σ and π Electronic Structures in the Ground, Triplet, and Ionic States of Ethylene

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Abstract: The ground, lowest triplet, and π-ionic states of ethylene have been studied by the LCAO SCF MO method with an extended basis set. The triplet and ion were also studied *via* a π-only SCF procedure with fixed ground-state σ core. In all states the σ core has been subsequently transformed to localized orbital form. Expectation values of the electronic position operators were calculated for the localized σ orbitals as well as for the π orbitals in the various states. Rearrangement upon excitation to the triplet is almost entirely accounted for by π rearrangement alone, as shown by energy, population, and expectation value analysis. (There is some C–C σ overlap decrease in the triplet, but this does not affect energy and expectation values.) But similar analysis shows that π ionization involves substantial σ and π rearrangements which are not just localized in the C–C bond. Comparison of the results with previous studies of benzene and pyridine suggests that the fixed σ-core π-electron methods are valid for excitations to low-lying states in larger π-electron systems, contrary to recent speculation.

We shall consider in this paper the electronic structure of the π-electron molecule ethylene in its ground, first excited triplet, and lowest ionic states. This work has been particularly motivated by the π-electron approximation[2] and the consequent desire to study a simple π-electron molecule *via ab initio* quantum mechanical methods. Analyses of wave functions obtained from the nonempirical LCAO SCF MO model[3] will be given. We shall examine the σ and π electronic rearrangement from the ground state to the triplet and ion, as well as the effects of using a common σ core for all three states. In addition to energy and population analysis[4] considerations, we shall relate our study to simple "textbook" bonding concepts by examining σ cores which have been transformed[5] to localized orbital form (C inner-shell, C–C, and C–H bonds). Calculations of expectation values of various electronic position operators for the π orbitals and the localized σ cores will thus exhibit directly the electronic rearrangement for the different states.

There have been several recent *ab initio* LCAO SCF MO calculations on ethylene. Dunning, Hunt, and Goddard (DHG)[6a] summarize these results and their own extensive direct *ab initio* calculations on both the ground and the first two excited states. The reader is referred to that paper and the paper of Schulman, Moskowitz, and Hollister[6b] for further references. We shall later discuss some results of DHG which are relevant to our work. Experimentally, ethylene has been studied exhaustively, and an excellent comprehensive review article has just appeared.[7]

The π-electron approximation has also been reviewed extensively.[2] Since it is really intended for semiempirical quantum chemistry, we emphasize that our study is related to examination of electronic rearrangement in different states, and to the basic assumption that a common σ core may be used for different π states. Griffith and Goodman[8] performed the first *ab initio* study of σ and π rearrangement by LCAO SCF MO calculations on ground, singly (π) excited, anionic, and cationic states of acetylene. They also summarized earlier semiempirical work. A minimum Slater orbital basis set was used, exponents being optimized for each of the states considered. They found nonnegligible rearrangement energies of 5.5 eV for anion and 0.9 eV for cation, and essentially none for the singly excited states. (Rearrangement is here defined as the difference between the state energy computed by appropriately occupying orbitals from the ground state, and that from the optimized wave functions.) Population analysis suggested a substantial σ rearrangement in cation and anion, and very little for excited states. Because of the limited basis set, π rearrangement occurred entirely because of exponent changes in the π basis functions. Use of a fixed σ core was not considered.

The ground state and two π ionic states of benzene were studied by Schulman and Moskowitz[9] with a contracted gaussian basis set somewhat larger than minimum size. From the population analysis they found a σ electron shift of about 0.05 electron from each H to its neighbor C in going from ground to either of the two ionic states. The total rearrangement energy was about 0.4 eV for both states. Clementi[10] similarly used a minimum contracted gaussian set for LCAO SCF studies of pyridine and its $^2A_2$ positive π ion. He analyzed the electronic rearrangement in detail *via* population analysis, and also found marked shifts of about 0.08–0.12 σ electron from H to the ring upon ionization. The total rearrangement energy was about 0.6 eV. Neither Schulman and Moskowitz nor

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(3) (a) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); (b) G. G. Hall, *Proc. Roy. Soc., Ser. A*, **205**, 541 (1951); (c) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 28 (1960).

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Clementi studied any of the neutral molecule excited states between ground state and ion, nor did they consider explicitly any assumptions of the π-electron approximation. On the other hand, the SCF MO ground state σ core in benzene was fixed in extensive configuration interaction calculations by Buenker, Whitten, and Petke (BWP)[11] on many excited states. Gilman and de Heer[12] did the same for an *ab initio* alternate molecular orbital calculation on the first triplet state. The triplet excitation energy was good in both calculations, suggesting that σ-core rearrangement was unimportant. Results for the higher excited states obtained by BWP are more ambiguous, since the limited π basis set may have been too inflexible.

Clementi[13] has subsequently concluded that "... the π-electron approximation is untenable ...." However, because he had studied only a highly excited state (an ion) of one molecule with essentially a minimum basis set, this conclusion should be considered preliminary and it is probably overly pessimistic. In the present paper we shall examine the more "gentle" π electronic excitation to the lowest triplet state, as well as the "severe" process of π ionization. These are obviously two extreme cases.

The Quantum Mechanical Calculations

The nuclear geometry was in all cases fixed at R(CH) = 2.0236, R(C–C) = 2.551 au, θ(HCH) = 117°, the molecule lying in the xy plane with the origin at the C–C midpoint and the x axis along the C–C line. With 1 au = 0.52917 Å, this geometry is close to the experimental one.[7] This orientation differs from standard recommendations,[7] but it is consistent with previous ethylene studies.[6] Basis functions for the LCAO calculations were taken from several sources: at each carbon the three groups of s gaussians found by Whitten[14] in atomic SCF calculations were used, the long-range group being decomposed into a two-term group and the single, most diffuse gaussian; the five-term gaussian 2p SCF AO's of Huzinaga[15] were likewise split into four-term and one-term (most diffuse) groups; further, d-type gaussians of x^2, y^2, z^2, xy, and xz dependence and exponents of 1.0 were used (the yz function was not used, since by symmetry it does not contribute to any states considered). At hydrogen we used the five-gaussian 1s function,[14] scaled by 1.414, and split into four-term and one-term (most diffuse) functions.

From open-shell atomic SCF calculations[3c] we found that the unsplit groups of Whitten and Huzinaga give a carbon atomic SCF energy of −37.6811 au, essentially "double ζ" quality.[14] This extended basis set (four s, six p, and five d functions at each carbon; two s functions at each hydrogen) should accordingly be a very good molecular basis set. Note that there are three π-type basis functions at each carbon (two $2p_z$ and the d_{xz}), and that the four other d functions at each carbon contribute to the σ molecular orbitals. All calculations (integral generations, SCF, localized orbital transformations, and properties) were done with the MOLE quantum chemistry system.[16]

Table I. Summary of Energy Results[a] for Ground, Triplet, and Ionic States of Ethylene from Full SCF Calculations

	Ground	Triplet	Ion
	Energies		
E_t	−78.0333	−77.9095	−77.7060
E_{el}	−111.3591	−111.2353	−111.0317
V_{nn}	33.3257	33.3257	33.3257
V_{ne}	−247.9595	−248.2374	−242.7349
V_{ee}	58.5435	58.5096	53.6857
T	78.0569	78.4926	78.0175
$-V/2T$	0.99985	0.99629	0.99800
	Orbital energies		
$1a_g$	−11.2325	−11.2124	−11.5757
$2a_g$	−1.0301	−1.0291	−1.3590
$3a_g$	−0.5862	−0.5856	−0.9097
$1b_{3u}$	−11.2309	−11.2111	−11.5741
$2b_{3u}$	−0.7997	−0.7950	−1.1049
$1b_{2u}$	−0.6455	−0.6457	−0.9618
$1b_{1g}$	−0.5137	−0.5093	−0.8163
$1b_{1u}$ (π)	−0.3692	−0.5132	−0.7427
$1b_{2g}$ (π^*)	+0.1471	−0.2361	

[a] In atomic units: 1 au = 27.21 eV.

Table I summarizes the energy results from the full SCF calculations on the three states. The notation for the orbital symmetries is based on the molecular orientation mentioned previously, and is consistent with previous calculations by others.[6] The energies of all three states are lower than any previously published results, due to the extended basis set we have used.

To examine the effect of the σ core we did SCF calculations on the triplet and ion in which the π orbitals only were iterated to self-consistency in the field of the fixed ground-state σ core. These results are summarized in Table II, along with the results obtained by using the solutions of the ground-state problem for the excited states (virtual π^* for triplet, Koopmans' theorem for ion).

Table II. Total Energies of Triplet and Ionic States Calculated with Ground-State Orbitals, π-Only SCF, and Full SCF (from Table I).

	Triplet	Ion
Ground-state orbitals	−77.8795	−77.6641
π-only SCF	−77.9079	−77.6760
Full SCF (Table I)	−77.9095	−77.7060

To examine the electronic rearrangement in more detail, we have done a population analysis of the full SCF wave functions for the three states, as displayed in Table III. Because the σ core is always doubly occupied in the three states, the minimum exchange energy criterion[5] can be applied straightforwardly to localize the σ orbitals. This is, of course, the sort of qualitative transformation most chemists intuitively use: localized σ bonds, delocalized π bonds. Table IV summarizes expectation values of various electronic position operators for the localized σ orbitals found in this way for the three states. Included in the same table are similar expectation values for the π and π^* orbitals from the ground state, as well as for full SCF and π-only SCF wave functions for the excited states.

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[15] S. Huzinaga, *ibid.*, **42**, 1293 (1965).

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Table III. Population Analysis on the Full SCF Wave Functions for the Ground, Triplet, and Ionic States of Ethylene

	Ground	Triplet	Ion
	Gross atomic		
C	6.3734	6.3892	6.0511
H	0.8133	0.8054	0.7245
	Overlap[a]		
C–H	0.8123	0.8231	0.7744
C′–C (σ)	0.6510	0.5574	0.5318
C′–C (π)	0.5435	0.2451	0.2468
C′–C(π*)		−0.9001	
C–H″	−0.0721	−0.0776	−0.0647
H–H′	−0.0398	−0.0333	−0.0316
H–H″	0.0024	0.0025	0.0024
H–H‴	−0.0051	−0.0043	−0.0065

[a] Notation:

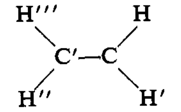

Table IV. Expectation Values[a] of Electronic Position Operators in Various States of Ethylene

	Ground	Triplet	Ion
	σ Core		
C–H[b] $\langle x\rangle$	0.7177	0.7086	0.6614
$\langle y\rangle$	1.1744	1.1789	1.1208
$\lvert r\rvert$	1.3763	1.3755	1.3014
θ	58° 34′	58° 59′	59° 27′
C–C $\langle x^2\rangle$	0.7742	0.7658	0.7368
$\langle y^2\rangle$	0.5838	0.5717	0.5467
$\langle z^2\rangle$	0.6042	0.5850	0.5596
C_{is} $\langle x^2\rangle$	1.6705	1.6707	1.6705
$\langle y^2\rangle$	0.0423	0.0424	0.0425
$\langle z^2\rangle$	0.0364	0.0364	0.0364
	π Orbitals		
Full SCF			
π $\langle x^2\rangle$	2.0805	2.0072	1.9331
$\langle y^2\rangle$	0.8891	0.7583	0.7430
$\langle z^2\rangle$	2.6673	2.2749	2.2290
π^* $\langle x^2\rangle$	10.1440	3.8381	
$\langle y^2\rangle$	2.6578	0.8925	
$\langle z^2\rangle$	7.9733	2.6774	
π-only SCF			
π $\langle x^2\rangle$		1.9989	1.8604
$\langle y^2\rangle$		0.7558	0.6740
$\langle z^2\rangle$		2.2673	2.0221
π^* $\langle x^2\rangle$		3.8287	
$\langle y^2\rangle$		0.8904	
$\langle z^2\rangle$		2.6713	

[a] In atomic units. First moments for C–H are with respect to C as origin. All second moments are with respect to C–C midpoint. [b] $|r| = [\langle x\rangle^2 + \langle y\rangle^2]^{1/2}$ = magnitude of electronic dipole moment. θ = angle of $|r|$ with x(C–C) axis; $\tan\theta = \langle y\rangle/\langle x\rangle$. The C–H internuclear line has a length of 2.0236, θ = 58° 30′.

Discussion

First we consider the ground state. The localized C–H bond orbitals have been discussed recently by one of us,[17] but we note here (*cf.* Table IV) that the average electronic dipole points almost exactly along the C–H internuclear line, lying about one-third of the way from H toward C. The C–C σ bond is nearly cylindrical (on the average) about the internuclear line, as judged from $\langle y^2\rangle$ and $\langle z^2\rangle$. The spatial distribution of the carbon inner-shell orbitals is essentially fixed for all three states.

From Table II we note that the π-only SCF accounts for almost all of the rearrangement energy (0.77 eV out of 0.82 eV) of excitation from ground state to triplet. Accordingly, the population analysis (Table III) and the electronic position properties (Table IV) show small rearrangement of the σ core based upon the full SCF wave functions for the two states. Furthermore, the spatial distributions of the π and π^* orbitals (Table IV) are nearly the same both for the full and the π-only SCF wave functions. There is a noted decrease in C–C σ overlap in the triplet relative to the ground state, but this does not show up in either energy or expectation value calculations. For this case, then, the use of a fixed σ core is an unimportant restriction: the fixed core assumption is "valid."

For the process of π ionization Table II shows that π-only SCF cannot account for the rearrangement: only about 30% of the energy (0.33 of 1.14 eV) is gained thereby. It is no surprise, then, that the full SCF wave functions show appreciable σ rearrangement upon π ionization. Though the carbons each lose formally 0.5 electron upon π ionization, a shift of about 0.09 electron from each hydrogen (Table III) means the net gross electron population shift at each carbon is just −0.32 electron. Table IV shows this shift nicely: the C–H bond dipole is contracted about 0.075 au, and changes direction by about +1° in the ionization process. The C–C σ bond also contracts somewhat. Note further from the expectation values in Table IV that the π-only SCF π orbitals are spatially rather different from the full SCF π orbitals. For π ionization, then, it is clear that one cannot usefully assume a fixed σ core: rearrangement is too great.

DHG[6a] found some interesting results pertinent to the present discussion. In their studies of the first excited singlet of ethylene they found a quite diffuse π^* orbital. Complete π-electron configuration interaction on the excited singlet in the field of the σ core from the excited singlet SCF gave an energy 0.62 eV lower than the similar calculation in which the ground-state σ core was used. Since the π^* orbital is so diffuse here, and π–π^* correlation so small (DHG found an energy lowering of 7×10^{-4} au owing to this configuration interaction), it is no surprise that our studies for the ion give a similar error of 0.81 eV in the ground-state σ core approximation.

Clearly one will have to take care in fixing the σ core to see whether the excited π states are "valence" or "ionic (Rydberg)" in nature.

It is worth noting that the error of the excitation energy is 1.24 eV (ΔE_{SCF} = 3.36, experiment[7] = 4.6 eV), while the ionization energy error is 1.60 eV (ΔE_{SCF} = 8.91, experimental[7] = 10.51 eV). This reflects the difference in correlation energy changes for the two different processes and is, of course, outside of the LCAO SCF MO model. Studies of these differences including electron correlation would be quite interesting.

Conclusion

In summary, we have found that only π-electron rearrangement is important for excitation from ground state to triplet state in ethylene, while both σ and π rearrangements are important in π ionization. Because ethylene is such a "small" π-electron molecule, we find for π ionization a rather larger rearrangement energy

[17] S. Rothenberg, manuscript in preparation.

(1.14 eV) than was found (with more limited basis sets) for π ionization of benzene[9] (0.4 eV) or pyridine[10] (0.6 eV). We therefore expect that π excitation to low-lying states in these (and other) larger π-electron systems will cause σ rearrangement of relatively less importance than the already small amount found in ethylene. This will then mean that one can indeed use the fixed core, π-electron approximation as a quantitatively accurate quantum chemical method for such problems (this is implicit in previous work[11,12]). It would be most interesting to see accurate *ab initio* calculations for larger π systems (*e.g.*, naphthalene) using the procedures we used for ethylene: it may be that for such large systems even π excitation to Rydberg states or π ionization would be moderately well represented with the fixed σ-core restriction.

Acknowledgment. M. E. S. acknowledges partial support of this work through a grant from the Petroleum Research Fund, administered by the American Chemical Society. We are also grateful to University Computing Company for a grant from the Chemical Applications Department, which enabled us to perform these calculations. Thanks are due Dr. R. Gilman for a preprint of his paper.[12]

Experimental and Theoretical Comparison of the Electronic Structures of Ethylene and Diborane

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Received January 17, 1970

Abstract: The high-resolution He(I) and He(II) photoelectron spectra of the isoelectronic molecules C_2H_4 and B_2H_6 are compared with each other and the results of near-Hartree–Fock calculations of their spectra using Koopmans' theorem. The agreement with experiment for the first six bands observed for each compound is very good, and lends considerable support to Pitzer's idea that the electronic structure of diborane is derived directly from that of ethylene, but with the $1b_{2u}$ π MO shifted below the first three σ MO's. The relevance of the photoelectron spectra of these molecules to their optical spectra is also demonstrated.

In the last 5 years, two techniques of electronic structure analysis, molecular SCF calculations using gaussian-type orbitals (GTO's) and high-resolution photoelectron spectroscopy, have proved to be of ever-increasing importance, especially when used in concert. In this study, these techniques are applied to the ethylene and diborane molecules, in an effort to trace experimentally and theoretically the correlation between the various orbitals of these two isoelectronic systems. A large number of calculations of the electronic structure of ethylene have already appeared,[2] of course, and the photoelectron spectrum up to 21 eV has been recorded and interpreted in terms of the latest of these calculations.[3] To this, we add the He(II) spectrum of ethylene, and the He(I) spectrum of ethylene-d_4. Nearly as much effort has been expended on theoretical work on diborane,[4] and to this we add a somewhat improved calculation, and the He(I) and He(II) photoelectron spectra.

Photoelectron spectra were recorded using a high-resolution, 127° spectrometer,[5] having a dc capillary discharge lamp operated to maximize the intensities of either the He(I) (21.21 eV) or the He(II) (40.8 eV) resonance line. Under the best conditions, the He(II) line is no more than $^1/_{50}$ as intense as that of He(I). Molecular orbital energies of ethylene and diborane in their established ground state geometries were calculated using the POLYATOM programs. The boron and carbon atom basic sets used here are those given in ref 6, except that the seven-term p set was split 5,2 rather than 4,3 as done in that reference. The hydrogen ls orbital is a five-term fit to a Slater orbital having an exponent of $(1.8)^{1/2}$.[7] Our past experience with such calculations strongly supports the idea that trustworthy estimates of valence shell ionization potentials can be obtained by empirically multiplying the Koopmans' theorem values by 0.92 for first row elements; the theoretical IP's reported here have been so treated. The total energies computed for ethylene and diborane were -78.0188 and -52.7758 au.

The experimental He(II) spectra and the theoretical IP's are compared in Figure 1, and the He(I) spectra showing the IP's up to 21 eV at a higher resolution are given in Figure 2. The lower resolution of the He(II)

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(1) (a) Bell Telephone Laboratories; (b) Ford Motor Company; (c) Rutgers University.

(2) See, for example, M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968); or A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

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