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THE ACETYL CATION AND ITS GEOMETRICAL ISOMERS

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THE ACETYL CATION AND ITS GEOMETRICAL ISOMERS.

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ABSTRACT

Ab initio self-consistent-field (SCF) calculations are reported on the acetyl cation (CH_3CO^+) and three of its possible geometrical isomers. The wave functions are discussed in terms of Mulliken populations and simple valence bond arguments. The energies of the low-lying electronic states of CH_3CO^+ are estimated and compared with those of CO. The similarities and differences are explained in terms of simple chemical arguments. Finally an accurate 2 configuration wave function for the CH_3CO^+ fragmentation is presented, showing unambiguously the dissociation products to be the expected ones CH_3^+ and CO.

I. INTRODUCTION

The existence of the acetyl cation has long been known to the organic chemist, as evidenced by the omnipresent 43 peak in mass spectrum of various organic precursors.[1] However this ion and its various geometrical isomers have taken on an increasing importance with the advent of ion cyclotron resonance spectroscopy,[2] which permits the elucidation of the various intermediate structures involved in the complex rearrangement of an organic molecule. In fact '43 peaks' attributed to several of the possible geometrical isomers of the acetyl cation have been observed.[3]

With regard to these isomers two questions naturally arise: (1) What are the relative energies of the isomers at their equilibrium geometries, and (2) How rapidly do the various structures interconvert? An auxiliary question then also arises concerning the relative positions of the excited electronic states of these species. Were adequate information available, the appearance or disappearance of each isomer might be monitored by appropriate spectroscopic techniques. Considering the importance of these questions, there have been relatively few attempts to answer them by theoretical methods.[4]

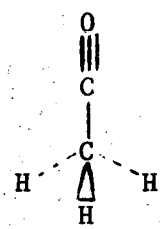
In this work we report the results of <u>ab initio</u> calculations on the four most stable geometrical configurations of $C_2H_3O^+$ and also investigate the electronic spectrum of the most stable arrangement, CH_3CO^+. The dissociation of CH_3CO^+ into CH_3^+ and

CO is also considered. Section II defines the systems to be considered and the technical aspects of the calculations; in Section III the results of the calculations on the ground electronic states are presented and discussed in terms of Mulliken populations and simple valence bond ideas; in Section IV the discussion turns to the spectrum of CH_3CO^+, where estimates of the electronic energies of several excited states are presented and compared to the well studied system CO with a eye to a simple understanding of the manifold of states; finally in Section V, we present some concluding remarks and the direction of future research on this system is outlined.

II. THEORETICAL APPROACH

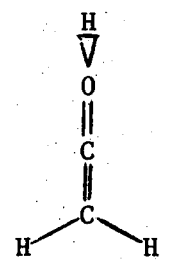
Traditional ideas of chemical bonding indicate four reasonable geometrical configurations of C_2H_3O are possible. They are illustrated below together with their space point group designations:

I.



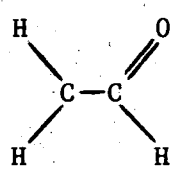
C_{3v}

II.



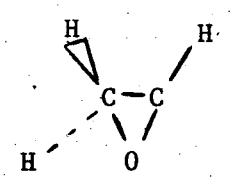
C_s

III.



C_s

IV.



C_s

The electron occupancies which give rise to the ground state single determinant wave functions for the four structures in question are given below:

I. $1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1^2\ 1e^4\ 2e^4$ (1)

II., IV. $1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 9a'^2\ 1a''^2\ 2a''^2$ (2)

III. $1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 9a'^2\ 10a'^2\ 1a''^2$ (3)

Thus it is seen that with the nuclear symmetry as indicated above, the ground electronic state of each of the four isomers is a closed shell system and therefore the determination of the electronic wave function within the self consistent field (SCF) approximation follows from Roothaan's prescription.[5]

The calculation of an SCF wave function for the $CH_3 \cdots CO$ fragmentation is a little more involved. The valence bond formalism that leads to the ground state occupancy of I as above, predicts that the $7a_1$ orbital should describe the C-C sigma bond. Thus the description of the fragmentation reaction will involve, essentially, the description of the $7a_1$ orbital as the C-C bond is stretched. If this bond were to cleave heterolytically, i.e., into two closed shell species, then the single configuration approximation would remain valid. That this should be the case is in fact reasonably clear. However so as not to prejudice the calculation the possibility of homolytic cleavage, i.e., cleavage in two radicals, should be taken into consideration. This is accomplished by allowing the 2 electrons in the $7a_1$ orbital to occupy 2 distinct orbitals of the form $7a_1 = \alpha' \sigma_1 + \beta' \sigma_2$; $7a_1' = -\beta' \sigma_1 + \alpha' \sigma_2$. These orbitals are then singlet coupled and the result is a 2 configuration wave function

$$\chi = \alpha A \; 1a_1^2 \; 2a_1^2 \; 3a_1^2 \; 4a_1^2 \; 5a_1^2 \; 6a_1^2 \; \sigma_1^2 \; 1e^4 \; 2e^4$$

$$- \beta A \; 1a_1^2 \; 2a_1^2 \; 3a_1^2 \; 4a_1^2 \; 5a_1^2 \; 6a_1^2 \; \sigma_2^2 \; 1e^4 \; 2e^4 \qquad (4)$$

where A is a self adjoint projection operator[7] which maps a general N particle function onto the subspace containing only functions such that $\chi(\phi_1, \phi_2 \ldots \phi_i, \phi_j \ldots \phi_N) = -\chi(\phi_1, \phi_2 \ldots \phi_j, \phi_i \ldots \phi_N)$.

The determination of χ is then given by the prescription of Goddard.[6] Note that if $\beta = 0$ our original single determinant approximation is recovered so that if χ is calculated in this way the calculation will be 'unprejudiced' as to the type of cleavage.

The determination of the excited electronic states of CH_3CO^+ turns out to be a much more difficult matter. The results of the calculation on the ground state of CH_3CO^+, to be described in the following section, indicate the highest occupied molecular orbital to be the 2e orbital (see Table III); it is given approximately as a linear combination of atomic orbitals by

$$2e_x = (e_{x_{CH_3}} + 0. \cdot P_{x_C} - P_{x_0}) \tag{5a}$$

and

$$2e_y = (e_{y_{CH_3}} + 0. \cdot p_{y_C} - P_{y_0}) \quad , \tag{5b}$$

where the lower subscript indicates the spatial location of the basis functions. Note that these functions contain one node. Thus the lowest lying virtual or unoccupied orbitals should be the following, degenerate, two node, functions

$$3e_x = (e_{x_{CH_3}} - P_{x_C} + P_{x_0})$$

and

$$3e_y = (e_{y_{CH_3}} - P_{y_C} + P_{y_0}) \quad . \tag{6}$$

Of course, since the three functions being combined are not equivalent the coefficients of combination are not expected to

be equal as above. This point will be taken up in greater detail in Section IV.

Regardless of the exact nature of these orbitals the lowest lying excited electronic state should arise from the occupancy:

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1^2\ 1e^4\ 2e^3\ 3e \tag{7}$$

which represents a singly-excited occupancy corresponding to the excitation $2e \rightarrow 3e$.

This occupancy gives rise to six distinct electronic states with the following wave functions (closed shell orbitals omitted for clarity):

$$^3A_1 \ : \ \frac{1}{\sqrt{2}} \mathcal{A}\ (2e_x\alpha\ 2e_y^2\ 3e_x\alpha + 2e_x^2\ 2e_y\alpha\ 3e_y\alpha) \tag{8}$$

$$^3E \ : \begin{cases} \frac{1}{\sqrt{2}} \mathcal{A}\ (2e_x\alpha\ 2e_y^2\ 3e_x\alpha - 2e_x^2\ 2e_y^2\alpha\ 3e_y\alpha) & (9a) \\ \frac{1}{\sqrt{2}} \mathcal{A}\ (2e_x\alpha\ 2e_y^2\ 3e_y\alpha + 2e_x^2\ 2e_y\alpha\ 3e_x\alpha) & (9b) \end{cases}$$

$$^3A_2 \ : \ \frac{1}{\sqrt{2}} \mathcal{A}\ (2e_x\alpha\ 2e_y^2\ 3e_y\alpha - 2e_x^2\ 2e_y\alpha\ 3e_x\alpha) \tag{10}$$

$$^1A_2 \ : \ \frac{1}{2} \mathcal{A}((2e_x\alpha\ 2e_y^2\ 3e_x\beta - 2e_x\beta\ 2e_y^2\ 3e_x\alpha) + (2e_x^2\ 2e_y\alpha\ 3e_y\beta - 2e_x^2\ 2e_y\beta\ 3e_y\alpha)) \tag{11}$$

$$^1E \ : \begin{cases} \frac{1}{2} \mathcal{A}((2e_x\alpha\ 2e_y^2\ 3e_x\beta - 2e_x\beta\ 2e_y^2\ 3e_x\alpha) - (2e_x^2\ 2e_y\alpha\ 3e_y\beta - 2e_x^2\ 2e_y\beta\ 3e_y\alpha)) & (12a) \\ \frac{1}{2} \mathcal{A}((2e_x\alpha\ 2e_y^2\ 3e_y\beta - 2e_x\beta\ 2e_y^2\ 3e_y\alpha) - (2e_x^2\ 2e_y\alpha\ 3e_x\beta - 2e_x^2\ 2e_y\beta\ 3e_x\alpha)) & (12b) \end{cases}$$

$$^1A_1 \;:\; \frac{1}{2} A((2e_x\alpha\; 2e_y^2\; 3e_y\beta - 2e_x\beta\; 2e_y^2\; 3e_y^2\alpha) - (2e_x^2\; 2e_y\alpha\; 3e_x\beta - 2e_x^2\; 2e_y\beta\; 3e_y\alpha)) \tag{13}$$

Note that the wave functions representing the ^1E and ^3E states can, in fact, be degenerate only to zeroth order in the nuclear displacements as required by the theorem of Jahn and Teller.[8]

We now consider the problem of determining the one-electron orbitals required for the above wave functions by an SCF procedure. To appreciate the difficulties involved one must retreat to the basic assumptions of the theory. The first step in carrying out any of the currently existing Roothaan-type SCF procedures is to express

$$E_{SCF} \equiv \langle \chi_{SCF} | H | \chi_{SCF} \rangle \tag{14}$$

as a linear combination of matrix elements of the form[5]

$$E_{SCF} = \sum_{i=1}^{N} f_i \langle \phi_i | 2h + \sum_{k=1}^{N} (2a_{ki}\, J_k - b_{ki}\, K_k) | \phi_i \rangle \tag{15}$$

where N = number of occupied orbitals,

J_k = coulomb operator for kth molecular orbital

K_k = exchange operator for kth molecular orbital

h = one electron kinetic energy and nuclear attraction energy operator

ϕ_i = ith molecular orbital

and

f_i = occupation number of the ith molecular orbital.

For example, if χ is a closed shell wave function $a_{ki} = 1 = b_{ki}$ for all i, k and $f_i = 1$ for all i.[5]

E_{SCF} is then regarded as a functional[9] of the set $\{\phi_i\}_{i=1}^{N}$ i.e., $E_{SCF} = E(\{\phi_i\})$ and the equations that result from the requirement that $E(\{\phi_i\})$ be stable with respect to all first order changes[10] in the set $\{\phi_i\}$ are solved for ϕ_i's. However if $E(\{\phi_i\})$ cannot be written in the form of equation (15) these standard procedures break down.

Appendix I gives the energy functionals corresponding to the wave functions in equations 8-13. Reference to this Appendix shows that in none of the eight cases does an energy functional of the form of equation (15) emerge. Further it can be readily seen that the reason for the difficulty lies in the occurence of more than one fractionally occupied multiply degenerate molecular orbital. However, for the particular case of the ^3E state the situation is not hopeless. In fact, Appendix II shows that if the wave function for this state is chosen to be $\chi = \frac{1}{2}(\chi_{^3E_x} + \chi_{^3E_y})$ then the resulting energy functional is of the required form. Therefore the molecular orbitals appropriate for this wave function can be obtained by the self consistent procedure due to Goddard.[11] Further since it is not unreasonable to expect that the individual molecular orbitals will not change too drastically as the space and spin couplings are changed to produce the remaining five electronic states, the energies of these states can

can be estimated by simply evaluating $E = \langle\chi|H|\chi\rangle$ according to the prescription of Appendix I with the χ's constructed using the molecular orbitals from the ^3E wave function. The viability of this approximation will be discussed in Section IV and in a subsequent paper in which a technique for obtaining the energies of all six states based on the technique of annihilation of single excitations[12] will be investigated.

As Section IV will show we are also interested in the triplet state arising from the occupancy

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1\ 1e^4\ 2e^4\ 3e \quad . \tag{16}$$

This occupancy arises from the single excitation $7a_1 \rightarrow 3e$. The calculation of the optimum molecular orbitals for this state is fairly straightforward. The only difficulty is that of constraining the e_x and e_y type orbitals to remain equivalent.[13] This however can be readily accomplished by performing the minimization procedure on the energy functional corresponding to the wave function

$$\chi = \frac{1}{2}(\chi_{^3E_x} + \chi_{^3E_y}) \tag{17a}$$

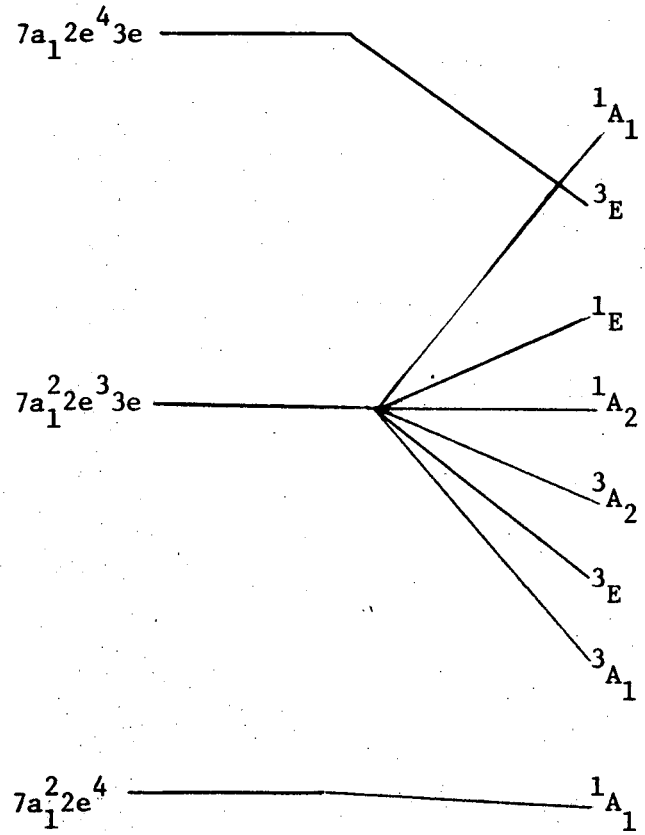
where

$$\chi_{^3E_x} = \mathcal{A}\ 7a_1\alpha\ 3e_x\alpha \tag{17b}$$

$$\chi_{^3E_y} = \mathcal{A}\ 7a_1\alpha\ 3e_y\alpha \tag{17c}$$

and again the closed shell orbitals have been omitted for clarity.

Thus to summarize, we propose to predict the total electronic energy of those electronic states depicted below:



All calculations were performed using a standard Dunning-[14] Huzinaga[15] basis set. Specifically, the (9s 5p/4s 2p) contraction was used for functions centered on carbon and oxygen atoms while the (4s/2s) contraction scaled by a factor of 1.2 was employed for functions centered on the three hydrogen atoms.

III. RESULTS: GROUND ELECTRONIC STATES

In Table I the results of geometry optimizations on the four isomers in question are displayed. In the case of isomers III (the aldehyde) and IV (the epoxide) deviations from C_s symmetry that did not involve the methylene hydrogens were permitted but were found to be energetically unfavorable. With the acetyl cation (I) taken as the reference level, protonated ketene (II) is seen to be the second most stable arrangement lying at 37 kcal, the aldehyde third at 64 kcal, and the epoxide fourth at 70 kcal.

While it is, in general, of questionable value to attempt to understand the quantitative results of the more exact Hartree-Fock-Roothaan theory with ideas arising from the simpler valence bond theory some very worthwhile sights into the nature of these systems can sometimes be gleaned from such an approach.

We start by asking the simple question: To what extent is CH_3CO^+ the union of CH_3^+ and CO? Within the context of our single configuration approximation to an electronic wave function the orbital occupancies to be considered are, in C_{3v} symmetry

$$CH_3^+ : \underset{C_{1s}}{1a_1^2}\ \underbrace{2a_1^2\ 1e^4}_{\sigma_{CH}} \tag{18a}$$

and

$$CO : \underset{O_{1s}}{1a_1^2}\ \underset{C_{1s}}{2a_1^2}\ \underset{O_{2s}}{3a_1^2}\ \underset{\sigma_{CO}}{4a_1^2}\ \underset{C_{sp}}{5a_1^2}\ \underset{\pi_{CO}}{1e^4} \quad . \tag{18b}$$

The designations under each orbital label the principal contributors to the molecular orbitals as might be predicted by valence bond theory. We remark that these designations are an interpretative convenience since the energy functional for a closed shell system is invariant under a unitary transformation of the orbitals.[5]

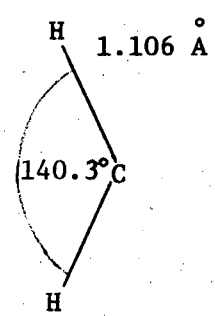
Now to form CH_3CO^+ we imagine the doubly occupied $5a_1(C_{sp})$ orbital of CO interacting with the empty $3a_1(C_p)$ orbital of CH_3^+ to form a σ bond. The CH_3 fragment will, naturally, deform from planarity and move toward a tetrahedral configuration corresponding to sp^3 hybridization while the CO fragment should remain basically unchanged since the $5a_1$ orbital is essentially nonbonding in character. To see the remarkable accuracy of this interpretation we note the following results from our ground state calculations on system I. The charge distributions presented in Table II indicate a significant transfer of charge from the CO carbon to the CH_3 cluster with little change in the oxygen charge from its approximately neutral condition in isolated CO.[16] The C-O distance in carbon monoxide is known experimentally to be 1.13 Å[17] while Table I shows the C-O bond in the acetyl cation to be 1.125 Å. Thus, as expected, the CO bond is not affected by the formation of the C-C bond. The CCH bond angle in CH_3CO^+ is found from Table I to be 109.5° which is the tetrahedral angle to 1 decimal place. Finally we note that in system I the C-C bond distance of 1.46 Å is precisely equal to that of the C-C single bond in methyl acetylene (CH_3-C≡C-H).[18]

This is very gratifying as in both cases the bond can be considered to originate from the joining of an sp with an sp^3 hybridized carbon.

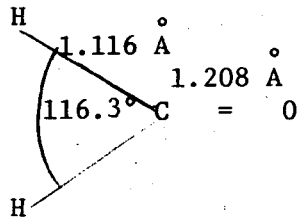
System III, the aldehyde, can also be interpreted in terms of this molecular fragments idea. The aldehyde structure can be viewed as a formaldehyde (H_2CO) with one of the hydrogens replaced by a CH_2^+ group. We begin our analysis by noting that accurate configuration interaction calculations on the CH_2^+ system[19] show that for the ground electronic state ($^2A_1$ in C_{2v} symmetry), corresponding principally to the orbital occupancy:

$$\begin{array}{ccccc} 1a_1^2 & \underbrace{2a_1^2 \; 1b_2^2} & 3a_1 \\ C_{1s} & \sigma_{C-H} & C_{sp^2} \end{array} \qquad (19)$$

the equilibrium geometry is as follows



Further ground state formaldehyde ($^1A_1$) is known experimentally to have the following structure[20]



Thus structure III can be viewed as arising from the interaction of the $3a_1$ orbital of CH_2^+ with an approximately sp^2 orbital from the carbon of $H_2C = O$, both of which contain one electron. Reference to Table I shows that the model does not work as well for this system as it did for the acetyl cation. Steric interactions force the bond angles around the formaldehyde carbon to become unsymmetrical. The CH_2 cluster which we might have predicted to have + 1 charge now carries a Mulliken charge of + 0.72. Various other geometrical parameters show deviations from their values in the isolated fragments. For example the C-O distance in formaldehyde is 1.208 Å[20] whereas in structure III it is found to be 1.221 Å; the CH distance in isolated CH_2^+ is 1.106 Å, in our case the distance is 1.077; finally the HCH angle is seen to exhibit an even larger deviation, changing from 140.3° in the unperturbed molecular fragment[19] to 120.° in structure III.

The molecular fragments model is not particularly well suited for the analysis of structures II and IV. However we can estimate the position of the unique hydrogen in system II by viewing it as a union of H^+ and $CH_2 = C = O$ fragments. If in the CH_2CO fragment, the oxygen is considered to be sp^2 hybridized, the plane defined by the hybrid orbitals must be perpendicular to the molecular plane

and the two equivalent non-bonding doubly occupied orbitals each make a 60° angle with the C_2 axis. The O-H bond is then formed as H^+ interacts with one of these two equivalent orbitals so that the unique hydrogen should be located in the plane containing the perpendicular bisector of the CH_2 bond and form a COH angle of 120°. Table I shows that this is in fact the case except that the COH angle is found to be 128.0°.

Thus we see that the idea of molecular fragments in conjunction with valence bond theory provides a useful starting point for the discussion of molecular structure. These ideas may prove increasingly useful as the size of system being investigated increases. Finally we note that Tables III, IV, V, VI present an analysis of the ground state wave functions of the four isomers in question in terms of orbital energies and Mulliken populations. Note that in these Tables the localized description of the orbitals used above does not emerge (see remarks following Eq. 18b). Rather, these delocalized orbitals are the appropriate starting point for the investigation of the spectral properties of $C_2H_3O^+$.

We conclude our discussion of the ground electronic states by investigating the dissociation reaction

$$CH_3\text{-}CO^+ \rightarrow CH_3^+ + CO \tag{20}$$

The bond cleavage is seen to proceed in an asymmetric manner as shown in Table VIII with the positive charge ultimately residing on the CH_3 cluster. It should be pointed out that, as in the case of Table II, the charge distributions are calculated with the aid of Mulliken populations. Also consistent with the asymmetric

bond cleavage is the large value of α ($0 \leq \alpha \leq 1$) (see Equation 4) at all points along the reaction coordinate--if the cleavage were to be symmetric a limiting value of $\alpha = {}^{1}/\sqrt{2}$ would be expected. The predicted strength of the C-C bond is 58.1 kcal and bond breaking is seen to be complete by $\Delta R = 3$ bohrs, with the CH_3^+ assuming the planar geometry characteristic of the isolated molecular fragment.[21] Finally we note that if viewed in the reverse direction reaction (20) proceeds with no activation energy.

IV. RESULTS: EXCITED STATES OF CH_3CO^+

In Table VII, a Mulliken population analysis of the single configuration wave function corresponding to the ^3E state arising from the occupancy in eq. (7) is presented. Since the corresponding energy functional is not invariant under a unitary transformation of the e-type molecular orbitals the localized nature of these orbitals is significant. In particular we observe that the 1e pair is strongly localized on the CH_3 cluster while the 2e and 3e pairs are strongly CO localized. Further, reference to the actual wave function (not presented here) shows the 2e pair to be an even combination of carbon p and oxygen p functions, i.e., to be a CO bonding orbital while the 3e pair is seen to be the corresponding odd combination of carbon and oxygen p functions i.e., to be a CO antibonding orbital. Thus the 2e $\rightarrow$ 3e excitation discussed in Section II is seen to be a $\pi \rightarrow \pi^*$ excitation within the CO cluster. The analog of this excitation in the isolated CO molecule is easily seen to be $1\pi \rightarrow 2\pi$ (see eq. 18b).

The second electron configuration of interest is that arising from the $7a_1 \rightarrow$ 3e excitation. In Section II we concluded that the $7a_1$ orbital should result from the formation of the σ bond between the CH_3^+ and CO fragments. In Table VII the $7a_1$ orbital is shown to be more delocalized than expected; however, this is a result of the method of calculation, i.e., the molecular orbitals are chosen to be eigenfunctions of the Fock operator.[5] Localization could be achieved by a unitary transformation (among the closed shell orbitals) which would leave the energy

functional unchanged. In any case, the $7a_1 \rightarrow 3e$ excitation is seen to be of $\sigma \rightarrow \pi^*$ type, the analogous excitation in CO being the $5\sigma \rightarrow 2\pi$ excitation. However, as noted in Section II to the $7a_1$ orbital should be stabilized relative to its 5σ precursor as a result of bond formation. In light of the above observations we can make the following predictions regarding the excited states of CH_3CO^+:

(1) Those states arising from the occupancy $7a_1^2\ 2e^3\ 3e$ should show a lengthening of C-O bond distance as compared to the ground state since an electron is being removed from a C-O bonding orbital and put into a C-O antibonding orbital.

(2) The C-C bond distance in the above states should remain essentially unchanged especially when compared to the change occuring in the ^3E state arising from the occupancy $7a_1\ 2e^4\ 3e$, since in the latter case an electron is being removed from a C-C bonding orbital.

(3) The CO bond distance in the $^3E(7a_1\ 1e^4\ 3e)$ state should be longer than in the ground electronic state but shorter than in those states arising from $(7a^2\ 2e^3\ 3e)$ since in the former case the electron being promoted does not originate from a C-O bonding orbital as it does in the latter.

(4) The manifold of states arising from the $(7a_1\ 2e^3\ 3e)$ occupancy in CH_3CO^+ should show splittings similar to those of the states arising from the $5\sigma^2\ 1\pi^3\ 2\pi$ occupancy in CO.

(5) The ^3E state originating from the $7a_1\ 2e^4\ 3e$ occupancy should be much higher in energy relative to the $7a_1^2\ 2e^3\ 3e$ manifold

than the $5\sigma\ 1\pi^4\ 2\pi$ is relative to the $5\sigma^2\ 1\pi^3\ 2\pi$ manifold owing to the stabilization of the $7a_1$ orbital described above.

(6) Finally, the method of calculating the excited states of CH_3CO^+ assumes that only small changes in the orbitals in the $7a_1^2\ 2e^3\ 3e$ manifold occur upon recoupling. This should be reflected in the case of the isolated CO molecule by only small changes in the CO distance among the various state arising from the $5\sigma^2\ 1\pi^3\ 2\pi$ electron occupancy.

Reference to Table IX shows predictions (1)-(3) to be quite valid, with the CO distance stretched 0.225 Å in states arising from the occupancy $7a_1^2\ 2e^3\ 3e$ while only 0.138 Å in the ^3E state arising from the $7a_1\ 2e^4\ 3e$ occupancy. The C-C bond predictions are seen to fare equally well, stretching only 0.015 Å in the former case, while stretching 0.063 or more than 4 times as much in the latter case.

The accuracy of the remaining predictions can be evaluated from Table X. The left hand part of the table presents the results of our calculations using the methods outlined in Section II. The right hand side is a compilation of the experimentally known[22] energy levels of the CO molecule with the principal electron occupancies being determined by comparison to the configuration interaction wave functions of O'Neil and Schaefer.[17]

We first note that with regard to prediction (6) we are encouraged as to the viability of our "fixed orbital" approximation in that in the five spectroscopic states O'Neil and Schaefer were able to identify the CO bond varies by only 0.05 Å and compares quite well to our calculated value of 1.35 Å.

Prediction (5) is also seen to be born out as reference to the entries in the final row of the table easily shows.

However, it is prediction (4) which provides the most stringent test of the ideas expounded in this work. If it were to be found accurate it would represent significant evidence of the viability of both the molecular fragments model and the "fixed orbital approximation" in describing this system.

Consider then a comparison of the five states of CO identified unambiguously by O'Neil and Schaefer as arising from the occupancy $5\sigma^2\ 1\pi^3\ 2\pi$ with the corresponding states of CH_3CO^+. To facilitate the comparison we uniformly translate the CO levels so that the $^3A_1$ state of CH_3CO^+ and the $^3\Sigma^+$ state of CO are at the same energy relative to the ground state. The results of this procedure are to be found in Table X in the column labeled $E_{(comp)}$.

We first note that the ordering of the terms within the two manifolds are the same. But we have done better than just obtaining the correct ordering. The ($^3A_2$, $^3\Sigma^-$) and (^1E, $^1\Delta$) pairs are seen to agree to $\leqslant$ 0.06 eV while the ($^1A_2$, $^1\Sigma^-$) and (^3E, $^3\Delta$) pairs agree to $\leqslant$ 0.17 eV. Thus not only is the proper ordering of states obtained but so is reasonable agreement as to their splittings.

V. CONCLUSIONS AND NEW DIRECTIONS

Thus, in conclusion, we believe that in many instances the molecular fragments model can provide a valuable tool for constructing equilibrium structures for complex molecules. With regard to the question of when the model is useful, it should be noted that we have made no attempt to define in any unambiguous or rigorous manner what constitutes a molecular fragment. The concept should be understood as a simple interpretative tool which under appropriate circumstances can be of predictive value. Thus we present no general rule for the applicability of the concept.

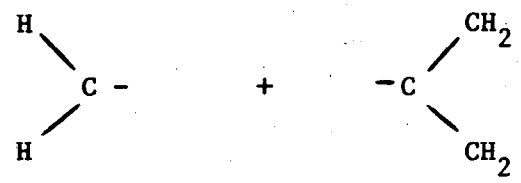
Further, we have attempted to show that the effects of different coupling on the molecular orbitals arising from a given electron occupancy may in many cases be neglible and that the energy of the various states arising from these occupancies can be computed within the fixed orbital approximation. However, a word of caution is in order. Our work on the trimethylenemethane system[23] demonstrates that under certain circumstances the fixed orbital approximation fails badly. In planar $C(CH_2)_3$ one is interested, amongst other things, in the following two states in C_{2v} symmetry (again closed shell orbitals omitted)

$$^3B_1 : \chi = A\, a_2\, b_2\, \alpha\alpha$$

and

$$^1B_1 : \chi = A\, a_2\, b_2\, \frac{(\alpha\beta-\beta\alpha)}{\sqrt{2}} \quad .$$

If $C(CH_2)_3$ is thought of as arising from



then it can be shown that the a_2 orbital is localized on the $C(CH_2)_2$ fragment while the b_2 orbital, which might be considered to originate on the CH_2 fragment, has the possibility of becoming delocalized when the fragments are combined. Reference to the molecular orbitals arising from SCF calculations on the above two states shows that the (a_2, b_2) pairs of the two wave function have quite similar a_2 orbitals but highly dissimilar b_2 orbitals. In one case the b_2 orbital remains localized, in the other case it delocalizes. Thus it should be clear that these two ideas, of molecular fragments and fixed orbitals, are intimately interrelated and that careful consideration should preceed their use.

The second question proposed in Section I, regards the rates of interconversion of the various systems. In this regard the geometry optimizations discussed in Section III represent the necessary first step in investigating these rates, i.e., the identification of the surface minima as a function of nuclear coordinate. The next crucial determination is that of the relevant "mini-max" or saddle points. This of course is a much more arduous task but hopefully not beyond theoretical treatment.

ACKNOWLEDGMENTS

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APPENDIX I

Let $$\chi \sum_{i=1}^{L} k_i D_i \tag{AI.1}$$

where D_i is a Slater determinant of orthogonal spinorbitals $\{\phi_i\}$ and $\sum_{i=1}^{L} |k_i|^2 = 1$. We will consider a spin orbital ϕ_i to be product of a spatial part s_i and a spin part $\gamma_i \varepsilon \{\alpha,\beta\}$ i.e.,

$$\phi_i = s_i \gamma_i \quad . \tag{AI.2}$$

It is then easily seen that

$$E \equiv \langle\chi|H|\chi\rangle = \sum_{i=1}^{L} |k_i|^2 \langle D_i|H|D_i\rangle + 2 \sum_{1\leq i<j\leq L} k_i k_j \langle D_j|H|D_i\rangle \quad . \tag{AI.3}$$

Expression (AI.2) for the energy functional E is then evaluated by means of Slater's method.[24]

For the evaluation of $\langle D_i|H|D_i\rangle$ we proceed as follows:

$$\text{let} \quad D = A(a_1\alpha\ a_1\beta \ldots a_N\alpha\ a_N\beta\ b_1\gamma_1 \ldots b_M\gamma_M) \tag{AI.4}$$

where again $\gamma_i \ \varepsilon\{\alpha,\beta\}$ and the a_i and b_i are functions of the spatial coordinates of the ith electron. In the usual terminology the a_i are referred to as doubly occupied orbitals while the b_i are said to be singly occupied. The matrix element $\langle D|H|D\rangle$ is then given by the following expression

$$\langle D|H|D\rangle = \sum_{i=1}^{N} h_i + \sum_{k=1}^{M} h_k + \sum_{ij=1}^{N} (2J_{ij} - K_{ij}) \tag{AI.5}$$

$$+ \sum_{\substack{i=1,N \\ k=1,M}} (2J_{ik} - K_{ik}) + \frac{1}{2} \sum_{k,\ell=1}^{M} (J_{k\ell} - K_{k\ell}\delta_{\gamma_k,\gamma_\ell})$$

where

$$h_i = \langle S_i|h|S_i\rangle \tag{AI.6}$$

$$J_{ik} = \langle S_i|J_i|S_i\rangle = \langle S_k|J_i|S_k\rangle \tag{AI.6b}$$

$$K_{ik} = \langle S_i|K_k|S_i\rangle = \langle S_k|K_i|S_k\rangle \tag{AI.6c}$$

N = number of doubly occupied orbitals

M = number of singly occupied orbitals

and $S \varepsilon \{\{a_i\}, \{b_i\}\}$.

In the cases we will be considering, if $i \neq j$ when D_j can be obtained from D_i by either (1) replacement of γ_i, γ_j by γ_i', γ_j' with the space parts unchanged or (2) replacement of ϕ_i, ϕ_j by ϕ_i', ϕ_j', i.e., both space and spin functions are altered.

Note that in neither case do we allow $i' = i$ or $j' = j$ so that we are dealing with double replacements only. Thus for case (1)

$$\langle D|H|D'\rangle = -\langle s_j|K_i|s_j\rangle = -\langle s_i|K_j|s_i\rangle \tag{AI.7a}$$

and for case (2)

$$\langle D|H|D'\rangle = \int d^3r_1 d^3r_2 \frac{s_i(1)s_j(2)s_i'(1)s_j'(2)}{r_{12}} \delta_{\gamma_i\gamma_i'}\delta_{\gamma_j\gamma_j'}$$

$$- \int d^3r_1 d^3r_2 \frac{s_1(1)s_j(2)s_j'(1)s_i'(2)}{r_{12}} \delta_{\gamma_i\gamma_j'}\delta_{\gamma_j\gamma_i'} \qquad \text{(AI.7b)}$$

$$\equiv (s_i s_i' || s_j s_j')\delta_{\gamma_i\gamma_i}\delta_{\gamma_j\gamma_j'}$$

$$- (s_i s_j' || s_j s_i')\delta_{\gamma_i\gamma_j}\delta_{\gamma_j\gamma_i'} \quad . \qquad \text{(AI.7c)}$$

With these tools in hand the requisite energy functionals are now easily evaluated. We shall work out the case of the $^3A_1$ state in detail and then merely tabulate the remaining results. Comparison of Eq. (8) of Section II with Eq. (AI.1) shows that for $\chi_{^3A_1}$ L = 2 and

$$k_1 = \frac{1}{\sqrt{2}} = - k_2 \qquad \text{(AI.8a)}$$

$$D_1 = A(1a_1\alpha 1a_1\beta \ldots 7a_1\alpha 7a_1\beta 1e_x\alpha \ldots 1e_y\beta 2e_x\alpha 2e_y\alpha 2e_y\beta 3e_x\alpha) \qquad \text{(AI.8b)}$$

$$D_2 = -A(1a_1\alpha 1a_1\beta \ldots 7a_1\alpha 7a_1\beta 1e_x\alpha \ldots 1e_y\beta 2e_x\alpha 2e_x\beta 2e_y\alpha 3e_y\alpha) \qquad \text{(AI.8c)}$$

$$= A(1a_1\alpha 1a_1\beta \ldots 7a_1\alpha 7a_1\beta 1e_x\alpha \ldots 1e_y\beta 2e_x\alpha 2e_y\alpha 2e_x\beta 3e_y\alpha) \quad . \qquad \text{(AI.8d)}$$

Therefore using (AI.7c) we get for $\langle D_1|H|D_2\rangle$

$$\langle D_1|H|D_2\rangle = (2e_x 2e_y || 3e_x 3e_y) \qquad \text{(AI.9)}$$

while using (AI.5) the diagonal matrix elements become

$$\langle D_1|H|D_1\rangle = 2 \sum_{i\varepsilon c'} h_i + \sum_{j\varepsilon o'} h_j + \sum_{i,j\varepsilon c'} (2J_{ij} - K_{ij})$$

$$+ \sum_{\substack{i\varepsilon c \\ j\varepsilon\{2e_x 3e_x)}} (2J_{ij} - K_{ij}) \qquad \text{(AI.10a)}$$

$$= 2 \sum_{i\varepsilon c} h_i + 2h_{2e_y} + h_{2e_x} + h_{3e_x} + \sum_{i,j\varepsilon c} (2J_{ij} - K_{ij})$$

$$+ 2 \sum_{i\varepsilon c} (2J_{i,2e_y} - K_{i,2e_y}) + \sum_{j\varepsilon\{2e_x,3e_x\}} (2J_{2e_y,j} - K_{2e_y,j})$$

$$+ (2J_{2e_y,2e_y} - K_{2e_y,2e_y}) + \sum_{\substack{i\varepsilon c \\ j\varepsilon\{2e_x,3e_x\}}} (2J_{ij} - K_{ij}) +$$

$$(J_{2e_x,3e_x} - K_{2e_x,3e_y}) \qquad \text{(AI.10b)}$$

where c' denotes the set of all doubly occupied orbitals, specifically

$$c' = \{1a_1, 2a_1, 3a_1, 4a_1, 5a_1, 6a_1, 7a_1, 1e_x, 1e_y, 2e_y\} \qquad \text{(AI.11a)}$$

and o' denotes those orbitals which are singly occupied, that is

$$o' = \{3e_x, 3e_y\} \quad . \qquad \text{(AI.11b)}$$

In (AI.10b) we have explicitly separated out the contribution of the $2e_y$ orbital from the other doubly occupied orbitals and have defined

the set c as

$$c = c' - \{2e_y\} \tag{AI.11c}$$

Similarly the matrix element corresponding to D_2 is:

$$\begin{aligned}
\langle D_2|H|D_2\rangle = {} & 2\sum_{i\varepsilon c} h_i + 2h_{2e_x} + h_{2e_y} + h_{3e_y} \\
& + \sum_{i,j\varepsilon c} (2J_{ij} - K_{ij}) + 2\sum_{i\varepsilon c} (2J_{i,2e_x} - K_{i,2e_x}) \\
& + \sum_{j\varepsilon\{2e_y,3e_y\}} (2J_{2e_x,j} - K_{2e_x,j}) + (2J_{2e_x,2e_x} - K_{2e_x,2e_x}) \\
& + \sum_{\substack{i\varepsilon c \\ j\varepsilon\{2e_y,3e_y\}}} (2J_{ij} - K_{ij}) + (J_{2e_y 3e_y} - K_{2e_y,3e_y}).
\end{aligned} \tag{AI.12}$$

Using Eq. (AI.3) the energy functional for the $^3A_1$ state is given as

$$E = \frac{\langle D_1|H|D_1\rangle}{2} + \frac{\langle D_2|H|D_2\rangle}{2} + 2(-\tfrac{1}{2})\ (2e_x 2e_y||3e_x 3e_y) \tag{AI.13a}$$

$$\begin{aligned}
= {} & 2\sum_{i\varepsilon c} h_i + \tfrac{1}{2}(3h_{2e_x} + 3h_{2e_y} + h_{3e_x} + h_{3e_y}) \\
& + \sum_{i,j\varepsilon c} (2J_{i,j} - K_{ij}) + \tfrac{3}{2}\sum_{\substack{i\varepsilon c \\ k\varepsilon\{2e_x,2e_y\}}} (2J_{ij} - K_{ik}) \\
& + \tfrac{1}{2}\sum_{\substack{i\varepsilon c \\ k\varepsilon\{3e_x,3e_y\}}} (2J_{ik} - K_{ik}) + \tfrac{1}{2}\sum_{k,\ell\varepsilon\{2e_x,2e_y\}} (2J_{k,\ell} - K_{k,\ell})
\end{aligned} \tag{AI.13b}$$

$$+ \frac{1}{2} (J_{2e_x,3e_x} + J_{2e_y,3e_y} + 2J_{2e_x,3e_y} + 2J_{2e_y,3e_x}$$

$$- (K_{2e_x,3e_x} + K_{2e_y,3e_y} + K_{2e_x3e_y} + K_{2e_y,3e_x}))$$

$$- (2e_x2e_y||3e_x3e_y) \quad .$$

The matrices $\underset{\approx}{a}$ and $\underset{\approx}{b}$ and the vector $\underset{\approx}{f}$ are then determined by comparison of (AI.13b) with Eq. (15) of Section II. Note that various choices of the $\underset{\approx}{a}$ and $\underset{\approx}{b}$ matrices are consistent with Eq. (AI.13b) and the final term in Eq. (AI.13b) cannot be expressed in terms of matrix elements of J and K operators.

Finally, we observe that it is possible to group the orbitals of the previous equation into classes such that for all i', $i \in I^{th}$ class and for all $j' \in J^{th}$ class the following equations hold for all I, J

(i) $a_{ij} = a_{i'j'}$ (AI.14a)

(ii) $b_{ij} = b_{i'j'}$ (AI.14b)

(iii) $f_i = f_{i'}$. (AI.14c)

Thus the energy functional for this case can be summarized as two 5 x 5 matrices, one 5 x 1 matrix and one additional integral. Table XI presents these matrices along with the corresponding partitioning of the orbitals into classes, for the $^3A_1$ and ^3E_x energy functionals.

The energy functionals for the six remaining states are summarized in Tables XII - XIV.

APPENDIX II

$$\text{Let } \chi_{3_E} = \frac{1}{2}\left(\chi_{3_{E_x}} + \chi_{3_{E_y}}\right) \tag{AII.1}$$

where $\chi_{3_{E_x}}$ and $\chi_{3_{E_y}}$ are given by Eqs. (9a) and (9b) of Section II respectively. The energy functional corresponding to χ_{3_E} is given by

$$\begin{aligned} E_{3_E} \equiv \langle\chi_{3_E}|H|\chi_{3_E}\rangle &= \frac{1}{2}\langle\chi_{3_{E_x}} + \chi_{3_{E_y}}|H|\chi_{3_{E_x}} + \chi_{3_{E_y}}\rangle \\ &= \frac{1}{2}\left(\langle\chi_{3_{E_x}}|H|\chi_{3_{E_x}}\rangle + \langle\chi_{3_{E_y}}|H|\chi_{3_{E_y}}\rangle\right) \quad . \end{aligned} \tag{AII.2}$$

since H is a scalar operator. The required matrix elements are evaluated by the methods of Appendix I and can be seen from Tables XI and XII to be

$$\begin{aligned} \langle\chi_{3_{E_x}}|H|\chi_{3_{E_x}}\rangle = {} & 2\sum_{i\varepsilon c} h_i + \frac{1}{2}(3h_{2e_x} + 3h_{2e_y} + h_{3e_x} + h_{3e_y}) \\ & + \sum_{i,j\varepsilon c}(2J_{ij} - K_{ij}) + \frac{3}{2}\sum_{\substack{i\varepsilon c \\ k\varepsilon\{2e_x,2e_y\}}}(2J_{ik} - K_{ik}) \\ & + \frac{1}{2}\sum_{\substack{i\varepsilon c \\ \ell\varepsilon\{3e_x,3e_y\}}}(2J_{i\ell} - K_{i\ell}) + \frac{1}{2}\sum_{k,\ell\varepsilon\{2e_x,2e_y\}}(2J_{k\ell} - K_{k\ell}) \\ & + \frac{1}{2}\left(J_{2e_x,3e_x} + J_{2e_y,3e_y} + 2J_{2e_x,3e_y} + 2J_{2e_y,3e_x}\right. \\ & \left. - (K_{2e_x,3e_x} + K_{2e_y,3e_y} + K_{2e_x,3e_y} + K_{2e_y,3e_x})\right) \end{aligned} \tag{AII.3a}$$

$$+ (2e_x 2e_y || 3e_x 3e_y)$$

$$\langle \chi_{3_{E_y}} | H | \chi_{3_{E_y}} \rangle = \sum_{i\varepsilon c} h_i + \frac{1}{2} (3h_{2x} + 3h_{2y} + h_{3x} + h_{3y})$$

$$+ \sum_{i,j\varepsilon c} (2J_{ij} - K_{ij}) + \frac{3}{2} \sum_{\substack{i\varepsilon c \\ k\varepsilon\{2e_x, 2e_y\}}} (2J_{ij} - K_{ij}) + \frac{1}{2} \sum_{\substack{i\varepsilon c \\ k\varepsilon\{3e_x, 3e_y\}}} (2J_{ik} - K_{ik})$$

$$+ \frac{1}{2} \sum_{k,\ell\varepsilon\{2e_x, 2e_y\}} (2J_{k,\ell} - K_{k,\ell})$$

$$+ \frac{1}{2} (J_{2e_x, 3e_y} + J_{2e_y, 3e_x} + 2J_{2e_y, 3e_y} + 2J_{2e_x, 3e_x}$$

$$- (K_{2e_x, 3e_y} + K_{2e_y, 3e_x} + K_{2e_y, 3e_y} + K_{2e_x, 3e_x}))$$

$$- (2e_x 2e_y || 3e_x 3e_y)$$

where the set c is as defined in Appendix I.

Inserting (AII3.a) and (AII3.b) into (AII.2) gives

$$E_{3E} = 2 \sum_{i\varepsilon c} h_i + \frac{1}{2} (3h_{2e_x} + 3h_{2e_y} + h_{3e_x} + h_{3e_y}) + \sum_{i,j\varepsilon c} (2J_{ij} - K_{ij})$$

$$+ \frac{3}{2} \sum_{\substack{i\varepsilon c \\ k\varepsilon\{2e_x, 2e_y\}}} (2J_{ik} - K_{ik}) + \frac{1}{2} \sum_{\substack{i\varepsilon c \\ k\varepsilon\{3e_x, 3e_y\}}} (2J_{ik} - K_{ik})$$

$$+ \frac{1}{4} \sum_{\substack{k\varepsilon\{2e_x, 2e_y\} \\ \ell\varepsilon\{3e_x, 3e_y\}}} (3J_{k,\ell} - 2K_{k,\ell}) \qquad \text{(AII.4)}$$

Thus the energy functional corresponding to χ_{3_E} has the form of Eq. (15) of Section II. It is summarized in Table XV in the matrix form discussed in Appendix I.

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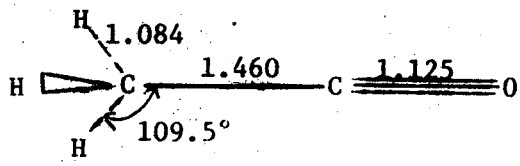
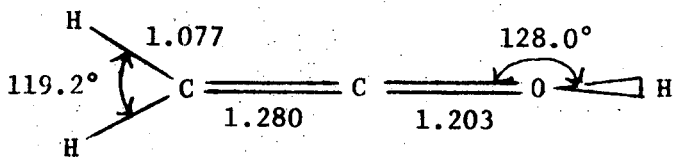
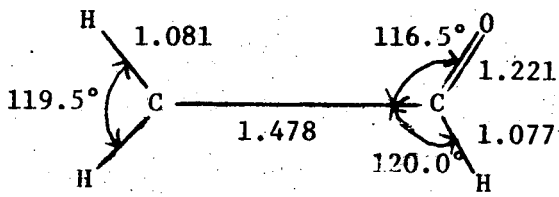
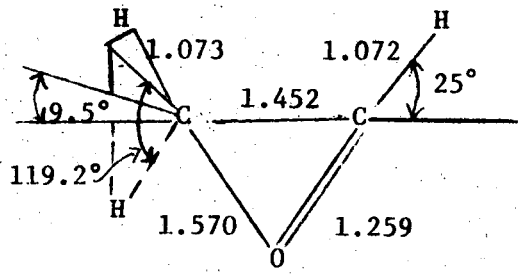
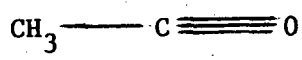
TABLE I. Ground State Geometries

	Symmetry	E(SCF)
	C_{3v}	-151.993808
	C_s	-151.935277
	C_s	-151.891656
	C_s	-151.883025

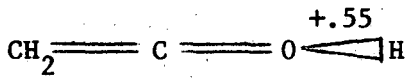
All distances in Å

Energies in Hartrees

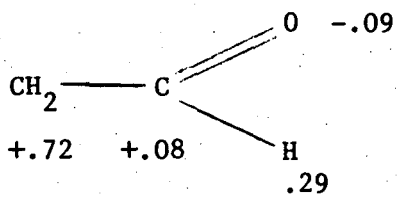
TABLE II. Charge Distributions



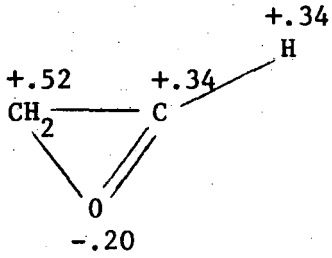
+.37	+.60	+.02	($^1A_1$:$7a^2$ $2e^4$)
+.40	+.57	+.03	(^3E:$7a^2$ $2e^3$ 3e)
+.45	+.59	-.04	(^3E:7a $2e^4$ 3e)



+.26 +.56 -.37 (^1A)



(^1A)



(^1A)

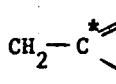
TABLE III. $CH_3-C^{*}\equiv O$ $1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1e^4 2e^4$ $^1A_1$

Orbital	Orbital Energy	s/p Populations C^*	O	C	H	H	H
$1a_1$	-20.9981	0.00	1.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
$2a_1$	-11.7528	1.00	0.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
$3a_1$	-11.5453	0.00	0.00	1.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
$4a_1$	-1.8620	0.31	0.61	0.01	0.00	0.00	0.00
		0.18	0.07	0.00	0.00	0.00	0.00
$5a_1$	-1.3455	0.12	0.01	0.62	0.03	0.03	0.03
		0.14	0.01	0.02	0.00	0.00	0.00
$6a_1$	-1.0690	0.16	0.25	0.06	0.02	0.02	0.02
		0.02	0.43	0.03	0.00	0.00	0.00
$7a_1$	-.9644	0.10	0.04	0.08	0.05	0.05	0.05
		0.22	0.13	0.30	0.00	0.00	0.00
$1e_x$	-.9614	0.00	0.00	0.00	0.04	0.01	0.01
		0.30	0.51	0.12	0.00	0.00	0.00
$2e_x$	-.8457	0.00	0.00	0.00	0.20	0.05	0.05
		0.01	0.21	0.48	0.00	0.00	0.00
$1e_y$	-.9614	0.00	0.00	0.00	0.00	0.03	0.03
		0.30	0.51	0.12	0.00	0.00	0.00
$2e_y$	-.8457	0.00	0.00	0.00	0.00	0.15	0.15
		0.01	0.21	0.48	0.00	0.00	0.00

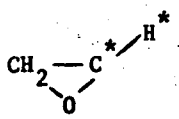
TABLE IV. $CH_2{=}C^*{=}O{-}H^*$ $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 8a'^2 9a'^2 1a''^2 2a''^2$ ^1A

s/p Populations

Orbital	Orbital Energy	C^*	O	H^*	C	H	H
1a'	-20.9453	0.00	1.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
2a'	-11.6856	1.00	0.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
3a'	-11.5354	0.00	0.00	0.00	1.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
4a'	-1.8131	0.10	0.73	0.02	0.00	0.00	0.00
		0.10	0.04	0.00	0.00	0.00	0.00
5a'	-1.3514	0.25	0.02	0.01	0.44	0.02	0.02
		0.12	0.06	0.00	0.05	0.00	0.00
6a'	-1.1958	0.04	0.04	0.16	0.07	0.01	0.01
		0.16	0.52	0.00	0.00	0.00	0.00
7a'	-.9775	0.05	0.05	0.01	0.06	0.05	0.05
		0.12	0.49	0.00	0.13	0.00	0.00
8a'	-.9486	0.04	0.02	0.00	0.10	0.09	0.09
		0.15	0.24	0.00	0.29	0.00	0.00
9a'	-.6690	0.00	0.01	0.02	0.00	0.00	0.00
		0.41	0.13	0.00	0.43	0.00	0.00
1a''	-.9451	0.00	0.00	0.00	0.00	0.04	0.04
		0.20	0.52	0.00	0.19	0.00	0.00
2a''	-.8478	0.00	0.00	0.00	0.00	0.12	0.12
		0.00	0.32	0.00	0.44	0.00	0.00

TABLE V.  $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 8a'^2 9a'^2 10a'^2 11a''^2 \; {}^1A$

Orbital	Orbital Energy	s/p Populations O	C*	H*	C	H	H
1a'	-20.8853	1.00	0.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
2a'	-11.6736	0.00	0.00	0.00	1.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
3a'	-11.6143	0.00	1.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
4a'	-1.7066	0.66	0.20	0.00	0.01	0.00	0.00
		0.06	0.07	0.00	0.01	0.00	0.00
5a'	-1.3213	0.06	0.10	0.00	0.62	0.05	0.05
		0.01	0.10	0.00	0.01	0.00	0.00
6a'	-1.0994	0.07	0.29	0.11	0.09	0.09	0.03
		0.07	0.09	0.00	0.16	0.00	0.00
7a'	-1.0007	0.02	0.00	0.05	0.01	0.01	0.15
		0.18	0.22	0.00	0.37	0.00	0.00
8a'	-.9417	0.05	0.01	0.01	0.00	0.13	0.01
		0.25	0.18	0.00	0.35	0.00	0.00
9a'	-.8927	0.07	0.01	0.07	0.00	0.06	0.09
		0.36	0.18	0.00	0.16	0.00	0.00
10a'	-.7360	0.00	0.01	0.11	0.01	0.01	0.01
		0.68	0.06	0.00	0.10	0.00	0.00
1a''	-.7912	0.00	0.00	0.00	0.00	0.00	0.00
		0.51	0.43	0.00	0.06	0.00	0.00

TABLE VI.  $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 7a'^2 8a'^2 9a'^2 1a''^2 2a''^2 \; {}^1A$

Orbital	Orbital Energy	O	C^*	H^*	C	H	H
		s Populations					
$1a'$	-20.9436	1.00	0.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
$2a'$	-11.7020	0.00	1.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
$3a'$	-11.6165	0.00	0.00	0.00	1.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
$4a'$	-1.8262	0.61	0.16	0.00	0.06	0.00	0.00
		0.07	0.08	0.00	0.03	0.00	0.00
$5a'$	-1.2605	0.16	0.05	0.00	0.50	0.04	0.04
		0.07	0.12	0.00	0.01	0.00	0.00
$6a'$	-1.1571	0.06	0.43	0.15	0.06	0.01	0.01
		0.15	0.09	0.00	0.03	0.00	0.00
$7a'$	-1.0120	0.08	0.00	0.10	0.07	0.05	0.05
		0.22	0.27	0.00	0.16	0.00	0.00
$8a'$	-.9105	0.02	0.01	0.03	0.02	0.05	0.05
		0.42	0.22	0.00	0.18	0.00	0.00
$9a'$	-.7744	0.01	0.01	0.05	0.00	0.00	0.00
		0.44	0.18	0.00	0.30	0.00	0.00
$1a''$	-.9786	0.00	0.00	0.00	0.00	0.08	0.08
		0.28	0.12	0.00	0.45	0.00	0.00
$2a''$	-.8084	0.00	0.00	0.00	0.00	0.10	0.10
		0.51	0.09	0.00	0.21	0.00	0.00

TABLE VII. CH_3CO^+ $1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1e^4 2e^3 3e$ ^3E

s/p Populations

	C1	O	C	H	H	H
$1a_1$	0.00	1.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00
$2a_1$	1.00	0.00	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00
$3a_1$	0.00	0.00	1.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00
$4a_1$	0.11	0.78	0.01	0.00	0.00	0.00
	0.06	0.05	0.00	0.00	0.00	0.00
$5a_1$	0.18	0.20	0.60	0.03	0.03	0.03
	0.10	0.01	0.02	0.00	0.00	0.00
$6a_1$	0.27	0.14	0.10	0.03	0.03	0.03
	0.02	0.34	0.05	0.00	0.00	0.00
$7a_1$	0.06	0.03	0.05	0.04	0.04	0.04
	0.26	0.22	0.27	0.00	0.00	0.00
$1e_x$	0.00	0.00	0.00	0.24	0.06	0.06
	0.05	0.00	0.59	0.00	0.00	0.00
$2e_x$	0.00	0.00	0.00	0.00	0.00	0.00
	0.09	0.90	0.00	0.00	0.00	0.00
$3e_x$	0.00	0.00	0.00	0.03	0.01	0.01
	0.86	0.09	0.00	0.00	0.00	0.00
$1e_y$	0.00	0.00	0.00	0.00	0.18	0.18
	0.05	0.00	0.59	0.00	0.00	0.00
$2e_y$	0.00	0.00	0.00	0.00	0.00	0.00
	0.09	0.90	0.00	0.00	0.00	0.00
$3e_y$	0.00	0.00	0.00	0.00	0.02	0.02
	0.86	0.09	0.01	0.00	0.00	0.00

TABLE VIII

$$CH_3CO^+ \rightarrow CH_3^+ + CO$$

$$\Delta R = R_{C-C} - 2.759 \text{ bohrs}$$

$$\chi = \alpha\, A\, 1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1e^4 2e^4 - \beta\, A\, 1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 8a_1^2 1e^4 2e^4$$

ΔR (bohrs)

	0	1	3	6	10	100
θ_{H-C-C}	109.5	99.0	90.0	90.0	90.0	90.0
Q_{CH_3}	+ 0.37	0.61	0.84	+1.0	+1.0	+1.0
α	0.997	0.994	0.997	0.998	0.998	0.998
$E_{(kcal)}$	0.	22.8	48.6	56.6	57.8	58.1

TABLE IX. CH_3CO^+ Geometries

Electron Occupancy	State	C-H	C-C	C-O	∢HCC	Energy
$7a_1^2 2e^4$	$^1A_1$	1.084	1.460	1.125	109.5	-151.993808
$7a_1^2 2e^3 3e$	^3E	1.086	1.475	1.350	109.5	-151.804622
$7a_1^1 2e^4 3e$	^3E	1.082	1.523	1.263	107.0	-151.684239

Energies in Hartrees

Bond distances in Angstroms

TABLE X. Electronic States of CH_3CO^+ and CO

CH_3CO^+ C_{3v}				CO $C_{\infty v}$				
Electron Occupancy	State	R_{CO} (Å)	$E_{(calc)}$ (eV)	$E_{(calc)}$ (eV)	$E_{(exp)}$ (eV)	R_{CO} (Å)	State	Principal Electron Occupancy
$7a_1^2 2e^4$	$^1A_1$	1.13	0	0	0	1.13	$^1\Sigma^+$	$5\sigma^2 1\pi^4$
$7a_1^2 2e^3 3e$	$^3A_1$	1.35	4.65	4.65	6.92	1.35	$^3\Sigma^+$	$5\sigma^2 1\pi^3 2\pi$
$7a_1^2 2e^3 3e$	^3E	1.35	5.14	5.31	7.58	1.37	$^3\Delta$	$5\sigma^2 1\pi^3 2\pi$
$7a_1^2 2e^3 3e$	$^3A_2$	1.35	5.63	5.69	7.96	1.38	$^3\Sigma^-$	$5\sigma^2 1\pi^3 2\pi$
$7a_1^2 2e^3 3e$	$^1A_2$	1.35	5.64	5.80	8.07	1.39	$^1\Sigma^-$	$5\sigma^2 1\pi^3 2\pi$
$7a_1^2 2e^3 3e$	^1E	1.35	5.89	5.91	8.18	1.40	$^1\Delta$	$5\sigma^2 1\pi^3 2\pi$
$7a_1^2 2e^3 3e$	$^1A_1$	1.35	12.31				$^1\Sigma^+$	
$7a_1^2 2e^4 3e$	^3E	1.26	8.42		6.04	1.21	$^3\pi$	$5\sigma 1\pi^4 2\pi$

Note: The method of calculation requires R_{CO} to remain fixed for all states arising from $7a_1^2 2e^3 3e$ occupancy.

TABLE XI. $^3A_1$, ^3E_x Energy Functionals

Classes: 1 = $\{1a_1, 2a_1, 3a_1, 4a_1, 5a_1, 6a_1, 7a_1, 1e_x, 1e_y\}$

2 = $\{2e_x\}$

3 = $\{2e_y\}$

4 = $\{3e_x\}$

5 = $\{3e_y\}$

$F^\dagger$ Vector (1.0 $^3/_4$ $^3/_4$ $^1/_4$ $^1/_4$)

A Matrix

1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
1.0	$^2/_3$	$^2/_3$	$^1/_6$	$^1/_3$
1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_6$
1.0	$^1/_2$	1.0	0.0	0.0
1.0	1.0	$^1/_2$	0.0	0.0

B Matrix

1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_3$
1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_3$
1.0	1.0	1.0	0.0	0.0
1.0	1.0	1.0	0.0	0.0

Additional Integral

$$\mp (2e_x 2e_y || 3e_x 3ey)$$

(- corresponds to $^3A_1$, + corresponds to ^3E_x)

TABLE XII. ^3E_y, $^3A_2$ Energy Functionals

Classes:	See Table XI				
$F^\dagger$ Vector					
A Matrix	1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_6$
	1.0	$^2/_3$	$^2/_3$	$^1/_6$	$^1/_3$
	1.0	1.0	$^1/_2$	0.0	0.0
	1.0	$^1/_2$	1.0	0.0	0.0
B Matrix	1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_3$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_3$
	1.0	1.0	1.0	0.0	0.0
	1.0	1.0	1.0	0.0	0.0

Additional Integral

$$\begin{matrix} - \\ + \end{matrix} (2e_x 2e_y || 3e_x 3e_y)$$

(- corresponds to ^3E_y, + corresponds to $^3A_2$)

TABLE XIII. $^1A_1$, ^1E_x Energy Functionals

Classes	See Table XI				
$F^\dagger$ Vector					
A Matrix	1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
	1.0	$^2/_3$	$^2/_3$	$^1/_6$	$^1/_3$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_6$
	1.0	$^1/_2$	1.0	0.0	0.0
	1.0	1.0	$^1/_2$	0.0	0.0
B Matrix	1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
	1.0	$^2/_3$	$^2/_3$	$-^1/_3$	$^1/_3$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$-^1/_3$
	1.0	-1.0	1.0	0.0	0.0
	1.0	1.0	-1.0	0.0	0.0

Additional Integrals

$$\pm\,(2(2e_x3e_x||2e_y3e_y) - (2e_x2e_y||3e_x3e_y))$$

(+ corresponds to $^1A_1$, - corresponds to ^1E_x)

TABLE XIV. ^1E_y, $^1A_2$ Energy Functionals

Classes $F^\dagger$ Vector	See Table XI				
A Matrix	1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$^1/_6$
	1.0	$^2/_3$	$^2/_3$	$^1/_6$	$^1/_3$
	1.0	1.0	$^1/_2$	0.0	0.0
	1.0	$^1/_2$	1.0	0.0	0.0
B Matrix	1.0	$^3/_4$	$^3/_4$	$^1/_4$	$^1/_4$
	1.0	$^2/_3$	$^2/_3$	$^1/_3$	$-^1/_3$
	1.0	$^2/_3$	$^2/_3$	$-^1/_3$	$^1/_3$
	1.0	1.0	-1.0	0.0	0.0
	1.0	-1.0	1.0	0.0	0.0

Additional Integrals

$$\pm(2(2e_x3e_y||3e_x2e_y) - (2e_x2e_y||3e_x3e_y))$$

(+ corresponds to ^1E_y, - corresponds to $^1A_2$)

TABLE XV. ^3E Energy Functional

Classes: 1 = $\{1a_1, 2a_1, 3a_1, 4a_1, 5a_1, 6a_1, 7a_1, 1e_x, 1e_y\}$

2 = $\{2e_x, 2e_y\}$

3 = $\{3e_x, 3e_y\}$

$F^\dagger$ Vector (1.0 $^3/_4$ $^1/_4$)

A Matrix

1.0	$^3/_4$	$^1/_4$
1.0	$^2/_3$	$^1/_4$
1.0	$^3/_4$	0.0

B Matrix

1.0	$^3/_4$	$^1/_4$
1.0	$^2/_3$	$^1/_3$
1.0	1.0	0.0

Additional Integrals

None

0 0 0 0 4 2 0 5 3 3 8

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