The Generalized Valence Bond Description of the Low-Lying States of Ketene[1]

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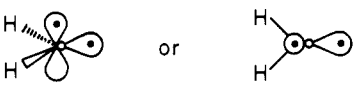
Abstract: The ground and valence excited states of ketene (H_2CCO) were studied using ab initio generalized valence bond (GVB) and configuration interaction (GVB-CI) wave functions. The character and properties of the states are analyzed in terms of the GVB wave functions. The calculated vertical excitation energies (in eV) are 3.62 $^3(n\rightarrow\bar{\pi}^*)$ or $^3A_2$, 3.69 $^1(n\rightarrow\bar{\pi}^*)$ or $^1A_2$, 5.39 $^3(\pi\rightarrow\pi^*)$ or 1 $^3A_1$, and 7.37 $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ or 2 $^3A_1$. (Here $\bar{\pi}$ indicates a π-like orbital in the plane of the molecule.) These results are in excellent agreement with the observed electron impact excitation energies, 3.8 ($^1A_2$) and 5.35 eV ($^3A_1$). Note in particular the small separation (0.07 eV) of the $^3A_2$ and $^1A_2$ states (0.5 eV for H_2CO) and the 2-eV separation in the $\pi\pi^*$ triplet states in the two planes. The calculated ground state dipole moment, 1.62 D, is in fair agreement with the experimental value of 1.41 D. The calculated dipole moments of the $^3A_2$, $^1A_2$, 1 $^3A_1$, and 2 $^3A_1$ excited states are 2.76, 3.43, 2.43, and 0.27 D, respectively.

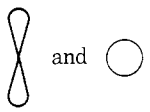
I. Introduction

The ground state of CH_2 ($^3B_1$) has the form[2-5]



(1)

consisting of two C-H bonds, a singly occupied p-like π orbital and an sp hybridized σ orbital (where

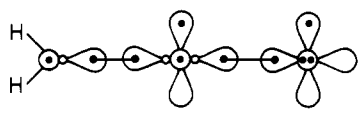


represent p orbitals in the plane and perpendicular to the plane, respectively). The ground states of atomic carbon and oxygen have the forms

(2)

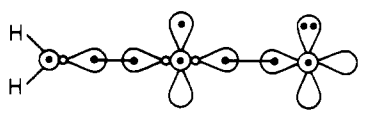
where the line connecting the singly occupied orbitals indicates singlet pairing.

Combining (1) and (2) we find only two orientations leading to two covalent σ bonds:



(3)

and



(4)

We will denote orbitals antisymmetric under reflection through the plane of the molecule (i.e., b_1 symmetry) as π and orbitals antisymmetric under reflection through the symmetry plane perpendicular to the molecule (i.e., b_2 symmetry) as $\bar{\pi}$ (ref 6 uses π' in place of $\bar{\pi}$).

Using (3) and allowing all possible couplings of the four singly occupied π and $\bar{\pi}$ orbitals leads to six states: two singlets, three triplets, and a quintet. Of these three, a singlet, a triplet, and the quintet result from triplet coupling of both the π and the $\bar{\pi}$ pairs and are therefore expected to be high lying. The remaining three states consist of the $^1A_1$ ground state (resulting from singlet coupling both the π and $\bar{\pi}$ pairs leading to a total of four bonds) and two $^3A_1$ states, $^3(\pi\rightarrow\pi^*)$ and $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ (resulting from triplet coupling the π pair with singlet coupling of the $\bar{\pi}$ pair, and vice versa, respectively).

Similarly, configuration 4 leads to six states of which we will consider only the lowest singlet and triplet. These two states will be denoted $^1A_2$ or $^1(n\rightarrow\bar{\pi}^*)$ and $^3A_2$ or $^3(n\rightarrow\bar{\pi}^*)$.

The above type analysis of the states of ketene in terms of atomic wave functions is referred to as a valence bond (VB) analysis. In this paper we report the results of generalized valence bond (GVB)[7,8] calculations in which the orbitals of valence bond-type wave functions are solved for self-consistently. The results indicate that (3) and (4) correctly describe the qualitative nature of the states but that polarization and delocalization effects are important for a quantitative description.

We also report configuration interaction (GVB-CI) calculations which include the most important orbital coupling and correlation effects neglected in the GVB wave function.

Some of the details of the calculations are discussed in section II, an analysis of the GVB orbitals is contained in section III, and the calculated excitation energies and dipole moments are reported in section IV.

II. Calculational Details

(A) Basis Set and Geometry. The double ζ (DZ) basis of Huzinaga[9] and Dunning,[10] (9s, 5p/4s) primitive Gaussians contracted to (4s, 2p/2s), was used in all calculations.

The geometry used was the experimental ground state geometry:[11] R_{CO} = 1.161 Å, R_{CC} = 1.314 Å, R_{CH} = 1.083 Å, ∠HCH = 123°, ∠CCO = 180°.

(B) The GVB Calculations.[12] The ground state HF wave function of ketene consists of 11 doubly occupied orbitals.

$$\psi_{HF} = \mathcal{A}[\phi_1^2\phi_2^2 \ldots \phi_{11}^2\alpha\beta \ldots \alpha\beta] \qquad (5)$$

The HF wave function of the low-lying excited states, though, consists of ten doubly occupied orbitals and two singly occupied orbitals. In general the correlation error in a closed shell HF ground state is significantly greater than the correlation error in open shell excited states. This differential correlation effect then leads to erroneously low HF excitation energies.

In the GVB wave function all orbitals are singly occupied and the spin function is completely general; for ketene this would lead to 22 nonorthogonal orbitals. However, one can also

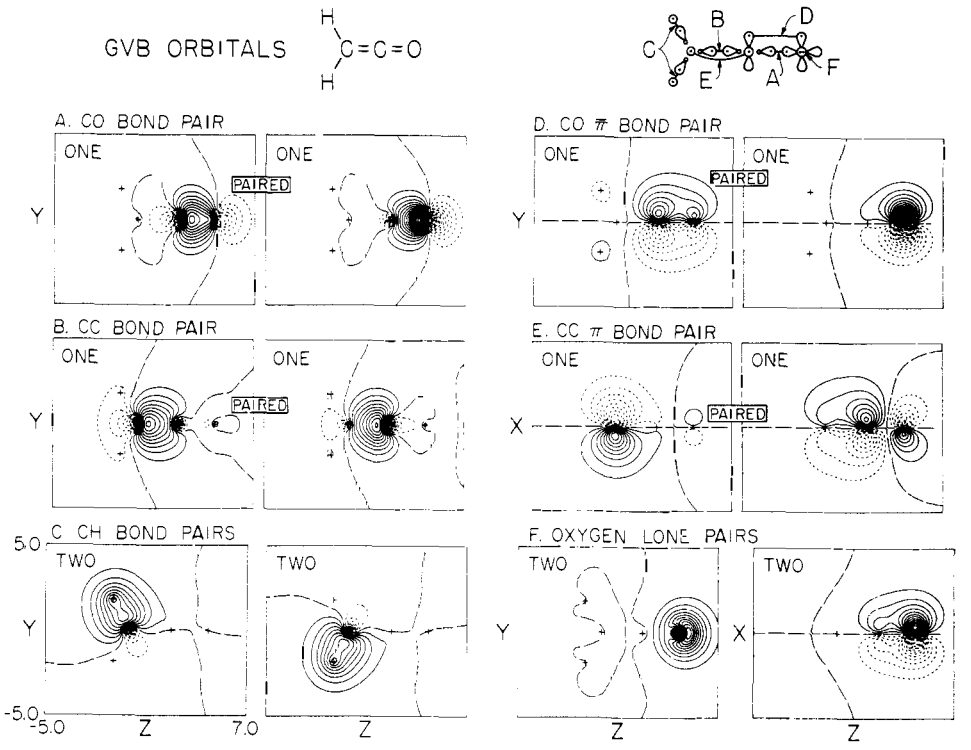


Figure 1. The ground state GVB(4/PP) orbitals of CH_2CO. The three 1s orbitals are not shown. The ONE and TWO indicate the number of electrons in the orbital. PAIRED connecting two orbitals indicates that the two orbitals are singlet paired. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au; the same conventions are used in all plots.

deal with intermediate cases in which some electrons are paired into doubly occupied orbitals as in the HF method while other electron pairs are allowed to split or correlate into nonorthogonal singly occupied orbitals. In addition, it has been found that two restrictions (perfect pairing and strong orthogonality)[7,13] can be imposed on the GVB wave function leading to a significant reduction in computational complexity without serious effects upon the quality of the wave function. The first approximation, perfect pairing, restricts the spin function to be the one in which as many orbital pairs as possible are singlet coupled for the given spin state. The strong orthogonality restriction requires orbitals of *different* singlet pairs to be orthogonal.

Table I. Configurations for the GVB-CI Calculations[a]

State	GVB natural orbitals				
	CO $\sigma\sigma^*$	CC $\sigma\sigma^*$	O n(π)	CC $\pi\pi^*$	CO $\bar{\pi}\bar{\pi}^*$
$^1A_1$ ground state	20	20	2	20	20
	11	20	2	20	20
	20	11	2	20	20
	20	20	2	11	20
	20	20	2	20	11
A_2 (n→π^*)	20	20	1	20	21
	11	20	1	20	21
	20	11	1	20	21
	20	20	1	11	21
	20	20	0	21	21
	20	20	2	10	21
	20	20	1	20	12
$^3A_1$ (π→π^*)	20	20	2	11	20
and ($\bar{\pi}$→$\bar{\pi}^*$)	11	20	2	11	20
	20	11	2	11	20
	20	20	2	11	11
	20	20	2	02	20
	20	20	2	20	20
	20	20	2	20	11
	20	11	2	20	11
	11	20	2	20	11
	20	20	2	20	02
	20	20	2	20	20

[a] The occupation numbers are shown for the orbitals of variable occupancy. Six other orbitals are doubly occupied.

In the calculations reported here the four pairs corresponding to σ, π and $\bar{\pi}$ bonds in the CO and CC regions were allowed to split into nonorthogonal, singly occupied, singlet coupled orbitals. This wave function is denoted as GVB(4/PP) to indicate that four pairs of electrons are split (correlated) and that the perfect pairing and strongly orthogonality restrictions (PP) are imposed. Thus the GVB(4/PP) ground state wave function is of the form

$$\mathcal{A}[\phi_1^2\phi_2^2 \ldots \phi_7^2(\phi_8\phi_9 + \phi_9\phi_8) \ldots (\phi_{14}\phi_{15} + \phi_{15}\phi_{14})\alpha\beta\alpha\beta \ldots \alpha\beta] \quad (6)$$

The perfect pairing restriction is generally adequate for systems with a single important VB structure. For systems with two or more important VB structures, such as allyl radical or benzene, the optimum orbital coupling often differs greatly from perfect pairing.[14] In the n→$\bar{\pi}^*$ states, the π system is formally that of allyl, and hence such effects could be expected to be important. For this reason we carried out additional calculations in which the PP restriction was relaxed (imposing only the strong orthogonality restriction on the π and $\bar{\pi}$ orbitals). These calculations are denoted as GVB(4/SO).[13] As expected there was little effect (0.0001 hartree) on the ground state but a significant effect (0.010 to 0.012 hartree) on the n→$\bar{\pi}^*$ states. However, we found (see section C) that CI calculations based on either PP or SO orbitals led to nearly identical absolute energies, indicating that the SO calculations are not necessary if an adequate CI is performed.

(C) The CI Calculations.[15] Wave functions of the valence bond form,

$$\phi_a\phi_b + \phi_b\phi_a$$

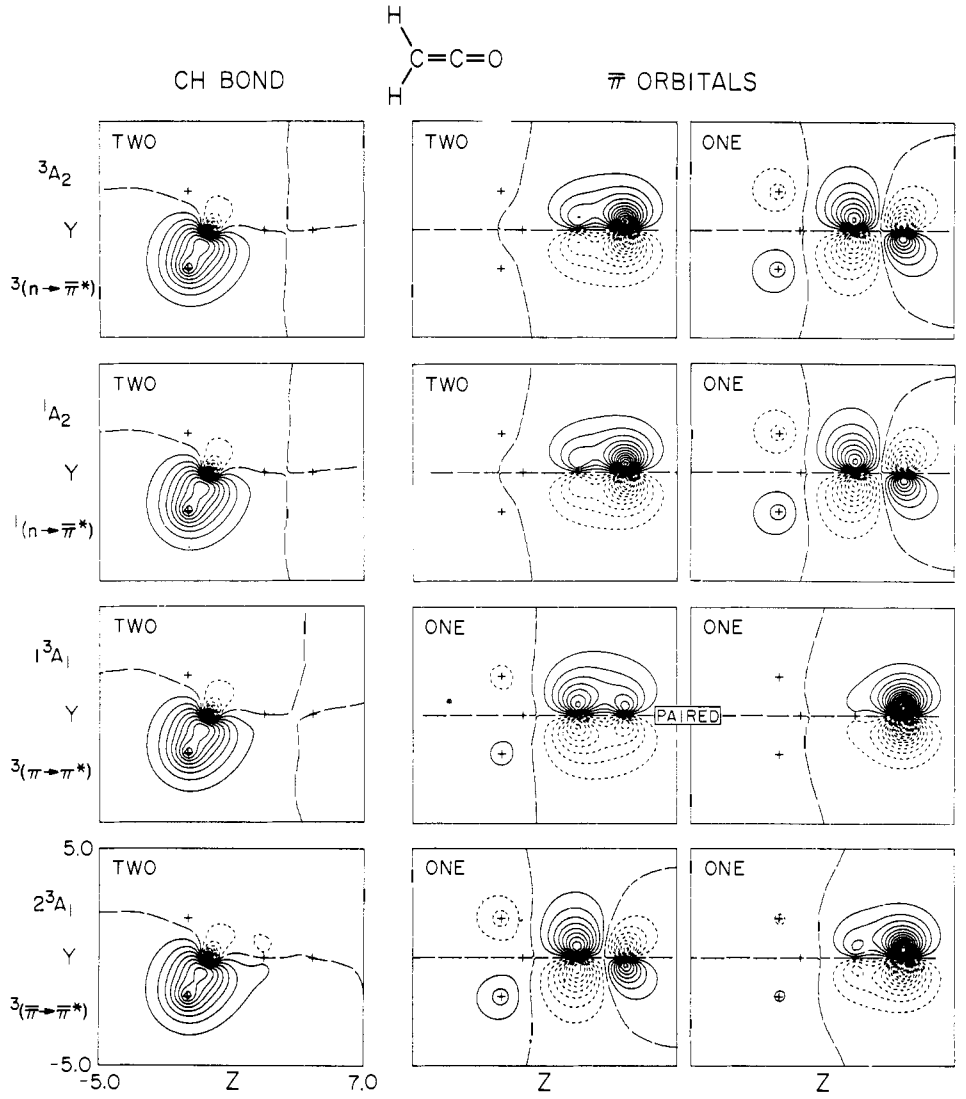


Figure 2. The CH and $\bar{\pi}$ orbitals of the valence states of CH_2CO (see ref 18).

where ϕ_a and ϕ_b are nonorthogonal, may be transformed to an equivalent natural orbital (NO) representation,

$$c_1\phi_1^2 - c_2\phi_2^2 \qquad (7)$$

where the NO's ϕ_1 and ϕ_2 are orthogonal. Generally the dominant NO of a GVB pair may be interpreted as a bonding orbital and the remaining NO as an antibonding or correlation orbital.

The basis for the GVB-CI calculations reported herein consists of all the GVB natural orbitals except the three lowest orbitals (one 1s-like orbital on each carbon and oxygen) together with all three virtual (unoccupied) π functions and virtual $\bar{\pi}$ functions on the two centers of the carbonyl. In all cases self-consistent orbitals for each state were used in the CI's. Within this basis all configurations resulting from single excitations from each of the configurations listed in Table I were included. These calculations relax the perfect pairing and strong orthogonality restrictions and include the important correlation effects neglected in the GVB wave function.

For the A_2 states, GVB-CI calculations using the GVB(4/PP) and the GVB(4/SO) orbitals were found to yield identical excitation energies (to 0.0004 hartree).

III. The GVB Orbitals

(A) The Ground State. The ground state GVB(4) orbitals of ketene are shown in Figure 1. The C-C and C-O σ bonds are found to be very similar to those of ethylene[4] and formaldehyde.[17] The C-O $\bar{\pi}$ bond is more strongly polarized toward the oxygen than the analogous π bond of formaldehyde. In addition the C-H bonds are noticeably polarized in the same direction resulting in a net $\bar{\pi}$ polarization toward the oxygen.

The π system consists of two singly occupied CC bonding orbitals and a doubly occupied orbital centered on the oxygen but somewhat delocalized into the CO π bonding region. In the VB model this latter orbital would correspond to a doubly occupied oxygen p orbital analogous to the n orbital of formaldehyde and other carbonyls. We therefore denote this orbital as n, noting, however, that the GVB orbital is found to have some π bonding character.

(B) The ($n\rightarrow\bar{\pi}^*$) States. The CH and $\bar{\pi}$ orbitals of the A_2 states are shown in Figure 2. In these plots the CH and $\bar{\pi}$ doubly occupied orbitals are obtained from approximate GVB(5) calculations.[18]

As expected from (4) the resulting CO $\bar{\pi}$ orbital is localized primarily on the oxygen; however, it does exhibit considerable CO $\bar{\pi}$ bonding character. The CO $\bar{\pi}^*$ orbital is centered primarily on the central carbon with some antibonding delocalization onto both the oxygen and the CH_2 group. With three electrons in the CO $\bar{\pi}$ bond region, the CH bonds cannot effectively delocalize toward the carbonyl, and hence the CH bonds are more localized in the $n\rightarrow\bar{\pi}^*$ states than in the ground state.

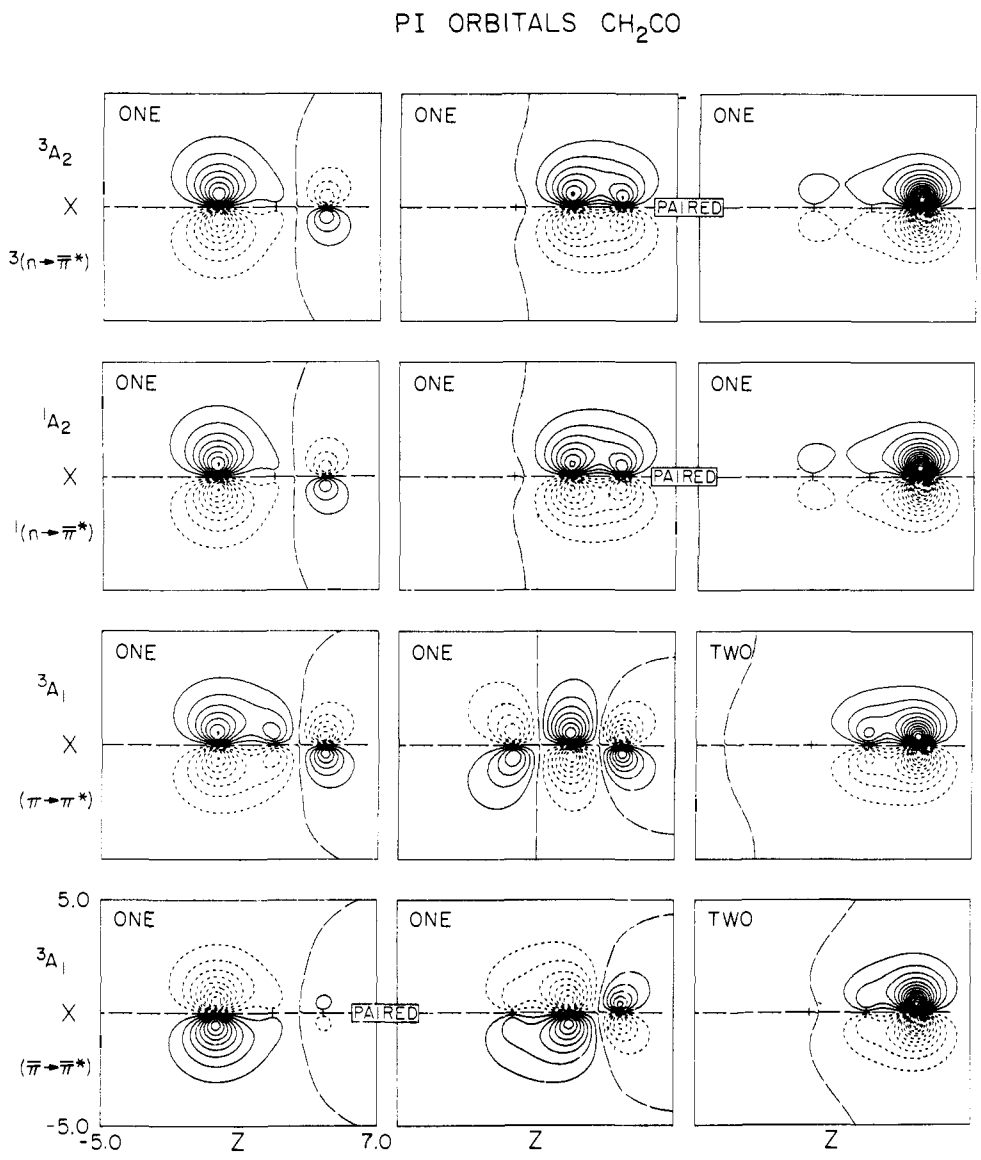


Figure 3. The GVB(4/PP) π orbitals of the valence states of CH_2CO.

In the π system, Figure 3, we find the singly occupied p orbital on the oxygen to be singlet paired with and highly overlapping (see Table II) the p orbital on the adjacent carbon, leading to a significant CO π bonding effect. Due to the strong orthogonality constraints, the remaining carbon p orbital must be orthogonal to the CO π bond and hence this orbital has C-O antibonding character. It should be emphasized that the strong orthogonality restriction results in an over-emphasis of the more favorable orbital coupling (in this case, singlet coupling of the carbonyl p orbitals) at the expense of the less favorable coupling (singlet coupling of the two carbon p orbitals).

(C) The $^3(\pi\rightarrow\pi^*)$ State. The σ and $\bar{\pi}$ orbitals of the $^3(\pi\rightarrow\pi^*)$ state, Figure 2, are nearly identical with those of the ground state, as expected from the VB description, (3).

In the π system, Figure 3, the oxygen lone pair has slightly more CO π bonding character than the ground state lone pair. As a result both the CC π and π^* orbitals are found to have a considerable amount of CO antibonding character.

(D) The $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ State. The CO $\bar{\pi}$ orbitals of the 2 $^3A_1$ state are slightly more delocalized into the C-H region than are the corresponding ground state orbitals. A much larger effect is the decrease in CO $\bar{\pi}$ bond polarity. A similar effect has been noted[17] in the $^3(\pi\rightarrow\pi^*)$ state of formaldehyde.

The π orbitals of this state (Figure 3) are slightly more localized than the ground state π orbitals, possibly representing a decrease in the π polarization away from the oxygen in conjunction with the decrease in $\bar{\pi}$ polarization toward the oxygen.

IV. Discussion

(A) Excitation Energies. The calculated GVB energies are listed in Table II along with GVB pair overlaps and splitting energies. In Table III the calculated excitation energies are compared with previous theoretical results and experiment. The $^1A_2$ and 1 $^3A_1$ excitation energies from GVB-CI are in excellent agreement with the results of recent electron impact experiments by Frueholz et al.[19] and, for the $^1A_2$ state, with the results of optical spectra.[20,21] We expect comparable accuracy in the $^3A_2$ and 2 $^3A_1$ excitation energies from GVB-CI, although neither of the states has been conclusively assigned in either the optical or electron impact spectra.[19]

Of particular interest is the calculated singlet-triplet splitting, 0.07 eV, of the $A_2(n\rightarrow\bar{\pi}^*)$ states. Previous calculations[6] and assignments of the optical spectra[20,21] have led to a splitting of 0.5 eV, comparable to the singlet-triplet $(n\rightarrow\pi^*)$ splitting in formaldehyde (0.47 eV) and other carbonyls. To a first approximation (not including orbital readjustments between the two states) the singlet-triplet splitting is equal to twice the exchange integral between the two "active" orbitals. In formaldehyde this exchange integral is 0.16 eV, and in ke-

Table II. Energies and GVB parameters for the GVB(4/PP) and GVB(4/SO) Wave Functions of CH_2CO (All Quantities Are in Atomic Units)

				GVB pair information		
Character	State	Calculation	Total energy	Pair	Overlap	ΔE^a
Ground state	$^1A_1$	PP	−151.7476	CO σ	0.874	0.0234
				CC σ	0.893	0.0085
				CO $\bar{\pi}$	0.696	0.0240
				CC π	0.693	0.0330
		SO	−151.7477	CO σ	0.874	0.0134
				CC σ	0.893	0.0085
				CO $\bar{\pi}$	0.696	
				CC π	0.693	
$^3(n\rightarrow\bar{\pi}^*)$	$^3A_2$	PP	−151.6016	CO σ	0.874	0.0133
				CC σ	0.891	0.0088
				CO π	0.768	0.0210
		SO	−151.6116	CO σ	0.875	0.0132
				CC σ	0.891	0.0087
				CO π	0.782	
$^1(n\rightarrow\bar{\pi}^*)$	$^1A_2$	PP	−151.5958	CO σ	0.874	0.0133
				CC σ	0.891	0.0088
				CO π	0.760	0.0222
		SO	−151.6082	CO σ	0.875	0.0132
				CC σ	0.892	0.0087
				CO π	0.769	
$^3(\pi\rightarrow\pi^*)$	$1\,^3A_1$	PP	−151.5494	CO σ	0.875	0.0132
				CC σ	0.891	0.0088
				CO $\bar{\pi}$	0.702	0.0313
$^3(\bar{\pi}\rightarrow\bar{\pi}^*)$	$2\,^3A_1$	PP	−151.4968	CO σ	0.875	0.0132
				CC σ	0.894	0.0083
				CC π	0.691	0.0246

[a] Energy increase upon replacing the GVB pair by a HF pair (averaging the GVB orbitals to obtain the HF orbital).

Table III. Vertical Excitation Energies (eV) for CH_2CO

						Single excitation CI	
State	Exptl[a]	GVB-CI	GVB(4/SO)	GVB(4/PP)	HF[b]	DZ	MBS[c]
$^3A_2(n\rightarrow\bar{\pi}^*)$		3.62[d]	3.70[d]	3.97[d]	3.12[d]	3.84[d]	3.71
$^1A_2(n\rightarrow\bar{\pi}^*)$	3.8	3.69	3.79	4.13	3.32	4.27	4.30
$1\,^3A_1(\pi\rightarrow\pi^*)$	5.35	5.39		5.39		4.95	4.88
$2\,^3A_1(\bar{\pi}\rightarrow\bar{\pi}^*)$		7.37		6.82		6.62	

[a] Electron impact results of R. P. Frueholz, W. M. Flicker, and A. Kuppermann, ref 19, [b] H. Basch, *Theor. Chim. Acta*, **28**, 151 (1973). [c] J. E. Del Bene, ref 6. [d] The calculated ground state ($^1A_1$) energies are −151.8271, −151.7477, −151.7476, −151.6721, and −151.6718 hartrees, respectively.

tene it is only 0.07 eV. The exchange integral is much smaller in ketene because the $\bar{\pi}^*$ orbital (Figure 2) has a node through the carbon on which the relevant π orbital is centered (Figure 3). Basically then, the small splitting is due to the $\bar{\pi}^*$ orbital being localized in the carbonyl region and the π orbital (to which it is either singlet or triplet coupled) being localized on the CH_2 carbon.

Excited states of closed shell systems are often treated in CI calculations including only single excitations from the higher-lying ground state occupied MO's to the lower-lying virtual MO's. Del Bene[6] has found that with a minimum basis set (MBS), this method leads to a singlet-triplet A_2 splitting of 0.59 eV. In order to test the possible basis set dependence of this result we have carried out similar calculations with our DZ basis and find a splitting of 0.43 eV.[22] In light of the explanation proposed above for the anomalously small splitting (0.07 eV) it is not surprising that calculations based on delocalized, ground-state, HF orbitals would lead to an erroneously large singlet-triplet splitting.

Laufer and Keller[23] have reported an extensive study of the low-energy optical spectrum of ketene using oxygen enhancement techniques. They find no evidence for a singlet-triplet transition in the 2-4-eV range and conclude that the $^3A_2$ transition is obscured by the $^1A_2$ transition.

Frueholz et al.[19] have recently reported the results of electron impact experiments at varying angles and impact energies. They were unable to resolve the $^3A_2$ transition from the $^1A_2$ transition and concluded the splitting to be much smaller than that normally found for carbonyl ($n\rightarrow\pi^*$) states. Their results indicate a singlet-triplet splitting of less than 0.2 eV and probably no bigger than 0.1 eV. These results are in agreement with our results but contradict those of Dixon and Kirby,[21] McGlynn and co-workers,[20] and Del Bene.[6]

McGlynn[20] has proposed the existence of two low-energy triplet states in the 2-4-eV range. Our results contradict this contention; indeed our calculations and the results of electron impact experiments place the second triplet state above 5 eV.

(B) Dipole Moments. The calculated GVB(4/PP) and GVB-CI dipole moments are listed in Table IV. The ground state GVB-CI dipole moment, 1.62 D, is found to be 0.21 D above the reported experimental value of 1.41 D.[24] A similar

Table IV. Calculated Total Dipole Moments[a]

State		Atomic units		Debye		
		GVB(4/PP)	GVB-CI	GVB(4/PP)	GVB-CI	Exptl
$^1A_1$	Ground state	0.77[b]	0.64	1.95	1.62	1.41
$^3A_2$	$^3(n\rightarrow\bar{\pi}^*)$	1.25	1.09	3.18	2.76	
$^1A_2$	$^1(n\rightarrow\bar{\pi}^*)$	1.19	1.35	3.03	3.43	
$1\,^3A_1$	$^3(\pi\rightarrow\pi^*)$	1.09	0.96	2.77	2.43	
$2\,^3A_1$	$^3(\bar{\pi}\rightarrow\bar{\pi}^*)$	0.008	0.11	0.19	0.27	

[a] The sign of the dipole moments indicates a shift of electron charge toward the oxygen for all states. [b] The dipole moment for the HF wave function is 2.00 D.

error (0.25 D) in the DZ GVB-CI dipole moment of formaldehyde was found to be due to a lack of d functions in the basis set.[17]

The ground state GVB-CI dipole moment, 1.62 D, is in significantly better agreement with experiment (1.41 D) than the GVB(4/PP) and HF results, 1.95 and 2.00 D, respectively. Previous HF calculations[25] with a different basis set led to the same dipole moment.

Partitioning the HF and GVB dipole moments into a_1, b_1, and b_2 components and associating with each the appropriate nuclear contributions [based on (3) and (4)], we find good agreement between the HF and GVB a_1 components, −0.89 and −0.87 au, respectively. The HF b_1 or π component, 1.40 au, is 0.31 au more *positive* than the GVB b_1 component, 1.09 au. The HF b_2 or $\bar{\pi}$ component, −1.30 au, is 0.31 au more *negative* than the GVB b_2 component. Thus in spite of the close agreement between the GVB(4/PP) and HF total dipole moments, the HF wave function contains appreciably more ionic character in both the π and $\bar{\pi}$ systems.

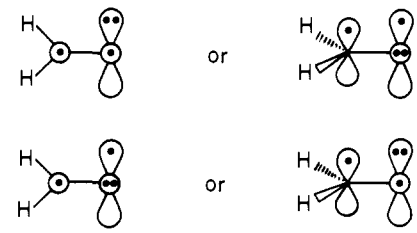
(C) Comparison of Theoretical Excitation Energies. In previous calculations on CH_2O[17] and H_2NCHO,[26] it was noted that the most important effects included in the GVB-CI wave functions but neglected in the GVB(/PP) wave functions were orbital coupling and interpair correlation terms. Of these the GVB(/SO) wave functions include only the important orbital coupling or resonance effects. From the results of Table III, we see the allylic resonance of the singlet and triplet $(n\rightarrow\bar{\pi}^*)$ states lowers these states by 7.9 and 6.2 kcal restrictively, indicating a resonance energy of ~7 kcal. For comparison, in allyl radical, where the two resonance structures are completely equivalent. the resonance stabilization was found to be 11.4 kcal.[14]

Considering now the GVB-CI excitation energies, we find only a small change in the $^{1,3}(n\rightarrow\bar{\pi}^*)$ excitation energies relative to the GVB(4/SO) results. This is in agreement with calculations on CH_2O and H_2NCHO in which it was found the $(n\rightarrow\pi^*)$ excitation energies were not greatly affected by the additional correlation effects in the CI.

Comparing the GVB(4/PP) $^3(\pi\rightarrow\pi^*)$ and $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ excitation energies to the GVB-CI results, we find the $^3(\pi\rightarrow\pi^*)$ energy to be unaffected by the CI whereas the $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ energy is increased by 0.55 eV. In calculations on formaldehyde[17] it was found that σ-π interpair correlations resulted in a lowering of the ground state energy 0.5 eV relative to the $^3(\pi\rightarrow\pi^*)$ state. The explanation for this differential effect is that σ-π interpair correlation corresponds to a concerted (correlated) movement of the two σ electrons to one center and the two π electrons to the opposite center. When the π pair is triplet coupled, the movement of both π electrons onto one center is unfavorable. In formamide[26] it was found that delocalization of the nitrogen π lone pair in the $^3(\pi\rightarrow\pi^*)$ state led to interpair correlation terms that canceled those in the ground state. In ketene the oxygen π lone pair is found to be greatly delocalized in the $^3(\pi\rightarrow\pi^*)$ state while no equivalent effect is found in the $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ state. Thus we would expect, as is found, a large (~0.5 eV) CI effect on the $^3(\bar{\pi}\rightarrow\bar{\pi}^*)$ excitation energy and little if any effect on the $^3(\pi\rightarrow\pi^*)$ excitation energy.

V. Comparisons to Formaldehyde and Ethylene

The VB diagrams for the valence states of formaldehyde are shown in (8).



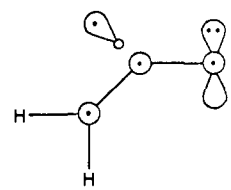
(8)

Coupling the two singly occupied orbitals into either a singlet or a triplet leads to the $^1A_1$ or ground state and $^3A_1$ or $^3(\pi\rightarrow\pi^*)$ state for the top of (8) and the $^1A_2$ or $^1(n\rightarrow\pi^*)$ and $^3A_2$ or $^3(n\rightarrow\pi^*)$ states for the bottom of (8).

In the A_2 states of formaldehyde it has been found that the hydrogens bend out of the plane of the molecule allowing the singly occupied π orbital to hybridize away from the doubly occupied π orbital thereby reducing the antibonding interaction.

Comparing the top of (8) to (3) then, we find the oxygen b_2 or $\bar{\pi}$ lone pair of formaldehyde corresponds to a b_1 or π orbital of ketene. Similarly, the π bond of formaldehyde corresponds to the $\bar{\pi}$ bond of ketene. Making this comparison we find the lone pair of ketene to have considerably more CO bonding character than the lone pair of formaldehyde (Figure 4).

Similarly comparing the bottom of (8) to (4) we would expect the antibonding character of the singly occupied $\bar{\pi}$ orbital to lead to a change in geometry analogous to that found in formaldehyde. In ketene this effect will lead to a decrease in



(9)

the CCO angle as shown in (9). Such an effect was in fact found in the calculations reported by Del Bene.[6]

In ref 20, comparisons are made between the $2b_2$ orbital of formaldehyde and the $2b_2$ orbital of ketene discussing the relative amounts of bonding and nonbonding character; from a simple VB analysis we conclude it is far more appropriate to compare the b_2 lone pair of formaldehyde and the b_1 lone pair of ketene. Similarly, Del Bene[6] argues that since the A_2 states of formaldehyde arise from a $b_2\rightarrow b_1$ transition while the A_2 states of ketene arise from a $b_1\rightarrow b_2$ transition, the A_2 states of ketene are not analogous to the A_2 states of formaldehyde. We find this argument to be incorrect.

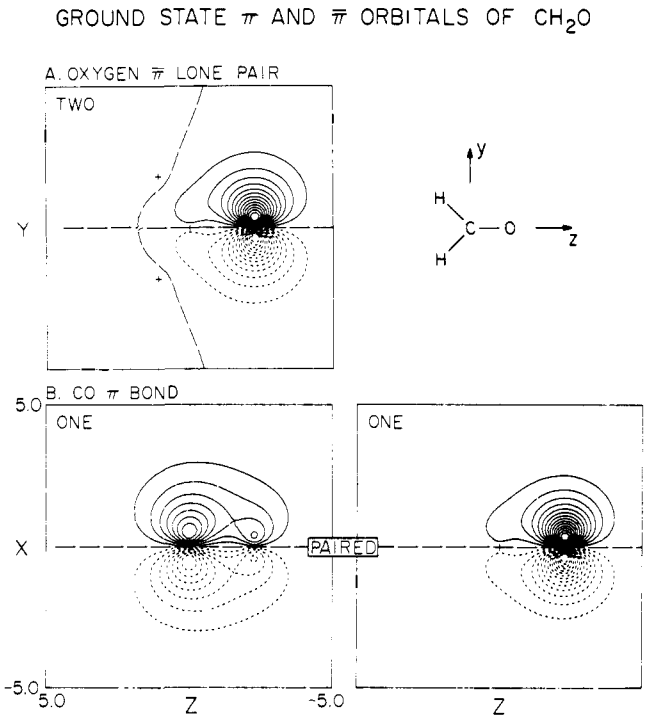


Figure 4. The $\bar{\pi}$ lone pair and CO π bond orbitals of CH_2O. All orbitals are from GVB(4/PP) calculations (see ref. 18).

Table V. Comparison of GVB-CI Vertical Excitation Energies of CH_2O, C_2H_4, and CH_2CO

	CH_2O[a]	C_2H_4[b]	CH_2CO
$^3A_2(n\rightarrow\pi^*)$	3.62		3.62
$^1A_2(n\rightarrow\pi^*)$	4.09		3.69
$1\ ^3A_1(CC\ \pi\rightarrow CC\ \pi^*)$		4.65	5.39
$2\ ^3A_1(CO\ \pi\rightarrow CO\ \pi^*)$	5.95		7.37

[a] L. B. Harding and W. A. Goddard, ref 17. [b] L. B. Harding and W. A. Goddard, manuscript in preparation.

It is also of interest to compare the excitation energies of ketene to those of the constituent chromophores ethylene and formaldehyde. From this analysis, Table V, we find a correct prediction of the ordering of the states. In particular we find fairly good agreement between the $(n\rightarrow\pi^*)$ excitation energies but the $^3(\pi\rightarrow\pi^*)$ energies of ketene are significantly higher than those of C_2H_4 and CH_2O. The difference in $^3(\pi\rightarrow\pi^*)$ excitation energies may be due to shorter CO and CC bond lengths in ketene. In the $(n\rightarrow\pi^*)$ states this effect is canceled by the previously mentioned allylic resonance stabilization.

VI. Summary

The GVB wave function leads to a consistent description of the valence states of ketene, and the GVB orbitals provide simple explanations of the character of the states. In addition, CI calculations based on the GVB orbitals include additional correlation and orbital coupling effects necessary for quantitatively accurate valence excitation energies.

References and Notes

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