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# Vertical Excitation Energy to the Lowest $^1\pi\pi^*$ State of Acrolein

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**Abstract:** In acrolein the use of orthogonal orbital SCF procedures on the lowest $^1\pi\pi^*$ state results in a configuration which has a low energy but a high overlap with the ground-state wave function. Variationally correct nonorthogonal SCF procedures give a much higher energy estimate for this state. Configuration interaction calculations with the correct SCF orbitals in a basis set without Rydberg orbitals gives 7.52 eV for the best estimate of the excitation energy compared with the observed value of 6.5 eV.

## Introduction

Acrolein $CH_2{=}CH{-}CH{=}O$ is a molecule with interacting ethylenic and carbonyl chromophores. In a recent paper in this journal, Dykstra reported extensive SCF calculations on several excited states of acrolein.[1] This was followed by a CI calculation for the lowest states of symmetry different from the ground state.[2] While most of the results in these papers seem correct, the ΔSCF results for the lowest $^1A'$ excited state produced energies much lower than CI results by other workers.[3,4] On the basis of these calculations, Dykstra concluded[1] that acrolein has a low-energy (3.52 eV) $^1\pi\pi^*$ excited state of the form $\cdot CH_2{-}CH{=}CH{-}O\cdot$, although he later recognized that there might be some problem with this result because the SCF wave functions for the excited state and ground state have nonzero overlap.[2]

Dykstra's calculations were performed by minimizing the energy subject to the constraint that $\pi$ and $\pi^*$ be orthogonal. We show here that this low energy is a rather extreme example of the well-known inapplicability of this SCF procedure to singlet states where both open shell orbitals are of the same symmetry.

## Procedure

Dunning's[5] [5s,3p] contraction of Huzinaga's[6] (9s,5p) Cartesian Gaussian basis plus a (2s,p,d) set of Rydberg functions[7] centered midway between the central carbon atoms were used. SCF calculations were done on the ground state and the lowest $^1\pi\pi^*$ state of acrolein at its equilibrium ground-state geometry.[8] At this geometry, the molecule has $C_s$ symmetry and both of these states are $^1A'$.

The $^1\pi\pi^*$ state energy was calculated by two different SCF procedures. One used the normal SCF procedure where the singly occupied orbitals are constrained to be orthogonal and the absolute minimum in the energy is sought subject to this constraint.[9] This procedure is correct for finding the lowest energy state of any symmetry except $^1A'$. The other method used the nonorthogonal SCF program developed by Davidson and Stenkamp.[10] In this procedure, the orbitals are not constrained to be orthogonal, but the $\pi^*$ orbital is constrained to be the second eigenfunction of its Fock operator.

Configuration interaction calculations were carried out by using all single replacements and selected double replacements from the dominant configuration. About 6000 configurations were included in most calculations. For the nonorthogonal SCF procedure, symmetrically orthogonalized $\pi$ and $\pi^*$ orbitals were used for the CI. It is easily shown that symmetrical orthogonalization leads to the pair of orbitals u and v for which the $^1uv$ configuration has maximum overlap with the nonorthogonal SCF function and the contribution from the $u^2$ and $v^2$ configurations is minimum.[11]

## Results

The energies from these calculations are summarized in Table I. The orthogonal SCF calculation gave a $\Delta E_{SCF}$ of 3.42

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**Table I.** Energies of Acrolein

| | ground state | nonorthogonal | | orthogonal | |
|---|---|---|---|---|---|
| | $E$, au | $E$ | $\Delta E$, eV[a] | $E$ | $\Delta E$, eV[a] |
| SCF | −190.7160 | −190.4673 | 6.76 | −190.5904 | 3.42 |
| Cl, root 1 | −190.9407 | −190.7712 | 4.61 | −190.9023 | 1.04 |
| Cl, root 2 | | −190.6642 | 7.52 | −190.5249 | 11.31 |

[a] Energy relative to the corresponding ground state calculation.

eV for the excitation energy in close agreement with the 3.52-eV value reported by Dykstra. The nonorthogonal SCF calculation, on the other hand, gave a $\Delta E_{\mathrm{SCF}}$ of 6.76 eV.

With orbitals for the nonorthogonal SCF calculation, the lowest root of the CI matrix is predominantly $\pi^2$ even though the energy is 4.61 eV above the CI energy using the ground state orbitals. The second root of the CI matrix is mostly the $^1\pi\pi^*$ configuration and lies 7.52 eV above the best ground-state calculation. The $^1\pi\pi^*$ state is experimentally observed[12] as a broad structureless band with an intensity maximum at 6.5 eV. This peak is undoubtedly a mixture of Rydberg and $^1\pi\pi^*$ transitions. The value calculated here is about 1 eV above the observed value. Such an error is normal because a correct prediction of $^1\pi\pi^*$ states requires a good description of valence-Rydberg mixing and a laborious recovery of correlation energy.[13]

The CI calculations using the orbitals from the orthogonal SCF calculation gave decidedly different results. The SCF configuration had a coefficient of 0.88 in the *lowest* root of the CI matrix and the lowest energy was only 1.04 eV above the best ground-state calculation. Root 2 of the CI matrix was 11.31 eV above the best ground state and did not contain much of the $^1\pi\pi^*$ configuration.

## Discussion

Excited state SCF procedures for open-shell singlets of the same symmetry as the ground state have received much attention in the simple context of the 1s2s $^1$S state of helium. In this context, it has been amply demonstrated that the nonorthogonal procedure is the correct one.

In order to show that a procedure gives an upper bound to an excited state, one must use one of the two variational theorems for excited states. The first of these is that any function which is orthogonal to an exact ground state gives an upper bound to the second state.[14] The other is that any function which occurs as the second root of a linear variation CI matrix is an upper bound to the second state.[15] Sharma and Coulson[16] analyzed the 1s2s $^1$S state of helium and concluded that, with orthogonal 1s and 2s orbitals, orthogonality to the ground state (here taken to be 1s$^2$ with a ground state 1s orbital) could not be established. With nonorthogonal orbitals, orthogonality of the ground and excited state wave functions through first order was shown. They concluded that orthogonality held for all orders so that the excited state SCF procedure gave an upper bound by the first variational theorem. Cohen and Dalgarno[17] showed that, in fact, nonorthogonality entered in second order so this "proof" was incorrect.

Nonorthogonal functions were computed by Trefftz et al.,[18] and by Davidson[19] for the lsns $^1$S sequence of helium. Davidson[19] gave an alternative proof of the variational theorem by showing that, if a CI matrix were constructed by using the lower energy virtual orbitals of the Fock operator for the ns orbital, then one of the CI eigenvalues would be the lsns SCF energy. Unfortunately the matrix elements of this CI matrix were incorrectly evaluated in this "proof" (orthogonality of the lsks configurations was assumed incorrectly).

More recently Davidson and co-workers[11,13,20] have applied the nonorthogonal SCF procedure to studies of $^1\pi\pi^*$ states of amides and carbonyls. More importantly, Davidson and Stenkamp[10] have given a correct proof that this procedure gives an upper bound to the excited state energy. Basically this proof consists of examining the nonorthogonal CI matrix formed from configurations like lsks where the ks orbitals occur as eigenfunctions of the Fock matrix for the ns orbital. It can be shown that the lsns $^1$S SCF energy occurs exactly as one of the eigenvalues of this CI problem. Consequently the nonorthogonal SCF procedure for $^1\pi\pi^*$ produces an upper bound to the second $^1$A′ state.

No such bound holds for the orthogonal SCF procedure. If in fact, however, the optimal $\pi$ orbital in the $^1\pi\pi^*$ calculation is nearly the same as the optimal $\pi$ orbital in the ground state (as is usual), then the overlap of the two configurations is small and so is the interaction matrix element. In this case a 2 × 2 CI calculation would give a second eigenvalue only a little higher than the excited state SCF energy. This is the situation for the 1s2s states of helium and many molecules.

If the optimal $\pi$ orbital in the orthogonal procedure for the $^1\pi\pi^*$ should turn out to be very different from the ground-state $\pi$ orbital, very large effects could be noticed, and, in fact, the orthogonal calculation could collapse to a poor approximation to the ground state. Acrolein presents an example of just such an effect. Dykstra indicated that the wave function from his calculation corresponds to the biradical $\cdot CH_2{-}CH{=}CH{-}O\cdot$. In the context of semiempirical valence bond theory (with neglect of two-center overlap), this configuration has an overlap of 0.5 with the configuration $CH_2{=}CH{-}CH{=}O$. Consequently, it contains a large amount of ground state character. It is also clear in such a description that the half-filled $\pi$ MO in the biradical is very different from the highest doubly occupied MO of the ground state. Consequently, his $^1\pi\pi^*$ SCF energy must be regarded as merely a poor approximation to the ground state. The nonorthogonal calculation, by the way, gave the biradical $\cdot CH_2{-}\dot{C}H{-}C{=}O$ as the excited state which is reasonable since the V state of ethylene lies several volts below the V state of formaldehyde.

These conclusions regarding the orthogonal SCF results are verified by the CI calculations. Use of these orbitals gave a CI matrix whose *lowest* root was predominantly the $^1\pi\pi^*$ configuration. This is further evidence that this configuration is an approximation to the ground state. The nonorthogonal SCF orbitals (with $\pi$ and $\pi^*$ symmetrically orthogonalized) gave a CI matrix whose *second* root was largely $^1\pi\pi^*$ verifying the essential correctness of this procedure.

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# Collisional Activation and Theoretical Studies of Gaseous $CSH_3^+$ Ions[1,2]

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**Abstract:** Collisional activation mass spectra of *m/z* 47 ions from a variety of sulfur-containing compounds demonstrate that both the protonated thioformaldehyde, $H_2C{=}SH^+$ (a), and thiomethoxy, $H_3C{-}S^+$ (b), ion structures are stable (lifetimes $>10^{-5}$ s). Formation of a occurs by $\alpha$ cleavage from thiols, as well as by low-energy anchimeric cleavage from methyl sulfides and by rearrangement of b at higher energies from methyl sulfides. The more stable isomer is indicated by CA to be a, in contrast to previously published thermochemical data. Ab initio calculations indicate that b is a triplet ion; empirical corrections allowing for neglect of correlation are necessary to give heat of formation values of a and b (205 and 215 kcal/mol, respectively) consistent with the experimental results. The activation energy for the rearrangement b → a is substantial (~40 kcal/mol).

## Introduction

A problem of long-standing interest in organic chemistry has been the difference in behavior between oxygen and sulfur. Based on solution-phase studies it has generally been accepted that oxygen is the more effective at stabilizing adjacent carbocation centers, while sulfur more effectively stabilizes carbanions and radicals or radical-like photoexcited states.[3] The major reasons for this trend, it has been argued, are the superior $\pi$-donating ability of oxygen vs. the $\pi$-accepting ability of sulfur, the latter attributed to $d\pi$-$p\pi$ overlap.[3,4] These conclusions have recently been questioned on the basis of theoretical studies,[5,6] which indicate sulfur to be as effective as oxygen in stabilizing cations,[5] and show that interactions involving d functions on sulfur are energetically less important than the greater polarizability associated with its larger, more diffuse orbitals.[6] A recent paper by Caserio and co-workers reviews these arguments.[7]

A number of gas-phase studies involving sulfur-containing positive ions have provided additional information,[7-16] but results have not led to a consistent interpretation. The fragmentation of $HOCH_2CH_2SH^{+\cdot}$ yields a higher abundance of $H_2C{=}SH^+$ (a) than of $H_2C{=}OH^+$,[8] supporting the theoretical conclusion[5a] that a is better stabilized by $\pi$ interaction. Similarly, recent ion cyclotron resonance studies[7] show that gas-phase formation from $CH_3YCH_2Cl^{+\cdot}$ of $CH_3SCH_2^+$ is preferred over that of $CH_3OCH_2^+$. Further support is provided by the observation that gaseous thioalkoxide ($R_2CH{-}S^+$) isomers of $C_2H_5S^+$ and $C_3H_7S^+$ ions rearrange rapidly to the more stable protonated thiocarbonyl structures $R_2C{=}SH^+$.[9] On the other hand, appearance potential studies of $CSH_3^+$ [11-16] indicate the $H_3C{-}S^+$ (b) structure to be as[11] or more[12] stable than a, in strong contrast to the situation regarding the oxygen analogues, in which there is little doubt that the $H_2C{=}OH^+$ structure is significantly more stable than other isomers.[17,18]

Combined experimental and theoretical investigations of $CSH_3^+$ and $COH_3^+$ are reported in this and the accompanying paper,[18] respectively. Collisional activation (CA) mass spectrometry[19] is used to distinguish between a and b formed under various conditions and ab initio molecular orbital theory to obtain detailed geometries and energies for these and related ions. The results indicate that the most stable form of $CSH_3^+$ is a, ~10 kcal/mol more stable than the triplet b.

## Experimental Section

CA measurements of *m/z* 47 were made as described previously[9,19] on a computerized double-focusing mass spectrometer of reversed geometry using 7.8-kV accelerating potential and 150 °C ion source temperature. Each spectrum (Table I) is the computer-averaged composite of at least 16 scans. Additional peaks present but not used were *m/z* 45 and 46, also formed by metastable ion decomposition; *m/z* 44, a large peak (~five times greater than *m/z* 33) whose abundance is independent of the mode of formation; *m/e* 34, which originates in part from $^{34}SCH^+$; and *m/z* 23.5 ($CSH_3^{2+}$, weak, very sharp, and of poor reproducibility). Standard deviations, estimated from several separate runs on methyl sulfide, are the larger of ±7% relative or ±0.5% absolute (greater for low-energy ionization). Mixture analysis was based on the *m/z* 15:14 ratio. $CH_3SD$ was prepared from $CH_3SH$ by exchange with $D_2O$ in the inlet system; the *m/z* 49:48 from low electron-energy ionization indicated ~92% isotopic purity. Other samples were obtained commercially.

Molecular orbital calculations were carried out using the GAUSSIAN 70 series of computer programs.[20] The minimal STO-3G basis set[21] was used for full geometry optimization of each structure, followed by single calculations with the 4-31G basis[22] at STO-3G geometries. In some cases further optimization was carried out with the 4-31G basis. Calculations of open-shell species employed the UHF procedure of Pople and Nesbet.[23] General discussions of the methodology are given by Pople;[24] for an evaluation of the accuracy of STO-3G and 4-31G calculated properties involving second-row elements (Na-Cl) see Collins et al.[25]

## Experimental Results and Discussion

**Collisional Activation Spectra.** In the CA spectra of *m/z* 47 ions from a variety of precursors (Table I) two patterns are evident. The spectrum assigned to protonated thioformaldehyde, $H_2C{=}SH^+$ (a), is that found for the thiols $RCH_2SH$ which should give a by R loss via $\alpha$ cleavage;[9] spectra identical within experimental error are found for R = H, $CH_3$, *n*-$C_3H_7$,

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