigma) & \text{CO}(\sigma) & \text{O}_{\text{LP}}(\sigma) & \text{O}_{\text{LP}}(\text{n}) & \text{O}(\pi) & \text{C}(\pi) \\ 1.0 & & & & & & & & & \\ & 1.0 & & & & & & & & \\ & & 1.0 & & & & & & & \\ & & & 1.0 & & & & & & \\ & & & & 0.5 & 0.5 & & & & \\ & & & & 0.5 & 0.5 & & & & \\ & & & & & & 1.0 & & & \\ & & & & & & & 1.0 & & \\ & & & & & & & & 1.0 & \\ & & & & & & & & & 1.0 \end{bmatrix} \quad (26)$$

$$\mathbf{P}^\beta(\lambda) = \begin{bmatrix} \text{O}(\text{IS}) & \text{C}(\text{IS}) & \text{CH}_1(\sigma) & \text{CH}_2(\sigma) & \text{CO}(\sigma) & \text{CO}(\sigma) & \text{O}_{\text{LP}}(\sigma) & \text{O}_{\text{LP}}(\text{n}) & \text{O}(\pi) & \text{C}(\pi) \\ 1.0 & & & & & & & & & \\ & 1.0 & & & & & & & & \\ & & 1.0 & & & & & & & \\ & & & 1.0 & & & & & & \\ & & & & 0.5 & 0.5 & & & & \\ & & & & 0.5 & 0.5 & & & & \\ & & & & & & 1.0 & & & \\ & & & & & & & 0 & & \\ & & & & & & & & 0.5 & 0.5 \\ & & & & & & & & 0.5 & 0.5 \end{bmatrix} \quad (27)$$

where elements not shown explicitly are taken to be zero. The initial $\mathbf{P}^\alpha(\chi)$ and $\mathbf{P}^\beta(\chi)$ matrices are then obtained di-

Table I. Formaldehyde Basis Orbital Parameters^a

Orbital ^b	Type	Distance from heavy atom ^c	Orbital radius ^c
1	O inner shell	O 0.00057129 ^d	0.24028227
2	C inner shell	C 0.0	0.32682735
3, 4	CH bonding	C 1.23379402	1.67251562
5	CO σ bonding	O 0.76467773	1.23671871
6	CO σ bonding	C 1.13093139	1.51399487
7	O σ lone pair	O 0.21614258	1.28753780
8	O π lone pair	O 0.1	1.19741696
9	O π bonding	O 0.1	1.12242182
10	C π bonding	C 0.1	1.80394801

^a Fragment parameter data taken from Table II of ref 7. ^b See Figure 1. ^c All distances are measured in Bohrs. ^d This distance is measured from the oxygen atom toward the carbon atom, along the CO bond axis.

rectly using eq 25. The initial $\mathbf{P}^\eta(\chi)$ matrices for a new conformer (K') can be estimated from the converged $\mathbf{P}^\eta(\chi)$ of a previous conformer (K) by

$$\mathbf{P}^\eta(\chi)_{K'} = \Delta_{K'}^{-1/2} \mathbf{P}^\eta(\chi)_K \Delta_{K'}^{-1/2} \quad (28)$$

where η equals either α or β and $\Delta_{K'}$ is the overlap matrix for the molecule in the new conformation (K').

Convergence to the desired state was eventually obtained for all cases in which the initial \mathbf{P} matrices were constructed by the above method. However, in most cases a large number of iterations were usually required to achieve convergence of the open-shell states, relative to the number usually required for the closed-shell states. The major problem at this stage of the calculation was to ensure that the wave function had the proper spatial symmetry behavior. In particular, it appears that rounding and differencing errors eventually develop in the \mathbf{P} matrix elements of sufficient magnitude to affect the nature of the solution. For example, the ${}^1\mathbf{B}_1$ wave function could not be obtained using direct substitution of the eigenvectors obtained at each iteration to form a new Fock matrix. In fact, after quite a large number of iterations, the calculation yielded the ${}^1\mathbf{A}_1$ ground-state wave function. This problem could have been overcome by periodically projecting out the components of desired symmetry. However, it was observed that the same result could be effected more simply by truncating the \mathbf{P} matrices to a small number of decimal places (usually four) after a chosen number of iterations. It was usually found necessary to truncate only once per conformation after *ca.* 40 iterations. Such slow convergence also indicates the appropriateness of extrapolation techniques for reducing the number of iterations needed for convergence.

III. Low-Lying States of Formaldehyde and Its Radical Ions

A. Franck-Condon Transitions, MO Ordering, and Charge Distributions. This section examines the Franck-Condon transitions of formaldehyde and its radical ions. In the ground state the HCH angle is 116° , the CH bond length is 2.109 B, the CO bond length is 2.2824 B,²⁶ and the molecule is planar. The fragment parameters used in all calculations of this paper are presented in Table I. The basis orbitals are also described pictorially in Figure 1, with σ -FSGO numbered 1-7, and p-type FSGO numbered 8-10.

The calculated vertical transition energies and the expectation values of S^2 are presented in Table II for the ${}^1,3\mathbf{A}_2(n \rightarrow \pi^*)$, ${}^3\mathbf{A}_1(\pi \rightarrow \pi^*)$, and ${}^1,3\mathbf{B}_1(\sigma \rightarrow \pi^*)$ states of formaldehyde, for the ${}^2\mathbf{B}_1(\text{GS})$ and ${}^2\mathbf{B}_2(n \rightarrow \pi^*)$ states of the anion, and for the ${}^2\mathbf{B}_2(\text{GS})$ and ${}^2\mathbf{B}_1(\pi \rightarrow n)$ states of the cation.²⁷ These values have been calculated both before and after single annihilation and are compared with other theoretical^{28,29} and experimental³⁰ values.

The α - and β -spin MO energies for the various states are compared in Tables III and IV, along with the MO energies for the RHF ground-state calculation of Neumann and Moskowitz³¹ (80 Gaussians contracted to 54 orbitals). This table illustrates the considerable MO reordering which takes place in going from one state to another. Accompanying this reordering, there are significant changes in the electron distributions of the individual MO's. Buenker and Peyerimhoff²⁸ have also observed such changes in their studies of formaldehyde. As an example, the electron distributions for the $\pi(1b_1)$ orbital of the various states are presented in Table V.

B. Equilibrium Structures and First-Order Electronic Properties. The energy has also been examined as a function of the "out-of-plane" angle (θ), where θ is defined as the angle between the CO bond and its projection onto the plane defined by the CH₂ group (see Figure 1). θ has been varied from 0 to 90° in increments of 10° in the region of the equilibrium position. It is possible to examine the energy of neutral formaldehyde as a function of θ for only four of the states being studied, *i.e.*, the ${}^1\mathbf{A}_1(\text{GS})$, ${}^1,3\mathbf{A}_2(n \rightarrow \pi^*)$, and ${}^3\mathbf{A}_1(\pi \rightarrow \pi^*)$ states. The ${}^2\mathbf{B}_1(\text{GS})$ and ${}^2\mathbf{B}_2(n \rightarrow \pi^*)$ states of the anion and ${}^2\mathbf{B}_2(\text{GS})$ and ${}^2\mathbf{B}_1(\pi \rightarrow n)$ states of the cation radicals were similarly investigated. The CO bond length in the excited states of the neutral molecule was taken to be 2.49 B, which is within the range of the reported experimental ${}^1,3\mathbf{A}_2$ values.^{32,33} All other geometrical parameters in the excited states studied were held fixed at their ground-state values. The potential curves are illustrated in Figures 2, 3, and 4, and the results are compared to those obtained by other workers^{28,32-34} in Table VI.

First-order electronic properties,³⁵ *i.e.*, dipole moments and Hellmann-Feynman field strengths at the nuclei, were also calculated at the equilibrium geometries. The results are presented in Tables VII and VIII, respectively.

IV. Discussion

A. Franck-Condon Transitions and Effect of Single Annihilation. From Table II, it is seen that the vertical transition energies of the H₂CO ${}^1,3\mathbf{A}_2(n \rightarrow \pi^*)$ states calculated by the UHF procedure before annihilation are smaller than the experimental values, as well as the CI results of Buenker and Peyerimhoff²⁸ and Whitten and Hackmeyer.²⁹ However, for the ${}^3\mathbf{A}_1(\pi \rightarrow \pi^*)$ and ${}^1,3\mathbf{B}_1(\sigma \rightarrow \pi^*)$ states where experimental values are not known, the UHF transition energies are larger than those reported in both of the CI studies. It is also interesting to note that the vertical transition energies calculated by the RHF procedure^{22,38} with a large basis set (60 Gaussian functions contracted to 22 orbitals) gave consistently smaller values for all the states examined. Despite these quantitative differences, the orderings of the states using any of the methods are in agreement with each other and with experiment.

This is an encouraging result, for it implies that it may be possible to obtain a small basis set that is sufficiently balanced to produce the correct ordering of states. It is interesting to note, however, that not all small basis sets will necessarily contain the proper balance. For example, in a recent *ab initio* CI study which considered only single excitations and employed an STO-nG basis,³⁹ the ordering of the ${}^3\mathbf{A}_1$ and ${}^3\mathbf{A}_2$ states was found to be reversed. Thus, care must be exercised in developing both the basis sets and the nature and extent of CI to be used so that the correct ordering of states can be obtained.

It is also of interest to compare the UHF and RHF results in greater detail. Since UHF excited states contain a limited amount of correlation energy over the normal RHF open-shell energy (see eq 23), it follows that the magnitude of the calculated vertical transition energies obtained from

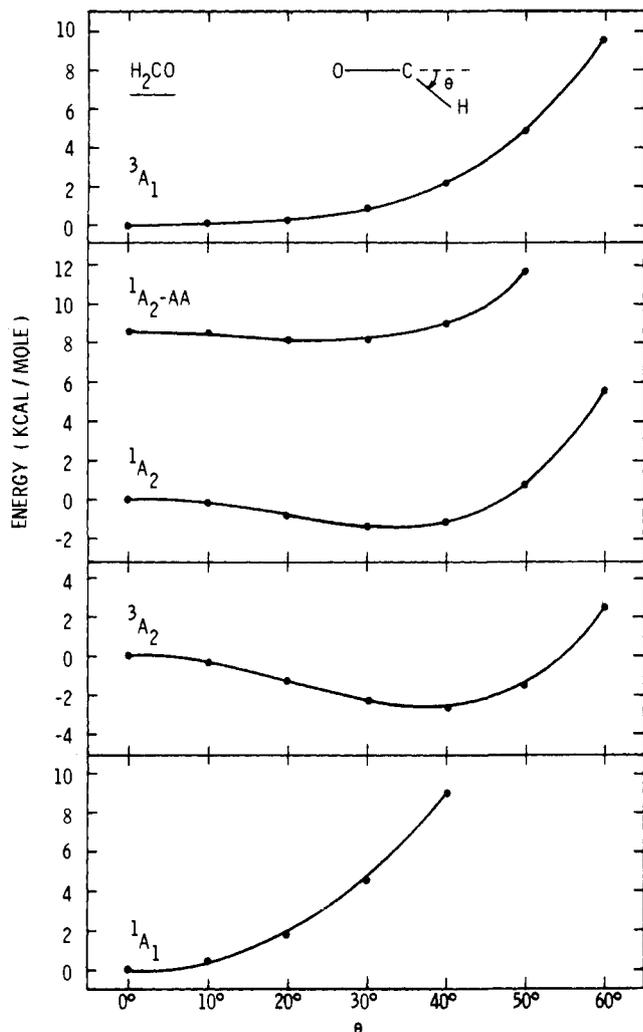


Figure 2. The total energy for several states of formaldehyde as a function of the out-of-plane angle, θ . The second hydrogen atom (behind the one depicted) has been deleted for clarity. The total energy (in hartrees) for each state when $\theta = 0^\circ$ is given by $E(^1A_1) = -96.937859$, $E(^3A_2) = -96.857209$, $E(^1A_2) = -96.841052$, and $E(^3A_1) = -96.747245$.

the UHF procedure should be expected to be smaller than those obtained by the RHF procedure, as long as equivalent basis sets are used. However, it is seen from Table II that each of the UHF transition energies are larger than the corresponding RHF values. Since the RHF studies employed a considerably larger basis (60 Gaussians contracted to 22 orbitals) than the molecular fragment basis (13 FSGO contracted to 10 orbitals), one must conclude that the larger

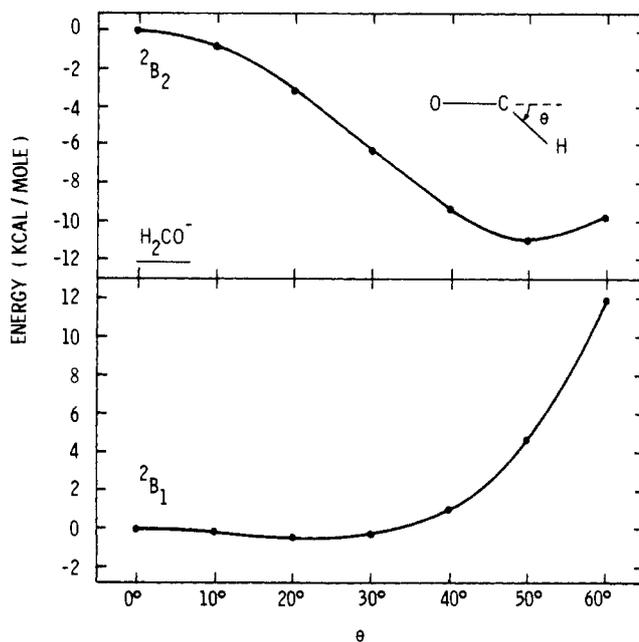


Figure 3. The total energy for the states of the formaldehyde anion as a function of the out-of-plane angle, θ . The second hydrogen atom (behind the one depicted) has been deleted for clarity. The total energy (in hartrees) for each state when $\theta = 0^\circ$ is given by $E(^2B_1) = -96.523482$ and $E(^2B_2) = -96.374485$.

UHF transition energies observed here are indicative of deficiencies in the FSGO basis. This is not surprising since, as pointed out by Whitten and Hackmeyer,²⁹ excited states with π^* character require diffuse π -type basis orbitals for their correct description. The present FSGO π -type basis is, however, quite localized in nature, and diffuse orbitals have not been added.

The doublet-doublet $n \rightarrow \pi^*$ transition can also be examined in the anion, for which the 2B_2 state is calculated to lie 4.05 eV above the 2B_1 ground state. This value is ≈ 0.5 eV greater than the corresponding observed singlet-singlet transition in neutral formaldehyde. This result is not unexpected, since the additional electron in the 2B_1 (GS) of the anion already occupies the $\pi^*(2b_1)$ orbital. Hence, the excitation of a nonbonded electron into an already partially filled π^* orbital would be expected to be energetically less favorable than the corresponding process into an empty π^* orbital in neutral formaldehyde. However, the calculated transition energy may be exaggerated due to the lack of diffuseness of the π -type FSGO's. Speaking qualitatively, this will tend to produce a more contracted π^* -type orbital, which should lead to a larger electron-electron repulsion

Table II. Vertical Transition Energies and Expectation Values of S^2 Before and After Single Annihilation for the Low-Lying States of Formaldehyde and its Anion and Cation Radicals

Molecule	State	Excitation	UHF total energy ^a	Vertical transition energies, eV						$\langle S^2 \rangle$	
				(Current study)						UHF	UHF-AA
				UHF	AA	RHF ^b	CI ^b	CI ^c	Obsd ^d		
H ₂ CO	¹ A ₁	GS	-96.937859								
	³ A ₂	$n \rightarrow \pi^*$	-96.842787	2.59	2.58	2.24	3.01	3.38	3.12	2.000442	2.000000
	¹ A ₂	$n \rightarrow \pi^*$	-96.825152	3.07	3.50	2.63	3.43	3.80	3.50	1.000555	0.004437
	³ A ₁	$\pi \rightarrow \pi^*$	-96.696279	6.57	6.57	4.20	4.99	5.66		2.000776	2.000000
	³ B ₁	$\sigma \rightarrow \pi^*$	-96.618614	8.69	8.69	6.91	7.62			2.000016	2.000000
H ₂ CO ⁻	¹ B ₁	$\sigma \rightarrow \pi^*$	-96.589041	9.49	10.23	7.84	8.61	9.35		1.001149	0.009180
	² B ₁	GS	-96.523482							0.750267	0.750000
H ₂ CO ⁺	² B ₂	$n \rightarrow \pi^*$	-96.374485	4.05	4.06					0.750127	0.750000
	² B ₂	GS	-96.823869							0.768421	0.750008
	² B ₁	$\pi \rightarrow n$	-96.636599	5.10	5.14					0.750112	0.750000

^a In hartrees. See ref 12. ^b Buenker and Peyrimhoff, ref 28. ^c Whitten and Hackmeyer, ref 29. ^d Reference 30.

Table III. Comparison of Molecular Orbital Energies for the Low-Lying States of Formaldehyde^a

MO ^b sym	RHF ^c		UHF		UHF		UHF		UHF	
	¹ A ₁ α and β	¹ A ₁ α and β	³ A ₂	³ A ₂	³ A ₁	³ A ₁	³ B ₁	³ B ₁	α	β
6a ₁	1.1241	1.1241	1.1366	1.1011	1.1244	1.0739	1.1427	1.0657	1.1323	1.0987
2b ₁ (π*)	0.4327	0.4327	0.4718 0.3738 (2b ₂)	0.3711 (2b ₂)	0.4532	1.0739	0.6162 0.1763 (1b ₁)	1.0739	0.4742 0.1353 (5a ₁)	(-0.1159 (5a ₁)) 1.1011
2b ₂ (n)	-0.4402	-0.4402	-0.0208 (2b ₁) -0.3032	-0.0056 (2b ₁) -0.4195 (5a ₁)	-0.2801	-0.0621 (2b ₁) -0.1911	-0.0621 (2b ₁) -0.1911	-0.0362 (2b ₁) -0.2522	-0.0123 (2b ₁) -0.1557 (2b ₂)	-0.2207 -0.3216
1b ₁ (π)	-0.5341	-0.5341	-0.2941	-0.4695 (5a ₁) -0.4377 (1b ₁)	-0.3264	-0.4772 (5a ₁) -0.4962 (1b ₁)	-0.1462 (2b ₂) -0.3674	-0.4939 -0.5073 (1b ₂)	-0.1876 (2b ₂) -0.2870 (1b ₁)	-0.4947 (1b ₂) -0.4421 (1b ₁)
5a ₁ (σ)	-0.6506	-0.4003	-0.4031	-0.4377 (1b ₁) -0.4412	-0.4392	-0.5145 -0.5083	-0.4791 -0.4791	-0.4902 -0.5311 (5a ₁)	-0.4421 (1b ₁) -0.4708	-0.4994 (5a ₁) -0.7429
1b ₂	-0.6893	-0.4893	-0.4196	-0.5338 -0.7303	-0.5145 -0.7057	-0.5083 -0.7792	-0.4791 -0.6978	-0.7934 -1.4722	-0.7188 -1.2686	-0.7188 -1.4072
4a ₁	-0.8646	-0.7327	-0.7568	-0.6739	-0.7057	-0.7792	-0.6978	-0.7934	-0.6602	-0.7188
3a ₁	-1.4038	-1.3268	-1.4600	-1.2888	-1.4017	-1.3982	-1.2481	-1.4722	-1.2686	-1.3084
2a ₁	-11.3431	-9.1936	-9.1458	-9.1549	-9.1508	-9.2191	-9.2130	-9.2387	-9.2285	-9.2530
1a ₁	-20.5738	-17.2048	-17.2933	-17.2800	-17.2632	-17.1679	-17.1576	-17.3047	-17.2797	-17.2641

^a A CO bond distance of 2.2824 Å with $\theta = 0^\circ$ (see Figure 1) was taken for the calculations reported in this table, maintaining an overall C_{2v} molecular symmetry. ^b MO's whose symmetry is different from those listed in this column are given in parentheses to the right of the orbital energy. Blank rows separate virtual, valence, and inner-shell MO's. Orbital energies are in hartrees. ^c Reference 31.

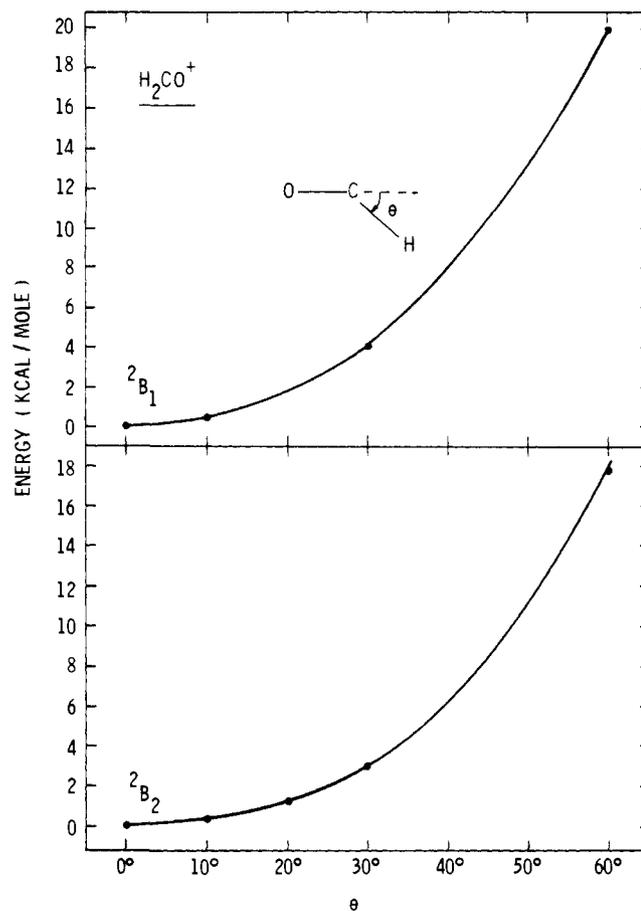


Figure 4. The total energy for the states of the formaldehyde cation as a function of the out-of-plane angle, θ . The second hydrogen atom (behind the one depicted) has been deleted for clarity. The total energy (in hartrees) for each state when $\theta = 0^\circ$ is given by $E(^2B_2) = -96.823869$ and $E(^2B_1) = -96.636599$.

between the two electrons in this MO in the $^2B_2(n \rightarrow \pi^*)$ excited state.

The $n \rightarrow \pi^*$ transition leading to a 2B_1 state cannot be examined in the cation, because the $\pi \rightarrow n$ transition leading also to a 2B_1 state is found to be of lower energy. The calculated vertical transition energy for the $\pi \rightarrow n$ state is 5.10 eV. Again the large transition energy is not surprising, since the $^2B_1(\pi \rightarrow n)$ state is formed by removing a electron from a delocalized π orbital and placing it in a partially filled, comparatively localized nonbonding orbital. Thus, as in the $n \rightarrow \pi^*$ transition, one expects qualitatively that the $\pi \rightarrow n$ transition will result in a substantial increase in electron-electron repulsion energy.

Both the open shell cation and anion ground state calculations also contain some correlation energy, as can be seen from the discussion of eq 23. Hence, it may be that the vertical transition energies calculated for the open shell cation and anion radical will be more reliable than the vertical transition energies calculated for molecules with a closed-shell ground state, where none of the correlation energy is recovered. This would, in fact, be possible if a more extensive basis set were used and the calculated correlation energy for the two states approximately canceled. However, due to the limited nature of the basis set used here, caution must be exercised in such interpretations.

The effect of spin contamination on the calculated transition energies can also be assessed. In Table II, all transition energies and expectation values of S^2 are given before and after single annihilation. It is obvious from the table that single annihilation is sufficient to obtain for each state a

Table IV. Comparison of Molecular Orbital Energies for the Low-Lying States of Formaldehyde Anion and Cation Radicals^a

MO ^b Sym	-UHF anion-				-UHF cation-			
	- ² B ₁ -		- ² B ₂ -		- ² B ₂ -		- ² B ₁ -	
	α	β	α	β	α	β	α	β
6a ₁	1.5521	1.5815	1.5455	1.5622	0.6684	0.6797	0.6498	0.6802
2b ₁		0.9564		0.8150 (2b ₂)	-0.0169	0.0047	-0.0572	0.1239
						-0.0495 (2b ₂)		-0.2932 (1b ₁)
2b ₂	0.4066 (2b ₁)		0.4483 (2b ₁)		-0.6929		-0.6124	
	0.2389	0.2705	0.1217	0.4651 (2b ₁)	-0.8236	-0.7598	-0.8362	-0.5877 (2b ₂)
1b ₁	0.0213 (5a ₁)	0.1693	0.0117	0.0428	-0.8793	-0.8176 (1b ₂)	-0.8544	-0.8218
5a ₁	-0.0098 (1b ₁)	0.0588	-0.0164	0.0271	-0.9311	-0.8335 (5a ₁)	-0.8916	-0.0764
1b ₂	-0.1067	-0.0965	-0.1188	-0.0513	-1.1392	-1.1071	-1.1524	-1.1221
4a ₁	-0.3548	-0.3161	-0.3282	-0.3033	-1.8975	-1.7666	-1.8595	-1.7538
3a ₁	-0.8963	-0.8096	-0.9547	-0.8282				
2a ₁	-8.6844	-8.6833	-8.6408	-8.6412	-9.6658	-9.6671	-9.7224	-9.7199
1a ₁	-16.6691	-16.6602	-16.7339	-16.7257	-17.7904	-17.7812	-17.7172	-17.7173

^a A CO bond distance of 2.2824 Å with $\theta = 0^\circ$ (see Figure 1) was taken for the calculations reported in this table, maintaining an overall C_{2v} molecular symmetry. ^b MO's whose symmetry is different from those listed in this column are given in parentheses to the right of the orbital energy. Blank rows separate the virtual, valence, and inner-shell MO's. Orbital energies are in hartrees.

Table V. Comparison of the Electron Populations of the $\pi(1b_1)$ Orbitals of Several Low-Lying States of Formaldehyde and Its Anion and Cation Radicals^a

Molecule	State	- α $\pi(1b_1)$ orbital-		- β $\pi(1b_1)$ orbital-	
		C	O	C	O
H ₂ CO	¹ A ₁ (GS)	0.558	0.442	0.558	0.442
	³ A ₂ (n → π^*)	0.297	0.703	0.430	0.570
	¹ A ₂ (n → π^*)	0.370	0.630	0.375	0.625
	³ A ₁ (π → π^*)	0.395	0.605	0.743	0.257
	³ B ₁ (σ → π^*)	0.306	0.694	0.492	0.508
H ₂ CO ⁻	³ B ₁ (σ → π^*)	0.389	0.611	0.444	0.556
	² B ₁ (GS)	0.410	0.590	0.733	0.267
H ₂ CO ⁺	² B ₂ (n → π^*)	0.361	0.639	0.411	0.589
	² B ₂ (GS)	0.303	0.697	0.433	0.567
	² B ₁ (π → n)	0.405	0.595	0.686	0.314

^a A CO bond distance of 2.2824 Å with $\theta = 0^\circ$ (see Figure 1) was taken for the calculations reported in this table, maintaining an overall C_{2v} molecular symmetry.

wave function which is nearly an eigenfunction of S². This result is not unexpected from the discussion concerning eq 19 to 22.

The excited singlet states, ¹A₂(n → π^*) and ¹B₁(σ → π^*), represent the cases with largest spin contamination in the current study. In these cases, the expectation value goes from 1.00 before annihilation to less than 0.01 after single annihilation. Consideration of eq 20, where $\Lambda \equiv S^2$, shows that each of the two major spin-state components of the total UHF wave function occur with approximately equal probabilities, i.e., $|C_s|^2 \approx |C_{s'+1}|^2 \approx 0.5$, with $s' = 0$. Since the expectation value of the Hamiltonian with respect to these pure spin component wave functions is always negative, it is clear that annihilating the more stable higher multiplicity components, in this case the ³A₂(n → π^*) or the ³B₁(σ → π^*) state, will produce an increase in the vertical transition energy, as is observed in Table II.

Table VI. Comparison of Equilibrium Angles (θ) and Barriers to Inversion for Several States of Formaldehyde and Its Anion and Cation Radicals

Molecule	State	-Equilibrium angle, deg-				Obsd	-Inversion barriers, kcal mol ⁻¹ -			
		UHF	UHF-AA	RHF ^a	CI ^a		UHF	UHF-AA	CI ^a	Observed ^c
H ₂ CO	¹ A ₁ (GS)	0.0	0.0	0.0	0.0	C				
	³ A ₂ (n → π^*)	37.6	37.6	32.0	32.7	35 ^b	2.814	2.814	2.076	2.215
	¹ A ₂ (n → π^*)	32.2	26.6	31.1	31.9	20, ^c 31 ^b	1.453	0.485	1.684	1.015
	³ A ₁ (π → π^*)	0.0	0.0	25.7	25.9					
H ₂ CO ⁻	² B ₁ (GS)	22.4 ^d	22.4 ^d				0.438	0.438		
	² B ₂ (n → π^*)	50.6	50.6				10.958	10.958		
H ₂ CO ⁺	² B ₂ (GS)	0.0	0.0							
	² B ₁ (π → n)	0.0	0.0							

^a Buenker and Peyerimhoff, ref 28. ^b Reference 32. ^c Reference 33. ^d A value of 22° was also obtained by Dobbs, *et al.*,³⁴ using the INDO method.

Table VII. Dipole Moments (in Debyes) for Several Low-Lying States of Formaldehyde^a

	¹ A ₁	³ A ₂	¹ A ₂	³ A ₁
UHF ^b	1.042	-1.204	-0.737	0.922
CI ^{c,d}	2.948	1.873	1.682	
CI ^{e,f}	3.125	1.921	2.068	
RHF ^{c,f}	2.821			
Obsd	2.338 ^g	1.560 ^h		

^a A positive dipole moment implies that the "negative end" of the dipole moment vector points toward the oxygen atom. ^b Calculated at the equilibrium geometry of the particular state. ^c Calculated at the equilibrium geometry of the ground state. ^d Reference 28. ^e Reference 29. ^f Reference 31. ^g Reference 36. ^h Reference 37.

The large contamination of the excited singlet states by their corresponding triplet states is probably the most extreme case that can occur since, as discussed by Nakatsuji and coworkers,²¹ the weight of the lowest contaminating spin state decreases with increasing spin multiplicity of the principal spin state.

B. Equilibrium Geometry and First-Order Electronic Properties. As seen in Table VI, the equilibrium values of θ calculated by the UHF procedure with and without single annihilation are in reasonable agreement with the known experimental evidence (see Figure 2). In particular, the ground state has a planar equilibrium geometry. Also, the ³A₂ state is calculated to be more bent than the ¹A₂ state,

Table VIII. Hellmann-Feynman Electric Field Strengths at the Nuclei for the Low-Lying States of Formaldehyde and its Anion and Cation Radicals^{a,b}

Molecule	State	Nuclei		
		O	C	H
H ₂ CO	¹ A ₁ (GS)	0.001	0.065	0.030
	² A ₂ (n → π*)	0.067	0.095	0.045
	¹ A ₂ (n → π*)	0.047	0.091	0.041
	³ A ₁ (π → π*)	0.030	0.087	0.028
H ₂ CO ⁻	² B ₁ (GS)	0.013	0.082	0.124
	² B ₂ (n → π*)	0.047	0.090	0.129
H ₂ CO ⁺	² B ₂ (GS)	0.012	0.011	0.058
	² B ₁ (π → n)	0.081	0.009	0.065

^a $|e_i| = [\epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2]^{1/2}$. ^b All values in hartree atomic units, see ref 12.

and the equilibrium angles for these states are close to those determined by other procedures. It is worth noting that the only significant change in the value of the equilibrium angle which occurs after single annihilation occurs for the ¹A₂(n → π*) state. As seen in Table II, this is the only state of those examined in Table VI with significant contamination of its principal pure spin component wave function. The above result indicates that caution should be used in geometry studies,⁴⁰ whenever the expectation value of S^2 is not quite close to that of a pure spin state.

Although conclusive experimental evidence is lacking, there are theoretical calculations²⁸ which indicate that the ³A₁(π → π*) state is also nonplanar, with an equilibrium angle of 26°. The current study indicates a planar equilibrium structure. However, these results may not be as contradictory as they first appear. In particular, the UHF calculations indicate that the total energy increases very slowly with increasing θ , the difference between the total energy at 0 and 30° being less than 1 kcal/mol (Figure 2). The FSGO basis employed in the current study may be inadequate to account properly for such shallow energy curves. Until a more complete basis set is studied, the question of the suitability of the UHF procedure for examination of such subtle geometric effects cannot be resolved definitively. Furthermore, the calculation of the equilibrium angle may be sensitive to the molecular geometry used. Other workers have observed this type of effect in studies of formaldehyde-excited states,⁴¹ and a complete structural study may be required to achieve conclusive results.

In the case of the anion, both states are found to be nonplanar, while the states of the cation are found to be planar. These results are in agreement with Walsh's diagrams for isoelectronic systems.⁴² Also, Dobbs, *et al.*,³⁴ have performed INDO calculations on the ground state of the anion and report that $\theta = 22^\circ$, in excellent agreement with the current results. However, the total energy curve obtained in the current study is extremely shallow (see Figure 2) and may require more extensive basis set calculations in order to determine the equilibrium angle accurately.

Before annihilation, the inversion barrier (see Table VI) for the ³A₂ state is about twice as large as that for the ¹A₂

state, 2.814 kcal mol⁻¹ vs. 1.453 kcal mol⁻¹. Although these calculated barriers are both slightly too large, the experimental values show the same trend, 2.215 kcal mol⁻¹ vs. 1.015 kcal mol⁻¹.³³ Unfortunately, after annihilation the ¹A₂ inversion barrier becomes too small. This may also be due to the limited nature of the basis set for the ¹A₂ state, as was discussed previously, but also indicates that spin contamination can also be a significant factor even in properties that are not explicitly spin dependent. Finally, although no experimental or theoretical values exist for the states of the anion, the current calculations indicate a very low barrier for the ground state and a very high barrier for the ²B₂ excited state.

In Table IX, ionization potentials and electron affinities are given for neutral formaldehyde⁴³ and its anion and cation radicals, using both the accurate theoretical expression and Koopmans' theorem.⁴⁴ In general, the values found by using the accurate theoretical expression are in reasonable agreement with the values predicted by Koopmans' theorem. The only experimental value available is for the ionization potential of neutral formaldehyde $IP_{\text{expt}} = 10.86$ eV.⁴³

The apparent low calculated ionization potentials that are reported in Tables IX, III, and IV are not particularly surprising, since they are consistent with results obtained in a large number of closed-shell systems.⁷ In particular, it has been found in studies of closed shell systems that, although the calculated values are shifted upward (resulting in low ionization potential estimates), the relative spacing between MO levels is very close to that of extensive basis set calculations. More quantitatively, it has been found that a linear relationship exists between the filled valence orbital energies of the molecular fragment procedure and the corresponding energies from extensive basis set calculations.^{7,45} When these linear relationships are employed, quite reasonable ionization potential estimates result. For example, when such a procedure is applied to the ground-state MO structure, a first ionization potential of 11.74 eV is found.

These observed linear relationships may also be responsible in part for the encouraging spectral results that were discussed earlier. In particular, if the primary effect of the use of a small molecular fragment basis set is to shift all MO energies uniformly upward then, *to a first approximation*, the spectral transitions will be well predicted since, *e.g.*,

$$\Delta E = E(n \rightarrow \pi^*) - E(\text{GS}) \cong \epsilon_{\pi^*} - \epsilon_n$$

and the additive constant that raises both the π* and n orbitals cancels out.

It must be remembered, however, when considering the MO structure of excited states and radical ions, that appropriate large basis set UHF calculations for comparison are not currently available. Hence, while experience with closed-shell states indicates that linear relationships to MO eigenvalues of more extensive basis sets are expected, such comparisons must await more extensive basis set calculations. Therefore, the apparent low calculated ionization potentials for some open-shell states (*e.g.*, the ¹A₂ state) are

Table IX. Vertical Ionization Potentials (IP) and Electron Affinities (EA) of Formaldehyde and Its Anion and Cation Radicals

Molecule	Ionization potentials, eV		Electron affinities, eV	
	$\Delta E_{\text{SCF}}(\text{IP})^b$	Approx ^d	$\Delta E_{\text{SCF}}(\text{EA})^c$	Approx ^d
H ₂ CO (¹ A ₁) ^a	3.10 (3.06)	4.75	11.28 (11.27)	11.77
H ₂ CO ⁻ (² B ₁)	-11.28 (-11.27)	-11.06		26.02
H ₂ CO ⁺ (² B ₂)		18.85	-3.10 (-3.06)	-1.35

^a The experimental value of $IP(\text{H}_2\text{CO}) = 10.86$ eV (see ref 45). ^b $\Delta E_{\text{SCF}}(\text{IP}) = E^{N-1} - E^N = \text{IP}$ of an N -electron system. Values listed in parentheses represent values obtained after single annihilation. ^c $\Delta E_{\text{SCF}}(\text{EA}) = E^N - E^{N+1} = \text{EA}$ of an N -electron system. Values listed in parentheses represent values obtained after single annihilation. ^d Approximate values of the IP and EA are obtained using Koopmans' theorem (see ref 46), which was also shown to hold for UHF wave functions by Amos and Hall (ref 14).

expected to be increased substantially when suitable orbital energy linear relationships are established.

Also of interest is the trend in ionization potential estimates using different procedures. Ignoring any anticipated linear relationship for extrapolation of MO eigenvalues, it is seen from Table IX that the ionization potential of H_2CO is estimated to be 4.75 and 3.10 eV, where the first estimate is from Koopmans' theorem and the second is from the difference in total energy of the ground states of H_2CO and H_2CO^+ . Since a separate SCF optimization is carried out on each state in the latter estimate, it is anticipated that the ionization potential estimate will be reduced from the Koopmans' theorem estimate. Such a result is observed, further substantiating the consistency of the description of both states.

One of the most surprising results of the current study is that the electron population⁴⁶ (see Table V) of the $\pi(1b_1)$ orbital for the UHF ground-state wave function is located on the carbon atom to a much greater extent than found by Neumann and Moskowitz (0.56 vs. 0.36, respectively). This situation is qualitatively reversed for the electron populations of the $n(2b_2)$ orbitals. Neumann and Moskowitz employed a very extensive atom-centered basis, while that used in the current calculations is a small localized FSGO basis set (see Table I). The nonatomic nature of the FSGO basis makes it difficult to assign an electron population to specific atoms, but some general comparisons can be made. First, qualitative estimates of the distributions over all the non- π MO's give a lower electron population on the carbon atom than that indicated in the results of Neumann and Moskowitz. This difference may also be related in part to the inadequacy of the calculated dipole moments (discussed below). Next, Neumann and Moskowitz observe that there are substantial differences in charge distributions on progressing from minimal to larger basis sets. Hence, some of these inconsistencies appear to be artifacts of using the initial closed-shell fragment basis for open-shell states and indicate that improvements in the basis may be needed for the description of some properties.

A more general examination of the total charge and bond-order matrix, $\mathbf{P}(\lambda)$, shows that, for all states considered, the values obtained before and after annihilation are almost identical, while those of the spin-density matrix, $\mathbf{P}^{\text{SD}}(\lambda)$, show large changes for the cases where S^2 is not close to the eigenvalue of the principal spin component of the UHF wave function. Such differences in behavior between $\mathbf{P}(\lambda)$ and $\mathbf{P}^{\text{SD}}(\lambda)$ before and after single annihilation have been discussed theoretically by a number of authors.^{14,15}

An important consequence of the lack of change in $\mathbf{P}(\lambda)$ after single annihilation is that all *spin-independent* first-order electronic properties which depend on $\mathbf{P}(\lambda)$ remain essentially unchanged after single annihilation. Examples of spin-independent first-order electronic properties calculated in the present study are given in Table VII (dipole moments) and Table VIII (Hellmann-Feynman electric fields).⁴⁷ An examination of the calculated dipole moments shows rather poor agreement with experiment and other calculated values. However, calculated dipole moments are sensitive both to geometry and basis set. Hence, they are often difficult to calculate accurately. For example, two *ab initio* calculations of the dipole moment of the ground state of H_2CO by Newton and Palke⁴⁸ and Dunning, *et al.*,⁴⁹ resulted in 0.554 and 3.036, respectively. Such variability in accuracy of dipole moment calculations is frequently observed and many basis sets have limited capabilities in this regard. However, in spite of such considerations, when combined with the observations concerning the charge distribution made earlier, it appears that improvements in the mo-

lecular fragment basis to better describe the charge distribution in open-shell states are desirable.

As seen in Table VIII, the calculated Hellmann-Feynman electric fields at the nuclei are generally small. They are of the same order of magnitude as observed in closed-shell studies^{7,35} and indicate that, at least as far as this measure is concerned, the FSGO basis is approximately as well suited for the description of open-shell systems as it is for closed-shell systems.

The limited basis set size (13 FSGO's contracted to 10 basis orbitals) is certainly responsible for some of the inadequacies in the calculated results described above. However, the questions concerning possible deficiencies in the size of the basis set cannot be answered separately from these concerning possible deficiencies in the types of orbitals used in the basis set. One possible shortcoming of the basis set is the lack of *diffuse* p orbitals. Whitten and Hackmeyer²⁹ have observed that the $\pi^*(2b_1)$ orbital becomes more diffuse when a larger and more flexible basis set is employed. The feasibility of adding diffuse π -type orbitals, obtained from CH_2^- and OH^- fragments where all other orbitals are fixed, is currently being examined, as well as the addition of double Gaussians in the inner-shell and CH-bond regions.⁵⁰

Whitten and Hackmeyer also point out that the lack of d-type polarization functions may be important. Although the basis set does not contain d orbitals explicitly, it has been observed⁷ that FSGO's which are not atom centered contain fixed components of all types of orbitals, *i.e.*, s, p, d, f, etc. While the importance of independent d orbitals is known, the significance of fixed d components in nonatom-centered Gaussians has not yet, however, been completely established.⁷

In summary, many aspects of the current study are quite promising. Geometric features, the ordering of states, and MO structure appear adequately predicted. Furthermore, new methodology for the formation of initial charge and bond-order matrices and subsequent SCF iteration provides an important tool for practical implementation of the method. In addition, the localized nature of the FSGO basis and the *ab initio* calculational framework allow a straightforward, yet detailed, analysis of the advantages and limitations of the basis along with suggestions where improvements are desirable. Finally, the UHF method with the FSGO basis is computationally relatively simple to implement compared to, *e.g.*, CI methods, and provides optimism that satisfactory methods for the description of open-shell states of large molecules can also be developed.

Further investigations regarding the application to other systems of chemical and biological interest and improvement of the FSGO basis as appropriate are currently in progress and will be reported at a later date.

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References and Notes

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- (2) (a) Department of Chemistry. (b) NSF Trainee, 1970-1974. (c) Supported in part by a USPHS Health Sciences Advancement Award [RR-06147] to the University of Kansas; Department of Biochemistry.
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Use of Semiempirical Models for Calculation of B Terms in Magnetic Circular Dichroic Spectra. IV. ^{1a} Substituted Benzenes in the Pariser–Parr–Pople Model

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Abstract: B terms in MCD spectra of the benzyl cation and anion are calculated in several approximations with the simple PPP model. Definite predictions are reached for signs of B terms of low energy transitions. The calculated signs of the first two B terms are easily understood in terms of a simple argument based on the well-known nodal properties of benzyl Hückel orbitals. A similar argument can be made for benzenes with a general conjugative substituent and suggests extrapolation of the calculated signs from the benzyl ions to isoelectronic substituted benzenes. This extrapolation is justified by numerical calculations and is in good agreement with experimental data, thus providing a simple intuitive rationalization of the well-known trends in MCD spectra of substituted benzenes. Unlike mesomeric effects of substituents, their inductive effects are calculated to have only very small influence on the lowest B terms. Finally, it is pointed out that the existence of these trends (in particular, of opposite effects of π -electron-donating and -withdrawing substitution) is related to general theorems concerning alternant pairing properties and that similar trends are to be expected for derivatives of other alternant hydrocarbons containing conjugative substituents.

At an early stage in the present surge of interest in MCD (magnetic circular dichroic) spectroscopy of organic compounds, it was noted that signs of bands in the MCD spectra of benzenes carrying ortho and para directing substituents are opposite to those found with meta directing substituents and a correlation between the maximum molar MCD of the first band and the Hammett σ_p constant was reported.^{1b} Other investigations followed,²⁻⁴ and it is now firmly established that substituted benzenes in which the substitu-

ent is electron donating have a positive lowest B term (the first transition corresponds to benzene ¹B_{2u} state) and a negative second B term (the second transition is believed to correspond to benzene ¹B_{1u} state), while the opposite is true for benzene with an electron-withdrawing substituent. Mesomeric substituent effect appears to be more important than inductive effect, since halobenzenes have a positive first B term.

A rationalization of these opposite trends in general