Interpretation of Open-Shell SCF Calculations on the T and V States of Ethylene

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Self-consistent field calculations are reported on (planar and perpendicular geometric conformers of) the lowest energy triplet and singlet (π, π^*) orbital configurations of ethylene, which are usually identified with the spectroscopic T and V states, respectively. For the planar conformation the calculation predicts a V state with the characteristics of a Rydberg state, but a T state of expected valence-shell character. The π^* orbital is much too large and the internuclear distance too small for the calculated V state, but are as expected for the T state. It is concluded that the calculated result for the supposed V state in the planar conformation is spurious due to the inadequacy of the Hartree–Fock single-configuration theory. The supposed V state here calculated may be identified with a Rydberg state which has been observed spectroscopically at $\sim$1.4 eV higher energy than the V state in the optical spectrum. For the perpendicular conformation, the calculations yield resonable results for both the T and V states. Calculations also have been carried out on a singlet (σ, π^*) state for planar ethylene; here the size of the π^* orbital is reasonable.

INTRODUCTION

The electronic spectrum of ethylene has been extensively studied both experimentally and theoretically. Merer and Mulliken[1] have given a comprehensive review of what is currently known experimentally about the ultraviolet absorption spectra and the excited states of ethylene. Some relevant aspects are briefly summarized below.

Three absorption systems have been identified in the wavelength range 3500–1560 Å.[2] The first is assigned as the T–N system and consists of a very weak progression of diffuse bands in the region 2700–3500 Å, peaking at an energy of about 4.6 eV. Starting around 2650 Å the absorption rises steeply, signalling the onset of the V–N system which consists of a long progression of broad, diffuse bands rising rapidly in intensity with decreasing wavelength and merging into a continuum which peaks broadly at $\sim$1620 Å (7.65 eV). This latter point may be considered the Franck–Condon maximum of the V–N transition. Beginning at about 1740 Å (7.1 eV) and superimposed on the underlying continuum are a set of fairly sharp bands which are easily identified as the $n=3$ member of a $\pi \rightarrow ns$ Rydberg series, π being the highest occupied molecular orbital (MO) in ethylene.

Spectroscopically, the V–N transition of ethylene is composed of a single progression of broad, diffuse bands, ostensibly resulting from excitation to coupled twisting and stretching vibrational modes in the upper state. In its equilibrium geometry, the molecule in the V state is apparently twisted with a 90° dihedral angle between CH$_2$ planes. The prediction of the positions and intensities of the bands for such an upper state is a difficult problem, but Merer and Mulliken[1,3] have shown that a model in which the twisting and stretching motions are coupled gives an excellent fit to the observed spectrum. Most convincingly, the model reproduces the observed difference in complexity between C_2H_4 and C_2D_4 spectra. From their analysis, Merer and Mulliken[1,3] are also able to deduce the equilibrium C–C bond distances in the V state for both the planar and perpendicular configurations.

The vibrational structure of the 1740-Å Rydberg transition has recently been examined in detail.[4] A vibrational analysis shows that the ethylene molecule is nonplanar at equilibrium in the upper electronic state with a C–C bond length of 1.41$\pm$0.01 Å and a dihedral twist angle $\sim$25°. This twist angle (as well as a potential barrier to inversion through the planar configuration of $\sim$280 cm^{-1}) had actually been predicted independently on theoretical grounds.[5] Based on the close similarity between the vibrational line frequencies, spacings, and intensities in the observed members of the $\pi \rightarrow ns$ Rydberg series and the first band in the ethylene photoelectron spectrum,[1,6,7] these geometric parameters are expected to be roughly appropriate to all Rydberg states leading up to the first ionization potential, as well as the ground state of the ethylene positive ion.[1,8,9]

With regard to Rydberg states it is necessary to have an operational definition of the term. From the orbital point of view[11] a Rydberg state is one in which the united atom (UA) representation is a sufficiently good approximation to the orbital character of the terminating MO such that the excitation energy to that state is found to be one member of a series of transitions that fit the atomlike (hydrogenic) Rydberg formula (in familiar notation),

$$\nu_n = \text{I.P.} - 13.605/(n-\delta)^2,$$

$$n = 3, 4, \cdots \infty \quad \text{for first-row atoms.} \quad (1)$$

The intimate relationship between the position of a Rydberg band (ν_n) and the ionization potential (I.P.) is to be noted. Experimentally, series of bands that fit

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the Rydberg formula have been recorded for many molecules,[12] including ethylene, which, as mentioned above, has the 1740-Å band as the $n=3$ member of an s-type ($\delta \sim 1$) Rydberg series.

There is another purely experimental diagnostic test for Rydbergs which reflects their spatially extended nature compared to non-Rydberg states. It has been variously reported[5,13,14] that well-identified Rydberg bands in the gas phase "disappear" in a dense medium, i.e., as a guest in a rare-gas matrix, neat or dissolved polycrystalline film, or under high pressure of an inert gas. Jortner and co-workers[15] have recently shown that in low-temperature rare-gas matrices, Rydberg states of guest organic molecules are actually shifted to substantially higher energy, but in mixed or pure crystals (or films) molecular Rydberg states are expected to be completely smeared out. More recently, Robin and Kuebler[16] have confirmed the pressure experiments. They find that modest (100–150 atm) pressures of an inert perturber gas cause no shift or broadening in the spectral features of non-Rydberg (valence shell)[11] transitions, whereas Rydberg transitions respond by broadening asymmetrically to the high-frequency side with only a very slight shift in wavelength of the absorption maximum. When applied to ethylene, by the above criteria the V–N band is valence shell and the 1740-Å band is a Rydberg.

Recently, Krauss and Mielczarek[17] and Miller[18] observed a dip in the angular dependence of the generalized oscillator strength in electron scattering experiments at an energy loss of 8.0 eV, from which, based on previous experience,[19] they conclude that the V state in ethylene has considerable Rydberg character. The observed minimum is attributed to the presence of radial nodes in certain MO's of the V state. In the simple MO description of the V state (see later) radial nodes are absent, whether the orbital character is pure Rydberg or valence shell. Presumably then, these radial nodes are introduced into the V state via configuration interaction with noded Rydberg states of the same symmetry but different electronic configuration.

If the V state itself were pure Rydberg, then it would be the first ($n=3$) member of a $\pi \rightarrow nd$ Rydberg series. In fact, Wilkinson[20] has identified the $n=4$ member of a $\pi \rightarrow nd_{\pi}$ Rydberg series, of the same symmetry as the V state, at 1370 Å (9.05 eV) with a quantum defect (δ) of 0.95 and r_e(C–C) = 1.406 Å.[21,22] Such a high value for the quantum defect of a d-type Rydberg series is characteristic of what Mulliken[11] has called "penetrating" Rydberg molecular orbitals, Rydberg MO's which can penetrate into core MO's of the same symmetry. Thus the valence-shell ("core") character of the V state is supported by Wilkinson's[20] assignment of the 1370-Å band in the optical spectrum of ethylene as $\pi \rightarrow 4d$. The united atom representation of the π^* MO in the V state as $3d$ has already been noted.[23]

In the simple orbital description of ethylene both the

T and V states arise from the excitation of an electron from a π molecular orbital to a π^* MO, where π and π^* are just the symmetric and antisymmetric combinations, respectively, of out-of-plane $2p$ atomic orbitals (AO's) on each carbon atom. The available parameters in the $2p\pi$ Slater-type orbitals, the exponents (ζ), are assumed to be the same in both the π and π^* combination of AO's. Vertical excitation energies to the (π, π^*) states are obtained by considering a planar excited state with a C–C bond distance of $\sim$1.34 Å, the equilibrium geometry of the ground state. In this way, Kaldor and Shavitt[10] calculate a $^1(\pi, \pi^*)$ vertical excitation energy of 13.20 eV in the nonempirical self-consistent field (SCF) approximation; in poor comparison with the experimental 7.65-eV value for the V–N transition. For $^3(\pi, \pi^*)$ an energy of 4.50 eV is calculated, to be compared with the experimental 4.6-eV value for the T–N transition.

An improved description of the excited states would be expected by using different orbital parameters for the $\pi(\zeta_u)$ and $\pi^*(\zeta_g)$ MO's, relaxing the pure atomic orbital origin of the carbon AO's to allow for differential orbital polarization and screening effects. This has been done by Huzinaga[24] using a π-electron Hamiltonian where the molecule is considered as consisting of 2 π electrons in the field of a σ-core skeleton, the effect of which is paramaterized. The very surprising result obtained is that a minimum in the energy of the $^1(\pi, \pi^*)$ state requires that the π^* MO be very diffuse. The optimum values obtained, $\zeta_u = 1.6$ and $\zeta_g = 0.2$, give an excitation energy of 6.97 eV. By comparison, the optimum free atomic orbital value is $\zeta = 1.6$. These results have been confirmed by a full nonempirical SCF calculation with configuration interaction where roughly the same optimized orbital parameters are obtained.[25]

Huzinaga[24] has also optimized the orbital parameters for the $^3(\pi, \pi^*)$ state for which he finds $\zeta_u = 1.4$, $\zeta_g = 1.2$, and a vertical excitation energy of 4.22 eV; here the π^* MO is not unusually diffuse. This great difference in spatial extension between the V and T states of ethylene is contrary to most previous assumptions.[5]

The most extensive nonempirical SCF–MO calculations on the (π, π^*) states of ethylene have been reported by Dunning et al.[26] using an atomic double-ζ basis of gaussian-type functions (GTF's) augmented in the π and π^* MO's by three successively diffuse $2p\pi$-type GTF's. In notation, it is now necessary to add a number prefix (sometimes represented by λ) to π and π^* since in the extended basis SCF calculation there is more than one of each type. With the molecule in the yz plane they report the values 42.08 and 2.74 (a.u.)^2 for the matrix element $\langle 1\pi^* \mid x^2 \mid 1\pi^* \rangle$ in the $^1(1\pi, 1\pi^*)$ and $^2(1\pi, 1\pi^*)$ states, respectively, with vertical excitation energies of 7.41 and 3.33 eV. Again the π^* orbital in the $^1(1\pi, 1\pi^*)$ state is found to be diffuse and very different from the π^* orbital in the

$^3(1\pi, 1\pi^*)$ state. The calculated excitation energy is also in good agreement with the position of the spectroscopic V–N band maximum.

At a similar level of approximation to that of Huzinaga's work,[24] Hansen,[27] with a valence bond wavefunction for the $^1(\pi, \pi^*)$ state of ethylene constructed from $2p\pi$ and $3d\pi$ atomic orbitals on the two carbon atoms, obtains a vertical excitation energy of 7.17 eV with optimum values for the parameters $\zeta(2p) = 1.55$ and $\zeta(3d) = 0.32$. This value of $\zeta(3d)$ is very close to the pure hydrogenic value $\zeta = \frac{1}{3}$, indicating that the wavefunction for the $^1(\pi, \pi^*)$ state contains a high degree of Rydberg character.

An analogous interpretation can be given to the MO results. Lefebvre-Brion, Moser, and Nesbet[28] had shown for diatomics, and it has also been found for ethylene,[15] formamide,[14,29] and water,[19,30] that augmenting the valence atomic orbital basis set with such diffuse-type basis functions as those used by Dunning et al.[26] leads to the construction of Rydberg states, i.e., series of states of a given symmetry can be found, with succeedingly more diffuse terminating MO's and with energies that fit the Rydberg formula, converging on the calculated ionization potential. Dunning et al.[26] report (frozen core) excitation energies of 7.41, 8.11, and 8.78 eV for the states $^1(1\pi, \lambda\pi^*)$, $\lambda = 1, 2, 3$, respectively. This series can, in fact, be fitted to the Rydberg formula, Eq. (1), with $\delta \sim 0$ and $n = 4, 3, 5$, leading up to a calculated ionization potential of ~ 9.0 eV. As will be reported subsequently in this paper, we find $\Delta E_{\text{SCF}}(\text{C}_2\text{H}_4{}^+ - \text{C}_2\text{H}_4) = 9.04$ eV, with a basis set similar to that used by Dunning et al.[26] Experimentally, the first ionization potential of ethylene is 10.51 eV.[6,7,12] This large discrepancy between calculated and observed ionization potentials is a measure of the increased correlation energy error in the ground-state neutral species over that found in the positive ion.

The formal similarity between the V and T states of ethylene and H_2 has often been stressed.[1,26] Thus, Huzinaga's results on ethylene[24] have their analog in the earlier work of Phillipson and Mulliken[31] on the (σ, σ^*) states of H_2 which arise from the excitation of an electron from a $\sigma(\zeta_g)$ to a $\sigma^*(\zeta_u)$ MO. σ and σ^* are just the symmetric and antisymmetric combinations, respectively, of $1s$ AO's on each hydrogen atom. In contradistinction to ethylene, Phillipson and Mulliken[31] find the optimum ζ_u diffuse for both the $^1(\sigma, \sigma^*)$ and $^3(\sigma, \sigma^*)$ states at the ground-state geometry. This can be partially explained by the behavior of the σ^* MO at small internuclear distances. Mulliken[1,11] refers to these states as semi-Rydberg because at r values near r_e of the ground state the UA description, $2p\sigma$, of the σ^* MO is already quite good, leading to a hydrogenic ζ_u. This is true for both V and T states of H_2.

The oxygen molecule is isoelectronic with ethylene and a one-to-one correspondence between the MO's and states of the two molecules can be drawn. Taketa et al.[32] find that in a minimal STO basis the observed $^3\Sigma_u{}^- - {}^3\Sigma_u{}^+$ energy separation in O_2 can be reasonably well reproduced only if the π_g MO in the $^3\Sigma_u{}^+$ state is diffuse. However, in a nonempirical calculation in the same basis but with free AO orbital parameters only, Schaefer and Harris[33] find that a valence configuration interaction calculation on all the states of O_2 gives an almost perfect $^3\Sigma_u{}^- - {}^3\Sigma_u{}^+$ energy interval. The diffuse π_g MO in the $^3\Sigma_u{}^+$ state of O_2 would then seem to require further study.

Thus the appearance of a diffuse terminating MO in only one state of an electronically isoconfigurational set is apparently without precedent in molecules and must be explained. Although the V state of ethylene is certainly expected to have a greater spatial extension than the T state in the ground-state geometry, the large difference obtained in the SCF π^* MO's seems unreasonable.

In this paper we contend that the lowest $^1(\pi, \pi^*)$ state obtained by direct SCF calculation in the ground-state geometry of ethylene is actually the first member of a Rydberg series and should not be identified with the spectroscopically observed V state. This SCF Rydberg state can actually be identified with a spectroscopically observed state of the same symmetry as the V state located ~ 1.5 eV above the Rydberg excitation energy in the SCF approximation. The thrust of the arguments presented here in support of this thesis are directed towards demonstrating that:

(a) a Rydberg of the same symmetry and electronic configuration is expected to lie below the spectroscopic V state in Hartree–Fock theory, in contradiction to experiment;

(b) whereas the geometry of the T and 1740-Å Rydberg states are accurately described by the $^3(\pi, \pi^*)$ and $^1(\pi, 3s)$ configurations, respectively, in the SCF approximation, the lowest $^1(\pi, \pi^*)$ state does not have the equilibrium C–C bond distance in the planar configuration expected for the spectroscopic V state but rather has the general characteristics found for known Rydbergs. In the more stable perpendicular configuration, where the π and π^* MO's are degenerate and neither is diffuse in the $^1(1\pi, 1\pi^*)$ state, the expected equilibrium C–C bond distance is better calculated;

(c) the early members of the manifold of calculated $^1(1\pi, \lambda\pi^*)$ states form a series which can be fitted to the Rydberg formula. This last point has already been noted in the results of Dunning et al.[26]

The term "diffuse" has not been defined or delimited explicitly. In order to avoid confusion and contentious argumentation about how diffuse is "diffuse," we identify "diffuse" with "Rydberg." The critical point of difference with previous interpretations[26] lies in the recognition that there are two spectroscopic states of the same symmetry, a valence shell (V) state and a Rydberg state, separated by ~ 1.4 eV.

TABLE I. Total energies for various states of ethylene.[a]

Geometry	r(C–C)[b]	State	Total energies (a.u.)	Energy difference (eV)[d]
Planar	r_0	$^1A_{1g}$	−78.02158	0.00
	r_0	$^3B_{1u}$	−77.89552	3.43
	r_0	$^1B_{1u}$	−77.74858	7.43
	r_0	$^1B_{1g}$	−77.68341	9.20
	r_0	$^2B_{3u}$	−77.68941	9.04
	r_0	$^2B_{3g}$	−77.54012	13.08
	$r_0+0.4$	$^3B_{1u}$	−77.92608	
	$r_0+0.8$	$^3B_{1u}$	−77.90497	
	$r_0+0.4$	$^1B_{1u}$	−77.74003	
	$r_0+0.8$	$^1B_{1u}$	−77.68934	
Perpendicular[c]	r_0	$^3A_2$	−77.93728	
	$r_0+0.4$	$^3A_2$	−77.94731	
	$r_0+0.8$	$^3A_2$	−77.91603	
	r_0	$^1B_2$	−77.77067	
	$r_0+0.4$	$^1B_2$	−77.75831	
	$r_0+0.8$	$^1B_2$	−77.70707	

[a] The C–H bond length (=1.086 Å) and HCH angle (=117.6°) [12] are the same for all calculations.

[b] r_0(C–C) =2.530378 a.u. =1.339 Å [12]; increments in atomic units.

[c] 90° dihedral angle between methylene planes.

[d] Relative to ground state ($^1A_{1g}$) in its equilibrium geometry.

Hartree–Fock theory gives the wrong one as lower in energy. A single level which is "more" or "less" spatially extended is inadequate to compare the Hartree–Fock results with experiment.

THEORETICAL AND COMPUTATIONAL ASPECTS

In its ground state the ethylene molecule is planar.[12] With the x axis perpendicular to the plane of the molecule and the z axis through the 2 carbon atoms the electronic configuration of the ground state in D_{2h} symmetry is given by

$$| ^1A_{1g}\rangle = (1a_{1g})^2(1b_{1u})^2(2a_{1g})^2(2b_{1u})^2(1b_{2u})^2(3a_{1g})^2$$

$$\times (1b_{3g})^2(1b_{3u})^2$$

$$= (\Sigma)(1b_{3u})^2. \qquad (2)$$

The $1b_{3u}$ orbital is to be identified with the 1π MO. Excitation of an electron from the 1π MO to the $1\pi^*$ MO gives the lowest-energy $^3B_{1u}$ and $^1B_{1u}$ states, $^3(1\pi, 1\pi^*)$ and $^1(1\pi, 1\pi^*)$, respectively, in the planar geometry:

$$| ^3B_{1u}\rangle = \tfrac{1}{2}(\Sigma)[1b_{3u}(1)1b_{2g}(2)-1b_{2g}(1)1b_{3u}(2)]$$

$$\times[\alpha(1)\beta(2)+\beta(1)\alpha(2)],$$

$$| ^1B_{1u}\rangle = \tfrac{1}{2}(\Sigma)[1b_{3u}(1)1b_{2g}(2)+1b_{2g}(1)1b_{3u}(2)]$$

$$\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)].$$

The $1b_{2g}$ orbital is just the $1\pi^*$ MO. Another state also considered is the lowest-energy $^1(\sigma, 1\pi^*)$ state, derived from a $1b_{3g}{\rightarrow}1b_{2g}$ excitation and of symmetry $^1B_{1g}$.

In the perpendicular geometric configuration which

is the more stable configuration for the $^{3,1}(1\pi, 1\pi^*)$ states, the 1π and $1\pi^*$ orbitals are electronically degenerate. It turns out to be more convenient to consider the individual x and y components, corresponding to the coordinate axes, of the degenerate e representation in D_{2d} symmetry. With the definition

$$\Sigma' = (1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(1e_x)^2(1e_y)^2,$$

the $^3B_{1u}$ and $^1B_{1u}$ states of the planar geometry go, respectively, into

$$| ^3A_2\rangle = \tfrac{1}{2}(\Sigma')[2e_x(1)2e_y(2)-2e_y(1)2e_x(2)]$$

$$\times[\alpha(1)\beta(2)+\beta(1)\alpha(2)],$$

$$| ^1B_2\rangle = \tfrac{1}{2}(\Sigma')[2e_x(1)2e_x(2)-2e_y(1)2e_y(2)]$$

$$\times[\alpha(1)\beta(1)-\beta(2)\alpha(2)].$$

The SCF equations for the open-shell singlet states were solved by the method of Hunt et al.,[30] which is a further development of the ideas of Huzinaga.[34] By this method, the off-diagonal Lagrangian multipliers, which guarantee orthogonality between open- and closed-shell MO's of the same symmetry, are eliminated. This avoids the difficulties of the coupling operator approach.[34–36] Actually, for all the states in the planar geometry considered here (see Table I) no special precautions are necessary since there are no open- and closed-shell MO's of the same symmetry. All of the open-shell doublet (positive ion) and triplet states were initially calculated using Roothaan's single-Hamiltonian SCF formalism.[36] In every case for which a comparison was made both[33,36] SCF method gave identical total energies and MO's. The orbital energies,
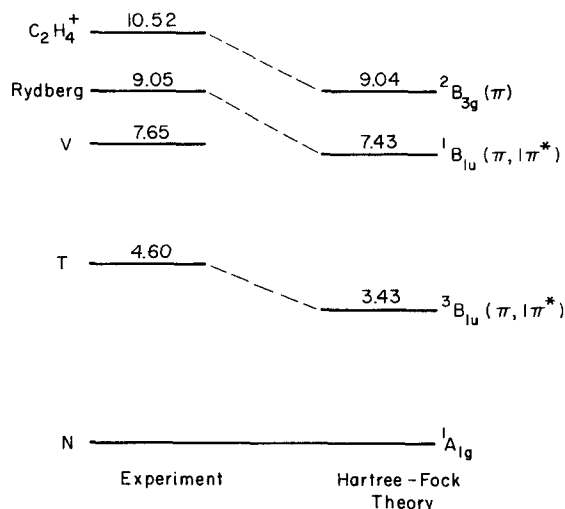
FIG. 1. Orbital configuration diagram for ethylene; correlation between theory and experiment according to assignments in text. π is sometimes labeled 1π in the text.

of course, are different for the two methods due to the different definitions of the Fock operator.

For the $^1B_2$ state, the SCF formulation used here[30] does not *necessarily* lead to an absolute variational minimum in the total energy and optimum MO's. This behavior manifests itself as a slight dependence of the self-consistent result on the initial input guess vector (MO's). In particular, the mixing between the open- and closed-shell MO's of the same symmetry is not *necessarily* optimal. Of course, for initial guess values of the MO's sufficiently close to the true variational result the minimum energy result is obtained. The effect of this uncertainty on the conclusions drawn based on the $^1B_2$ state calculations is discussed later.

Our experience in implementing the SCF calculations on the $^1B_2$ state of ethylene is sufficiently novel to merit mention. If the closed-shell MO's are denoted by the indices k and l, and the two open-shell MO's, $2e_{x,y}$, by the indices m and n, then the Hartree–Fock SCF equations to be solved for the $^1B_2$ state are (in the notation of Roothaan[36])

$$\left[H+\sum_l(2J_l-K_l)+\tfrac{1}{2}(2J_n-K_m+2J_n-K_n)\right]\varphi_k=\epsilon_k\varphi_k$$

$$\left(H+\sum_l(2J_l-K_l)+\begin{Bmatrix}K_m\\J_m\end{Bmatrix}-K_n\right)\varphi_m=\epsilon_m\varphi_m,$$

and an equation identical to the last one with m and n interchanged. Note the ambiguity in the definition of φ_m. In practice, it was not found possible to converge these equations using K_m, but rapid convergence to self-consistency was obtained using J_m. The wavefunction for the $^1B_2$ state has the aspects of a multiconfiguration function admitting only pair substitutions from a closed-shell structure and with the configuration

expansion coefficients fixed. All previous formulations of the multiconfiguration SCF equations[37] have used K_m. It is therefore possible that this experience can be of some use in helping find converged solutions to these-type multiconfiguration SCF equations.

Initially, calculations were carried out on both ground, $^3B_{1u}$, and $^1B_{1u}$ states with several large-atom Gaussian basis sets, including polarization d-type functions on the carbon and p-type functions on the hydrogen atoms. The best ground-state total energy obtained was -78.04732 a.u., which is only slightly lower than that calculated by Neumann.[38] The augmenting polarization functions were found not to materially affect the results obtained for the $^1B_{1u}$ state calculated in the atom basis sets alone and were discarded. It was also clear from this preliminary work that orbitals more diffuse than those usually found in the Hartree–Fock atom set (plus polarization) were needed for the $^1B_{1u}$ state.

The final basis set used for all calculations reported here, for all states and geometries, was taken mainly from the tabulations of Huzinaga.[39,40] The basis set on carbon is taken from Table XI of Ref. 39, but with the smallest exponent member of $\phi_{s,3}$ and largest exponent member of $\phi_{p,2}$ (in Huzinaga's notation[39]) split off to form separate basis functions. This gives 5^s3^p GTF's contracted from 11^37^p Gaussians. On hydrogen, a five-term fit to a Slater-type $1s$ orbital with $\zeta^2=1.8$ was split 4:1 in the manner of Whitten.[41] In both the planar and perpendicular geometries the p basis set on each carbon atom in the direction normal to the CH_2 plane was enlarged by (1) dividing the two-term outermost p-type GTF into two separate GTF's and (2) augmenting the AO basis by three diffuse Gaussians obtained by successively applying the constant ratio 0.405 to the smallest exponent Gaussian previously obtained. This ratio is found for the three smallest exponent members of the original AO set.[39] The added p-type functions have exponents 0.022536, 0.0091272, 0.0036965, and are, coincidentally, very near to the augmenting diffuse functions chosen by Dunning *et al.*[26] The final basis in the normal direction is thus seven GTF's contracted from 10 p-type Gaussians on each carbon atom.

RESULTS AND DISCUSSION

The total energies obtained for the relevant SCF calculations on ethylene are tabulated in Table I. Figure 1 compares some of the (vertical) excited-state energies with the spectroscopically observed states. At lowest energy is the $^3B_{1u}(1\pi, 1\pi^*)$ state, which is calculated $\sim$1.2 eV below the spectroscopic T state. This substantial discrepancy parallels that found for the ionization potentials and can be attributed to the same cause: a larger correlation energy error in the ground-state neutral species over that found in the

TABLE II. π and π^* orbital energies for various states in ethylene.[a]

Geometry	Planar					Perpendicular	
State	$^1A_{1g}$	$^2B_{3u}$	$^3B_{1u}$	$^1B_{1u}$	$^1B_{1g}$	$^3A_2$	$^1B_2$
Orbital energy (a.u.)							
1π	-0.3753	-0.7438	-0.5196	-0.6012	-0.3992	-0.3533	-0.6184
$1\pi^*$	$+0.0115$	-0.1429	-0.2397	-0.0593	-0.1719	-0.3533	-0.6184
$2\pi^*$		-0.0477	-0.0511	-0.0336	-0.0491	-0.0905	-0.1933
$3\pi^*$		-0.0270	-0.0287	-0.0148	-0.0277	-0.0438	-0.0830
$4\pi^*$		$+0.0064$	$+0.0001$	$+0.0422$	$+0.0037$	-0.0202	-0.0416
$5\pi^*$						$+0.0709$	-0.0176
$6\pi^*$							$+0.0815$
$7\pi^*$							

[a] Only orbital energies up to and including the first positive value are listed. These orbital energies have not been obtained using the SCF method of Ref. 36, but rather the alternate method described in the text.

triplet or positive ion. In the case of the positive ion this decreased correlation energy error can be qualitatively understood as being due to the fewer number of electrons whose instantaneous relative motions are incorrectly treated in Hartree–Fock theory.[42] For the *T* state the Fermi hole diminishes the correlation energy for the pair of electrons coupled to give a triplet state.

In a Rydberg state one electron is in an orbit which is large compared to the dimensions of the molecule and therefore almost independent of the instantaneous motion of all the other electrons in the molecule. It would be expected that calculated Rydberg state energies would suffer a discrepancy analogous to that of the positive ion, in comparison with experiment. This, in fact, has been observed by Miller *et al.*[43] in nonempirical SCF calculations on the electronic states of the water molecule. They find a difference of 1.3 eV between theory and experiment for the positive ion and an error of 1.0 eV for the lowest singlet Rydberg state. In analogous fashion for ethylene, with reference

TABLE III. Equilibrium C–C bond distances in the $^{3,1}(1\pi, 1\pi^*)$ states of ethylene.

Geometry	State	$r_{\min}$ (C–C) (Å)	
		Calculated	Observed[a]
Planar	$^3B_{1u}$	1.57	$1.58(T)$[e,f]
	$^1B_{1u}$	1.40	$1.80(V)$[e,d]
			$1.41(9.05\text{ eV}$ Rydberg)[e,f]
Perpendicular[b]	$^3A_2$	1.50	$?(T)$
	$^1B_2$	1.38	$1.44(V)$[e,d]

[a] See text.
[b] 90° dihedral angle between methylene planes.
[c] From Ref. 1.
[d] From Ref. 3.
[e] From Ref. 20.
[f] See Ref. 21.

to Fig. 1, the calculated $^1B_{1u}(1\pi, 1\pi^*)$ state should then be identified with a spectroscopic state at least 1.0 eV above its calculated position on the energy scale, if it can be shown that it is the first member of a Rydberg series.

The π and π^* orbital energies for various states of ethylene are displayed in Table II. The MO's for the $b_{2g}(\pi^*)$ manifold obtained in the $^1B_{1u}$ state SCF calculation have the convenient property that in the approximation that the Σ core [Eq. (2)] and 1π MO's are held constant, each of the $\lambda\pi^*$ MO's ($\lambda=1, 2, \cdots 7$) are the variationally correct orbitals for the $^1(1\pi, \lambda\pi^*)$ state. This arises from the form of the SCF equations which determine the open-shell orbitals:

$$[H+\sum_l (2J_l-K_l)+J_{1\pi}+K_{1\pi}]\varphi_{\pi}^* = \epsilon_\pi^*\varphi_\pi^*.$$

Thus each of the π^* MO's is determined in the field of $N-1$ electrons, where N is the total number of electrons in the molecule, and are expected to be excellent approximations to the higher excited orbitals of that symmetry. The excitation energy for the $^1(1\pi, \lambda\pi^*) \rightarrow$ $^1(1\pi, [\lambda+1]\pi^*)$ transition is just $\epsilon_{[\lambda+1]\pi^*} - \epsilon_{\lambda\pi^*}$.

Combining the lowest $^1B_{1u}$ total energy in Table I with the orbital energy differences gleaned from Table II gives 7.43, 8.13, and 8.64 eV for the first three $^1B_{1u}$ excited states arising out of the $(1\pi, \lambda\pi^*)$ electronic configuration. These numbers can be fitted to the Rydberg formula, Eq. (1), based on the calculated ionization potential with $\delta=0.1$ and $n=3$, 4, and 5. Only the first three states (out of seven) can be fitted to the Rydberg formula because only three diffuse functions (on each center) were included in the basis set. As expected, the $n=5$ member is a poorer fit than the previous two members because it was determined with the least degree of variational freedom. Nonetheless, there is no doubt that if the basis set were to be augmented with successively more diffuse functions, a correspondingly increasing number of states would be

TABLE IV. Molecular orbitals for perpendicular ethylene (E representation).

Basis function[a]	Exponent[b]	Molecular orbitals			
		$1e_x(^3A_2)$	$2e_x(^3A_2)$	$1e_x(^1B_2)$	$2e_x(^1B_2)$
H1 $1s$		−0.22999	0.09868	−0.22736	0.12741
$1s'$	0.1823562	−0.16780	0.14209	−0.16483	0.40898
H2 $1s$		0.22999	−0.09868	0.22736	−0.12741
$1s'$	0.1823562	0.16780	−0.14209	0.16483	−0.40898
C1 $2px$		0.28256	−0.03411	0.29408	−0.01400
$2px'$	0.338303	0.28775	−0.02416	0.29954	0.04487
$2px''$		0.12382	−0.10308	0.10760	0.17439
C2 $2px$		0.06185	0.38169	0.06355	0.29862
$2px'$	0.338303	0.04026	0.42067	0.04362	0.33317
$2px''$	0.137610	0.00067	0.36103	0.00363	0.32582
$2px'''$	0.055645	0.00128	0.09715	−0.00504	0.21958
$3px$	0.022536	0.00094	−0.02328	−0.00061	−0.03923
$4px$	0.0091272	0.00025	0.00907	−0.00028	0.02682
$5px$	0.0036965	0.00009	−0.00137	0.00008	−0.00850

[a] H1 and H2 are attached to C1 in the xz plane.   [b] Only the single-component members of the basis set are listed explicitly; see text for description of complete basis set.

generated which fit the Rydberg formula with increasing values of n, leading up to the 9.04-eV calculated ionization potential. The lowest energy $^1B_{1u}$ state at 7.43 eV is the first member of a Rydberg series.

Further evidence for this conclusion is obtained from the geometry dependence of the calculated lowest-energy $^1B_{1u}$ state and total oscillator strength of the $^1A_{1g} \rightarrow ^1B_{1u}$ transition. In Table III the calculated C–C bond distance for an energy minimum in the $^3(1\pi, 1\pi^*)$ and $^1(1\pi, 1\pi^*)$ states in both the planar and perpendicular configurations are displayed. These numbers are obtained by a parabolic fit through the three appropriate total energy values listed in Table I. The calculated equilibrium C–C bond distances should be reasonably accurate since in Hartree–Fock theory geometry is given correctly through first order in the wavefunction.[44] Although the wavefunctions and energies determined here are not quite of Hartree–Fock accuracy, they are believed to be sufficiently close that differences between these and the true Hartree–Fock results will be sufficiently small so as not to vitiate the arguments presented here. These sentiments are supported by the recent nonempirical SCF calculations on the 1740-Å Rydberg state of ethylene where the equilibrium dihedral twist angle and barrier to inversion through the planar configuration were predicted with great accuracy.[5]

Before presenting the comparison between theory and experiment the nature of the $^1B_2(1\pi, 1\pi^*)$ and both planar and perpendicular components of the $^3(1\pi, 1\pi^*)$ states should be described. In Table II it is apparent that the 1π and $1\pi^*$ orbital energies in the $^1B_2$ state are very similar to the 1π orbital energy in the $^1B_{1u}$ state. As would be expected from this comparison, both the π and π^* MO's in the $^1B_2$ state are composed al-

most exclusively of valence $(2p)$ atomic orbital functions. As pointed out previously, it is possible that in calculations on the $^1B_2$ states optimum variational mixing between the open$(2e)$- and closed$(1e)$-shell MO's of the same symmetry may not have been achieved. It is evident from Table IV, however, where the $1e_x$ and $2e_x$ MO's are explicitly tabulated, that no amount of $1e_x$–$2e_x$ mixing will significantly alter the Rydberg vs non-Rydberg character of the $2e$ MO's. The calculated $^1(1\pi, 1\pi^*)$ state in ethylene thus goes from pure Rydberg in the planar configuration to very much valence shell in the perpendicular configuration. Actually, valence-shell orbital character is expected for all geometric conformers of the V state.

All geometric conformers of the $^3(1\pi, 1\pi^*)$ state are also expected to be valencelike in orbital character and are so calculated. For the perpendicular lowest energy $^3A_2$ state this is shown by the explicit tabulation of vectors in Table IV. In the planar $^3B_{1u}(1\pi, 1\pi^*)$ state the energy eigenvalues in Table II, which also obey $\Delta E = \epsilon_{[\lambda+1]\pi^*} - \epsilon_{\lambda\pi^*}$ for the $^3(1\pi, \lambda\pi^3) \rightarrow ^3(1\pi, [\lambda+1]\pi^*)$ excitation, obviously do not fit the Rydberg formula, Eq. (1), with this state as the first member. The clearest indication of the non-Rydberg vs Rydberg character of π^* MO's is seen in Table V, where values of $\langle x^2 \rangle$ are displayed for individual MO's; $\langle 1\pi^* | x^2 | 1\pi^* \rangle$ for the $^3B_{1u}(1\pi, 1\pi^*)$ state is clearly much smaller than the corresponding value for the $^1B_{1u}(1\pi, 1\pi^*)$ state calculation.

As summarized in Table III, the comparison between calculated and observed equilibrium C–C bond distances is quite good for the $^3B_{1u}(1\pi, 1\pi^*)$ state and close for the $^1B_2(1\pi, 1\pi^*)$[45]; but the planar $^1(1\pi, 1\pi^*)$ state clearly is closer to the equilibrium C–C bond distance estimated[20,21] for the 9.05-eV spectroscopic

Rydberg than it is to the optical *V* state. Actually all the known Rydberg states of ethylene have an equilibrium C–C bond distance between 1.41 and 1.46 Å. That the comparison between theory and experiment is much closer for the $^1B_2$ state is taken as evidence that this state is being reasonably well described in the Hartree–Fock approximation.

The $^1B_2(1\pi, 1\pi^*)$ state is calculated to have an equilibrium C–C bond distance of 1.38 Å with a total energy of -77.7713 a.u. This point on an energy scale should correspond to the (0, 0) band of the *V* state at ~ 2650 Å (4.68 eV).[3] The $^1B_{1u}(1\pi, 1\pi^*)$ state using the ground-state C–C bond distance can be identified with the Franck–Condon maximum in the *V* state at ~ 1620 Å (7.65 eV). The energy separation between the calculated vibronic components of only 0.6 eV compares very poorly with the observed value of 3.0 eV, evidence that the $^1B_{1u}(1\pi, 1\pi^*)$ state is not the proper vertically excited state to be identified with the spectroscopic *V* state. Based on the assumption that the calculated $^1B_2(1\pi, 1\pi^*)$ state at its $r_{\min}$ is an accurate description of the vibrationless *V* state, it is possible to extract a calculated value of over 9 eV for the (hypothetical) Hartree–Fock analog of the vertically excited *V* state vibronic component. This value is the one typically found in nonempirical SCF calculations in a strictly valence-shell AO basis.[5] The implication that the correlation energy error is greater in the excited state than in the ground state, although possibly contrary to qualitative expectations,[26] must be accepted as real.[42] A state such as the *V* state of ethylene can have a larger correlation energy error than the ground state due to the presence of ionic components, e.g., $2p_a(1)2p_a(2)+2p_b(1)2p_b(2)$ in the Hartree–Fock wavefunction, and changes in the correlation energy of the Σ core on excitation.[46]

The total energy and $r_{\min}$ values for the $^1B_2$ state could be affected by improperly converged SCF solutions at the different C–C bond distances. The impact on the total energy is expected to be less than that on the vectors, by the variational principle. In calculations testing the input dependence of the SCF result on systems of similar size, as well as on perpendicular ethylene, a worst-case error of 0.005 a.u. (0.1 eV) in the total energy was obtained. It would require errors at least one order of magnitude larger in size to seriously affect the arguments presented here. Also, a consideration of differential correlation energy error in the planar and perpendicular geometric conformers of the $^1(1\pi, 1\pi^*)$ state will not alter these results.

The analogous energy separation for the *T* state is not known experimentally, but is calculated here as the difference in total energy for the $^3(1\pi, 1\pi^*)$ state between the planar, $r=r_0$, and perpendicular, $r=1.50$ Å (Table III), configurations to be ~ 1.5 eV. This number can be used to estimate the unobserved (0, 0) point for the *T* state, which is an important

TABLE V. $\langle x^2 \rangle$ for various MO's of planar ethylene.[a]

State MO	$^1A_{1g}$[b]	$^2B_{3u}$[c]	$^3B_{1u}$[d]	$^1B_{1u}$[e]	$^1B_{1g}$[f]
1π	2.1511	2.1737	2.0339	2.1516	2.1302
$1\pi^*$	244.63	2.8319	3.8417	41.891	4.6968
$2\pi^*$	123.91	70.738	69.973	174.03	77.133
$3\pi^*$	50.657	223.01	222.30	169.41	226.44
$4\pi^*$	25.135	125.05	127.08	55.539	118.29
$5\pi^*$	21.881	38.647	39.232	22.653	36.693
$6\pi^*$	9.9619	12.941	13.333	9.9707	12.584
$7\pi^*$	4.3491	4.111	4.6795	3.8260	4.6795

[a] E.g., $\langle 1\pi \mid x^2 \mid 1\pi \rangle$; in (a.u.)^2. The molecule is in the *yz* plane.
[b] Ground state.
[c] First positive ion; electron out of the π level.
[d] $^3(1\pi, 1\pi^*)$.
[e] $^1(1\pi, 1\pi^*)$.
[f] $^1(\sigma, 1\pi^*)$.

quantity in considering mechanisms for *cis–trans* isomerization.[1] Using 4.6 eV as the position of the Franck–Condon maximum for the *T* state gives 3.1 eV (~ 72 kcal) as the lowest energy of the *T* state relative to the vibrationless ground state.

In the approximation that the Σ core [Eq. (2)] is the same for both the ground and $^1(1\pi, 1\pi^*)$ states, the oscillator strength for the $^1A_{1g} \rightarrow ^1B_{1u}$ transition is easily calculated in the dipole approximation. There have been many discussions in the literature on whether the dipole length or velocity operators are more appropriate in using approximate wavefunctions and no consensus on, or resolution of, this question has been forthcoming. Since neither is to be preferred individually and there is some evidence[47] that the root mean square product value of the two operators has significance, we report the latter:

$$f = \tfrac{4}{3}\langle 1\pi \mid \mathbf{r} \mid 1\pi^* \rangle \langle 1\pi \mid \boldsymbol{\nabla} \mid 1\pi^* \rangle = 0.075.$$

The experimental value for the *V–N* oscillator strength is 0.34, while that for the 1740-Å (electric dipole allowed) Rydberg is 0.04. The experimental oscillator strength for the 9.04-eV Rydberg is not known, but Wilkinson's optical spectra[20] and the more recent energy loss spectra[22] indicate that it probably is somewhat less than that observed for the 1740-Å Rydberg.

The Rydberg nature of the lowest energy calculated $^1B_{1u}$ state in ethylene can be characterized by the value of $\langle 1\pi^* \mid x^2 \mid 1\pi^* \rangle = 41.891$ (a.u.)^2, shown in Table V. The corresponding value of that integral for the lowest-energy $^3B_{1u}$ state, which has $1\pi^*$ composed mainly of valence-shell AO components, is 3.8417 (a.u.)^2, and this can be taken as characteristic of a valence-type π^* MO. Another state which terminates on $1\pi^*$ in the orbital description is the lowest-energy $^1B_{1g}$ arising from a $\sigma \rightarrow \pi^*$ type transition, e.g.,

$$\cdots (1b_{3g})^2(1b_{3u})^2\ ^1A_{1g} \rightarrow \cdots (1b_{3g})(1b_{3u})^2(1b_{2g})\ ^1B_{1g}.$$
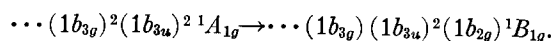
Direct SCF calculations on this state in the planar

geometry gives an excitation energy of 9.20 eV[48] and, in contrast to the $^1B_{1u}$ state, a valencelike $1\pi^*$ MO with $\langle 1\pi^* \mid x^2 \mid 1\pi^* \rangle = 4.6968$ (Table V). This result is consistent with and supports the arguments developed here. Ionization of an electron from the $1b_{3g}$ MO, corresponding to the second ionization potential of ethylene, is observed at $\sim$12.75 eV[6,7] but calculated (Table I) to require 13.10 eV. Thus there are no Rydberg states of $^1B_{1g}$ symmetry, leading up to ionization from the $1b_{3g}$ MO, expected in the region of 9 eV. The calculated direct SCF excitation energy for the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition is also in good agreement with previous virtual orbital (frozen ground-state MO's) results.[5]

If the lower-energy calculated $^1B_{1u}$ state is to be identified with a Rydberg found in the optical absorption spectrum at $\sim$9 eV,[49] what and where is the analog to the spectroscopic V state in Hartree–Fock theory? It is the basic contention of this paper that what would be the V state in Hartree–Fock theory is calculated to be beyond the Hartree–Fock ionization potential in energy and is so heavily contaminated with spuriously calculated lower-energy Rydberg components (because of orthogonality requirements) so as to be rendered unrecognizable as the true spectroscopic V state. Constraining the basis set to be chosen from SCF optimized AO's on the several atoms will not alter the situation since the SCF procedure will always try to converge on a Rydberg state, choosing from whatever basis functions are available.

What is obviously needed is to include electron correlation effects. Calculations have been carried out which give the approximate excitation energy between correlated ground and excited states. These results are obtained using the random phase approximation (RPA)[50] and its higher-order approximations, details of which will be published later. The RPA and renormalized RPA methods in the same basis used previously[26] give a $^1B_{1u}(\pi, \pi^*)$ state at 7.6–8.5 eV above the ground state but with a valencelike π^* orbital: $\langle \pi^* \mid x^2 \mid \pi^* \rangle \sim 7.5$ (a.u.)[2,50] This valencelike $^1(\pi, \pi^*)$ state must result from convergence to a $^1B_{1u}$ state unrelated to any bound state obtained in the Hartree–Fock approximation since the valencelike $^1B_{1u}$ SCF state is unbound.

A strong interaction between valence and Rydberg states of the same symmetry has been noted in Al,[51] N$_2$,[52] formaldehyde,[53] and CH$_3$,[54] offering copious evidence for the inadequacy of the single orbital configuration description in these molecules. All these cases, however, have involved the interaction of formally *different* orbital configurations of the same symmetry, one valence and one Rydberg type. The sorting out of the states is then a straightforward configuration mixing problem. The situation in ethylene is more complicated in that the two states arise out of the same type configuration [i.e., (π, π^*)] which

is already diagonal with respect to the molecular Hamiltonian. High-order pure (π, π^*) orbital configuration mixing will not solve the problem and (σ, σ^*)-type states, possibly of both Rydberg and valence character, must be involved in achieving an adequate theoretical description of the V state of ethylene.

Configuration mixing of a modest amount of Rydberg character into a predominantly valence $^1(\pi, \pi^*)$ configuration is not precluded by the pressure experiments.[5,16] The contribution to the oscillator strength of the Rydberg component could be a very small percentage of the total intensity. On the other hand, the electron scattering experiments[17,18] were carried out at an energy loss of 8.0 eV, which is beyond the Franck–Condon maximum in the V state and in the continuum region of the spectrum. Photodissociation of ethylene is known to begin at $\sim$7.2 eV,[1] and it is at about this energy value that the discrete part of the optical absorption spectrum merges into a continuum. The effect of the dissociation phenomenon on the angular dependence of the electron scattering should be studied. The influence of theoretically predicted,[5] optically forbidden Rydberg bands in the 8-eV energy region must also be considered. Finally, a quantitative correlation between the characteristic minimum in the angular dependence of the scattering and the amount of Rydberg character has yet to be established. It is clear that the experiments cannot yet tell us the extent of Rydberg character in the V state of ethylene. At the present time this information is probably best obtained theoretically, but not from Hartree–Fock theory.

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