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

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Abstract: The ground and valence excited states (n → π* and π → π*) 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 adiabatic excitation energies to the $^3A''(n \to \pi^*)$ and $^1A''(n \to \pi^*)$ states are 3.03 and 3.42 eV, in excellent agreement with the experimental values of 3.12 and 3.50 eV. The calculated vertical excitation energies of 3.62 and 4.09 eV, respectively, are in excellent agreement with the values from recent electron impact experiments (3.5 and 4.1 eV, respectively). With the best basis (double ζ plus d functions) the calculated dipole moment is 2.36 D (the double ζ basis leads to 2.59 D), in excellent agreement with the experimental value (2.32 D). For the double ζ basis the $^1A''$ and $^3A''$ states are found to have dipole moments of 1.71 and 1.59 D in reasonable agreement with the experimental values of 1.56 and 1.29 D, respectively. The $^3A_1$ ($\pi \to \pi^*$) state is found to have a vertical excitation energy of 5.95 eV, in excellent agreement with the result (5.9 eV) from recent electron impact experiments. The singlet $\pi \to \pi^*$ state is found to involve a diffuse π^* orbital and lies at 10.77 eV. This transition is not identified in the experimental studies; however, a broad peak in high energy electron impact spectra is observed around 10.5 eV.

I. Introduction

The ground state of $CH_2(^3B_1)$ has the form[3-6]

(1)
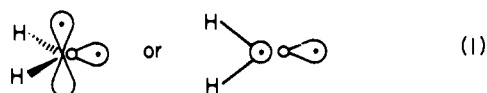
including a p-like singly occupied π orbital and an sp-hybridized singly occupied orbital (a p orbital perpendicular to the plane is indicated by a circle). The ground state of atomic oxygen has one doubly occupied p orbital and two singly occupied p orbitals.[6]

(2)
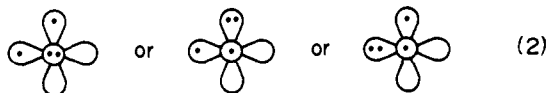
Combining (1) and (2) to form formaldehyde leads to

(3)

(4)

(5)
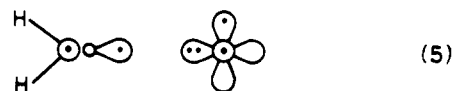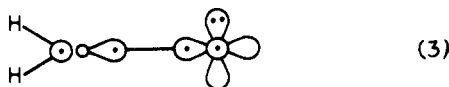
as the three possibilities. However, (3) and (4) are expected to form a strong covalent σ bond (indicated by a line in the diagrams) whereas (5) is not. Thus (3) and (4) are the most likely candidates for the low-lying valence states of H_2CO.

With the σ orbitals singlet paired, (3) and (4) each lead to a singlet state and a triplet state: $^3A_1$ and $^1A_1$ for (3) and $^3A_2$ and $^1A_2$ for (4). These states are expected to have charge distributions similar to the ground states of the atoms and hence will be referred to as *valence* states. The subject of this paper will be to examine the character of these states.

The above analysis of the formaldehyde wave functions in terms of the corresponding atomic orbitals is referred to as a valence bond analysis. In the theoretical studies of this paper we have used the generalized valence bond (GVB) method,[7,8] in which the orbitals of a valence bond type wave function are solved for self consistently. The results indicate that (3) and (4) correctly describe the basic character of the states, but that delocalization effects are important for some properties.

The GVB orbitals were also used in configuration interaction calculations to examine the correlation effects not included in the GVB wave function.

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

II. Calculational Details

A. Basis Set and Geometries. The double ζ (DZ) basis set of Huzinaga[9] and Dunning[10] [(9s,5p/4s) primitive Gaussians contracted to (4s,2p/2s)] was used for most of the calculations. A set of d basis functions (ζ_C = 0.6769, ζ_O = 0.8853) was also added to the DZ basis (denoted as the DZd basis) and used for a ground state calculation.

Two geometries were considered: (a) the experimental ground state geometry[11] R_{CO} = 1.2099 Å (2.2864a_0), R_{CH} = 1.1199 Å (2.1164a_0), and $\angle$ HCH = 118°; and (b) the n $\rightarrow$ π^* geometry with R_{CO} = 1.3068 Å (2.46958a_0), R_{CH} = 1.0961 Å (2.07143a_0), $\angle$HCH = 118°, and the C-O axis bent 30° away from the HCH plane. This represents a compromise between the experimental geometries of the n $\rightarrow$ π^* singlet[12,34] and triplet states.[13]

The observed[12] and calculated[22] barriers to inversion for both of these states are less than 0.1 eV and so we do not expect the use of this approximate geometry to significantly affect any of our calculated excitation energies.

B. The GVB Calculations. In describing the GVB calculations it is effective to compare them with the Hartree-Fock (HF) wave functions. For the ground state of formaldehyde, the HF wave function consists of eight doubly occupied orbitals.

$$\alpha[\phi_1^2\phi_2^2\phi_3^2 \ldots \phi_8^2\alpha\beta\alpha\beta \ldots \alpha\beta] \qquad (6)$$

The HF wave function describing the separated CH_2 and O species, (1) and (2), has six doubly occupied orbitals and four singly occupied orbitals. Consequently the HF wave function cannot properly describe the process of forming the C-O bond of formaldehyde.

In the full GVB wave function, every electron is allowed to have its own orbital, leading to 16 singly occupied orbitals for formaldehyde. One can also deal, however, with intermediate cases where some HF pairs are described with doubly occupied orbitals, while other HF pairs are allowed to split into nonorthogonal singly occupied orbitals.

In formaldehyde a comparison of (3) and (4) with (1) and (2) indicates that only four electrons require singly occupied orbitals. Thus we describe these states with a wave function of the form

$$\alpha[\phi_1^2\phi_2^2\phi_3^2\phi_4^2\phi_5^2\phi_6^2(\phi_7\phi_8)(\phi_9\phi_{10})\chi] \qquad (7)$$

where χ is an appropriate spin function. In the GVB method all the orbitals of (7) are solved for self consistently for each state. To indicate that only two pairs of (6) are described in terms of singly occupied orbitals, the self-consistent wave function (7), is denoted GVB(2) (indicating four singly occupied orbitals). In our calculations we took the spin function, χ, to be the simple spin function of a valence bond wave function. To indicate this restriction we use the symbol PP for perfect pairing, e.g., GVB(2/PP). [More generally PP also indicates that the orbitals of *different* pairs are required to be orthogonal; this is not a restriction for the GVB(2/PP) wave functions here.] Thus the GVB(2/PP) wave function for formaldehyde is of the form,

$$\alpha\{[\phi_1^2\phi_2^2 \ldots \phi_6^2\alpha\beta \ldots \alpha\beta](\phi_7\phi_8 + \phi_8\phi_7) \times$$
$$(\alpha\beta - \beta\alpha)(\phi_9\phi_{10} \pm \phi_{10}\phi_9)(\alpha\beta \mp \beta\alpha)\} \qquad (8)$$

The perfect pairing restriction was relaxed in the CI studies and was found to be of little importance (it would be

important for large CO separations, since both (1) and (2) require triplet pairing of the singly occupied orbitals).

The ground state was also studied with the GVB(4/PP) wave function, allowing eight singly occupied orbitals. This allows a VB-like description of the C-H bonding pairs but has little effect upon the orbitals of the CO pairs.

C. The CI Calculations.[16,17] Wave functions of the valence bond form,

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

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

$$c_1\phi_1^2 - c_2\phi_2^2$$

where the NO's, ϕ_1 and ϕ_2, are orthogonal. In general the first natural orbital of a GVB pair (the one with the dominating coefficient) may be interpreted as a bonding orbital and the second natural orbital as an antibonding or correlating orbital.

For the A_1 states the GVB-CI results reported here are simply full CI's within the C-O σ, σ^*, π, π^* natural orbital space. The GVB-CI's for A_2 and A'' states consist of a full CI within the preceding natural orbital space from the following two basic configurations,

	σ_{CO}	σ^*_{CO}	π	π^*	CH_{b_2}	n
(a)	2	0	2	1	2	1
(b)	2	0	2	1	1	2

It was found that allowing excitations out of the other orbitals (2s and CH_{a_1}) had little effect ($\sim$0.05 eV) on the excitation energies.

These calculations relax the perfect pairing restriction and include some of the correlation effects neglected in the GVB wave function.

III. The GVB Orbitals

A. The Ground State. The ground state, GVB(4) orbitals of CH_2O are shown in Figure 1. Although the GVB orbitals are allowed to delocalize over the molecule, we find that they localize in different regions leading to the basic character expected from VB wave functions.

There are clearly two types of σ bonding pairs. The C-H bonding pairs are each composed of one orbital which is essentially a hydrogen 1s orbital and a second orbital which is primarily on the carbon but hybridized in the direction of the corresponding hydrogen atom.

The second type of bonding pair is localized in the C-O region and clearly represents the C-O σ bonding pair. These two orbitals, although more delocalized than the orbitals of the C-H pair, still retain the character expected from the valence bond picture.

The remaining two σ pairs (which are not split in the GVB(4) calculation) represent the 2s and the 2pσ lone pairs on the oxygen.

The π bonding pair is found to consist of one orbital well localized onto the oxygen and a second more diffuse orbital showing π donation from the carbon to the oxygen.

B. The Excited States. 1. π Orbitals. As expected from the GVB diagrams (3) and (4), the orbitals of the excited states are generally quite similar to those of the ground state. The most significant changes occur in the π orbitals as shown in Figure 2.

In the A_2 states the doubly occupied orbital is primarily on the oxygen but is significantly delocalized in a bonding fashion onto the carbon. The singly occupied orbital is forced by the Pauli principle to be orthogonal to the doubly occupied orbital and hence must delocalize onto the oxygen in an antibonding way.
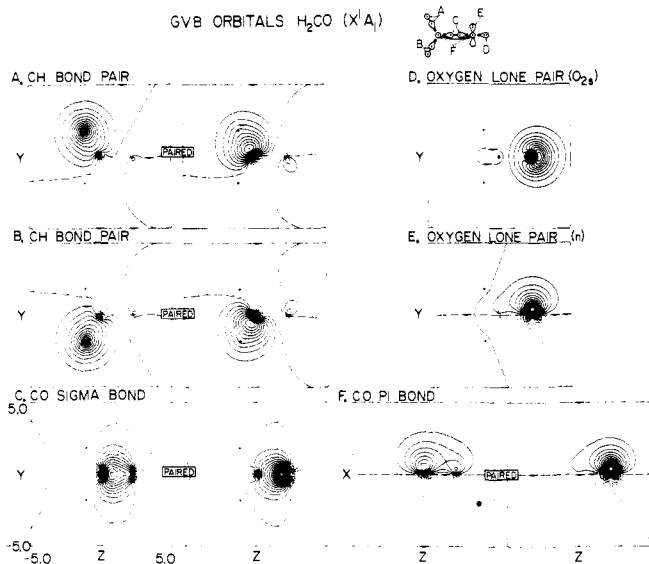
Figure 1. The ground state GVB(4) orbitals of CH$_2$O. The 1s orbitals are not shown. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au. The same conventions are used for all plots.

Some slight differences are expected in the π^* orbital of the A$_2$ states. Given a set of orbitals as in (4), the corresponding singlet and triplet states have energies

$$E(^1A_2) = E_0 + K_{n\pi^*}$$
$$E(^3A_2) = E_0 - K_{n\pi^*}$$

differing only in the exchange interaction. Thus in proceeding from atomic orbitals to the self-consistent GVB orbitals, we expect the orbitals of the triplet state to readjust so as to *increase* $K_{n\pi^*}$ while those of the singlet state readjust to *decrease* $K_{n\pi^*}$. The atomic orbitals of (4) already have the n and π^* orbitals on different centers and hence have a very small $K_{n\pi^*}$ ($\sim$0.1-0.2 eV for atomic orbitals on different centers). Delocalization of the π^* orbital onto the oxygen would result in a large increase in $K_{n\pi^*}$ ($\sim$0.9 eV for atomic orbitals on the same center). We therefore expect much more delocalization for the triplet state than for the singlet state, as observed.

The π orbitals of the $^3A_1(\pi \rightarrow \pi^*)$ state are also much more delocalized than those of the ground state. However, this is not significant because for a triplet state, a wave function with completely delocalized orbitals,

$$\pi = 1 + r$$
$$\pi^* = 1 - r$$

is equivalent to the state with localized orbitals,

$$(\pi\pi^* - \pi^*\pi)\alpha\alpha = (lr - rl)\alpha\alpha$$

2. n Orbitals. As shown in Figure 3 there is a characteristic difference between the n orbitals of the ground and excited states. In the ground state the n orbital is doubly occupied and delocalizes slightly into the C-H region, resulting in the slight antibonding character in the C-H orbitals. However, for the A$_2$ states, where the n orbital is only singly occupied, the C-H orbitals delocalize slightly in a bonding way onto the oxygen atom and the n orbital develops some antibonding character.

3. C-H Orbitals. In Figure 3 we note that the GVB(2) C-H orbitals of the A$_1$ and A$_2$ states are delocalized over two C-H bonds rather than localized as in the ground state GVB(4) calculation (Figure 1). In the GVB(2) calculations, the C-H bonds are described with doubly occupied orbitals; thus, since recombining doubly occupied orbitals
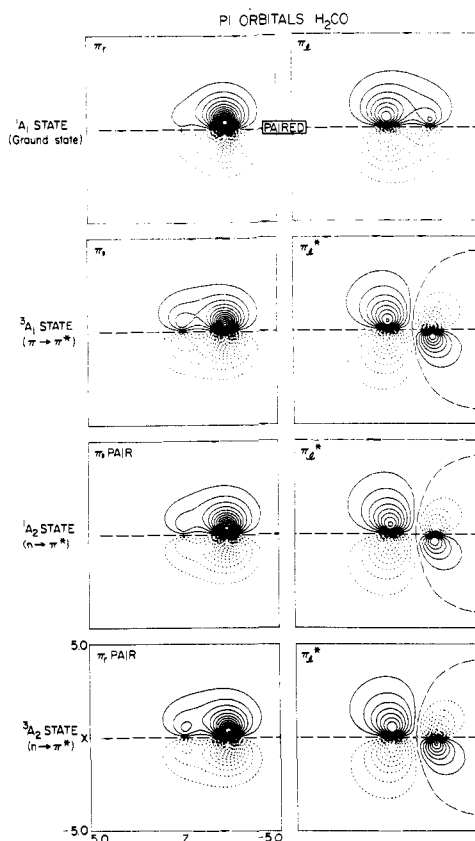

Figure 2. The π orbitals of the valence states of CH$_2$O. The $^1A_1$ orbitals are from the GVB(4) calculation and the remainder are GVB(2) orbitals.

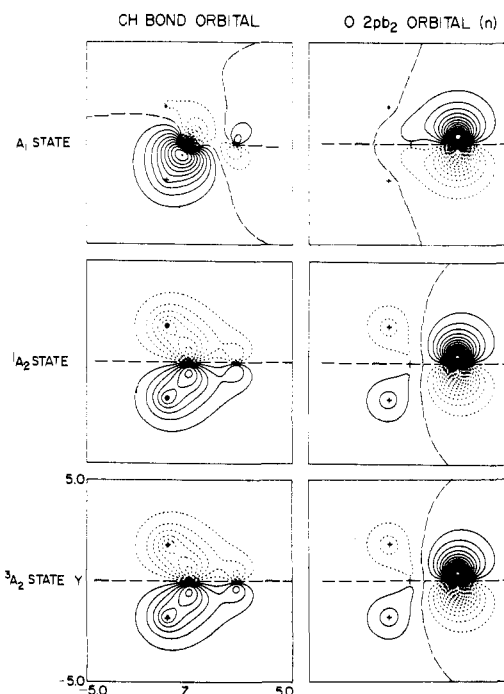Figure 3. The CH and n orbitals of the ground state and n-π^* states of CH$_2$O. The $^1A_1$ orbitals are from the GVB(4) calculation and the remainder are GVB(2) orbitals.

does not change the energy of the wave function, there is no unique set of orbitals. The usual choice is to require a stationary energy for the positive ion state obtained by removing an electron from a doubly occupied orbital. As is well

Table I. Energies and GVB Parameters for the GVB Wave Functions of CH_2O^a

Character	State	Geom	Calculation	Total energy	GVB pair information		
					Pair	Overlap	$\Delta E,^b$ hartrees
Ground state	$^1A_1$	A	HF	−113.8290			
		A	GVB(2)	−113.8850	C−O σ	0.858	0.0151
					C−O π	0.628	0.0427
		A	GVB(2)-DZd	−113.9409	C−O σ	0.867	0.0148
					C−O π	0.653	0.0378
		A	GVB(4)	−113.9162	C−O σ	0.863	0.0144
					C−O π	0.629	0.0425
					C−H $_l$	0.827	0.0161
					C−H$_r$	0.827	0.0161
$\pi \rightarrow \pi^*$	$^3A_1$	A	GVB(2)	−113.6875	C−O σ	0.859	0.0149
$n \rightarrow \pi^*$	$^1A_2$	A	GVB(2)	−113.7413	C−O σ	0.860	0.0147
	$^1A''$	B	GVB(2)	−113.7667	C−O σ	0.832	0.0181
$n \rightarrow \pi^*$	$^3A_2$	A	GVB(2)	−113.7551	C−O σ	0.861	0.0146
	$^3A''$	B	GVB(2)	−113.7780	C−O σ	0.833	0.0179

^{a} All quantities are in atomic units. ^{b} Energy increase upon replacing the GVB pair by a HF pair (averaging the GVB orbitals to obtain the HF orbital).

Table II. Excitation Energies (eV) for CH_2O

	Present work				Other theoretical results			
	HF	GVB(2)	GVB-CI^g	Exptl	CI(PCMO)^h I	CI(PCMO)^h II	WH^i	EOM^j
	Vertical Excitation Energies							
$^3(n \rightarrow \pi^*)$	2.25^h	3.54	3.62	3.5^a	3.01	3.41	3.38	3.46
$^1(n \rightarrow \pi^*)$	2.62^h	3.91	4.09	4.1^b	3.43	3.81	3.80	4.04
$^3(\pi \rightarrow \pi^*)$	4.17^h	5.41	5.95	6.0^a	4.99	5.56	5.66	5.29
$^1(\pi \rightarrow \pi^*)$			10.77^d	$(10.5)^e$	11.72	11.41	11.31	10.10
	Adiabatic Excitation Energies							
$^3(n \rightarrow \pi^*)$	$\sim1.84^f$	2.92	3.03	3.12^c				
$^1(n \rightarrow \pi^*)$	$\sim2.15^f$	3.23	3.42	3.50^c				

^{a} Reference 19. The numbers quoted here are our interpretations of experimental results, assuming that for the large angle (135°) and low energy (10.1 eV) the observed peak is essentially pure triplet. ^{b} Reference 20 (small angle, high-energy results). ^{c} Reference 21 numbers quoted are observed band origins. ^{d} Result of a much larger CI using diffuse functions (to be discussed in a subsequent paper). ^{e} Reference 23. This is our interpretation of experimental results (small angle 15°, high energy, 60 eV) which show a broad transition at this energy and should be considered speculative at this point. ^{f} Obtained by subtracting the pair splitting energies out of the GVB(2) excitation energies. ^{g} The number of spatial configurations for the $^1A_1$, $^3A_1$, $^1A_2$, $^3A_2$, $^1A''$, and $^3A''$ states are 11, 5, 16, 16, 32, and 32, respectively. ^{h} References 24 and 31 (HF-CI). ^{i} Reference 29 (HF-CI). ^{j} Reference 32 (equations of motion).

known, this tends to result in delocalized orbitals. This difficulty is overcome in the GVB(4) calculations where the variational condition uniquely defines the singly occupied orbitals.

4. C–O σ Orbitals. The C–O σ bonding orbitals are essentially the same for all four valence states (see Table I). This is expected from the valence bond description of the states, (3) and (4).

IV. Discussion

A. Excitation Energies. 1. Results. The calculated excitation energies are listed in Table II and compared with experiment. The adiabatic excitation energies to the nπ^* states (3.12 and 3.50 eV) are known accurately from experiment and these values are within 0.1 eV of the calculated (GVB-CI) values (3.03 and 3.43 eV, respectively).

We expect comparable accuracy in our calculated vertical excitation energies, which are about 0.6 eV higher than the adiabatic values. Assigning a vertical excitation energy from the experimental spectrum is ambiguous but the peak in the absorption spectrum is generally used (based on the Franck-Condon principle). The range usually quoted for the triplet n $\rightarrow$ π^* absorption is 3.12–3.44 eV,[22,29,30] whereas we calculate the vertical excitation energy to be 3.6 eV. However, we examined recent electron impact spectra by Chutjian[19,23] and found that for conditions that should emphasize triplet transitions with respect to singlet transitions

(123° scattering angle, 10.1 eV electrons), the peak of the n $\rightarrow$ π^* transition is at 3.5 eV. Taking this as the vertical excitation energy leads to good agreement with our value (3.62 eV).

Similarly experiments at small scattering angle (5°) and with high-energy electrons (250 eV) lead to a peak at 4.1 eV which we consider the vertical transition energy to the $^1(n\pi^*)$ state. This corresponds closely to the observed peak in the photon absorption spectrum, 4.1 eV.[30]

The electron impact experiments[19] also give a peak at 5.9 eV, in good agreement with the value we calculated (5.95 eV) for the $\pi\pi^*$ triplet state.

2. Comparison between Theoretical Values. The dominant configurations for the GVB-CI wave functions are listed in Table III along with their energy contributions (defined as the energy loss upon deleting the configuration).

The major correlation present in GVB-CI and missing in GVB(2/PP) is the (CO$\sigma \rightarrow \sigma^*$,CO$\pi \rightarrow \pi^*$) configuration. The significance of this configuration may be analyzed as follows,

$$\sigma^2\pi^2 - \lambda^2[\sigma\sigma^*][\pi\pi^*] = \frac{1}{2}\{[\sigma^2 + \lambda\sigma\sigma^*] \times$$

$$[\pi^2 - \lambda\pi\pi^*] + [\sigma^2 - \lambda\sigma\sigma^*][\pi^2 + \lambda\pi\pi^*]\} \quad (9)$$

where brackets indicate symmetric coupling, the antisymmetrizer and spin functions are understood, and the relative

phases of the orbitals are taken to be,

$$\sigma : \oplus \oplus \qquad \pi : \begin{matrix} \oplus & \oplus \\ \ominus & \ominus \end{matrix}$$

$$\sigma^* : \ominus \oplus \qquad \pi^* : \begin{matrix} \ominus & \oplus \\ \oplus & \ominus \end{matrix} \qquad (10)$$

The first term on the right-hand side of (9) may be rewritten as

$$[\sigma(\sigma + \lambda\sigma^*)][\pi(\pi - \lambda\pi^*)] \qquad (11)$$

and from (10) can be seen to correspond to a shift of σ electron density to the right and of π electron density to the left. Similarly the second term on the right of (9) corresponds to a shift of σ density to the left and π density to the right.

For the ground state this correlation results in a total energy decrease of 0.6 eV. For the n-π^* states, however, this effect is not as important since three π electrons cannot effectively move onto one center. Therefore, deleting these interpair correlation terms from both states [as in GVB(2)] would decrease the calculated excitation energy by approximately 0.4 eV. However, GVB(2) also omits the $CH_{b_2} \rightarrow \pi^*$ excitations that are important in describing the nπ^* states. The net result of deleting both these effects is a cancellation of errors so that the GVB(2) excitation energy is within 0.1 eV of the GVB-CI results.

The σ-π interpair correlation is also neglected in the GVB(2) triplet π-π^* excitation energy. Here there is no cancelling error and the net result is a GVB(2) excitation energy that is too low by 0.5 eV.

The Hartree-Fock excitation energies listed in Table II are all over 1 eV low, indicating a large difference in correlation energy for the closed shell ground state and the HF open shell excited states. The GVB-CI and GVB(2) results show this difference to be due primarily to the poor description of the π system in the HF ground state.

B. Dipole Moments. Using the DZ basis the ground state dipole moment from the GVB-CI calculation is found to be approximately 10% above the experimental value (Table IV), while the GVB(2) dipole moment is within 1% of the GVB-CI value. Addition of d functions to the basis brings the GVB(2) dipole moment to within 1% of the experimental value.

Dipole moments have also been reported for the singlet[26] and triplet[18] (n $\rightarrow$ π^*) states. In these experiments, though, the observed dipole moment is averaged over the inversion motion of the molecule.[18] Therefore we would expect the observed dipole moment to correspond more closely to the calculated z component. Indeed, for both cases the experimental dipole moment is bounded by the z component and total moment from the GVB-CI calculations.

One major advantage of the GVB wave functions is that since the orbitals are unique and have clear, valence bond characteristics, it is possible to analyze a property such as the dipole moment in terms of orbital contributions. [In order to do this consistently the nuclear contribution is partitioned among the orbital components by associating appropriate nuclear charges with each orbital. For example, we will define the oxygen 2s orbital contribution to the dipole moment as twice the orbital matrix element plus the contribution from a charge of 2+ centered at the oxygen nucleus.]

Applying this kind of analysis to the GVB(4) ground state wave function, we find both the CO σ and π bonds to be highly polar in the same direction, C^+O^-. The σ bond has a contribution of -0.75 au and the π bond -0.50 au. The contribution of the 2s lone pair, -0.73 au, clearly shows the effect of its hybridization away from the C-O σ

Table III. Summary of Important Contributions[a] to the GVB-CI Wave Functions

A. A₁ States (at Geometry A)

State	Configuration σ σ* π π*				Character	Energy contributions,[b] mhartrees[c]
¹A₁	2	0	2	0	GVB	
ground	2	0	0	2	GVB	31.5
state	0	2	2	0	GVB	11.1
	0	2	0	2	GVB	1.8
	1	1	1	1	$\sigma \rightarrow \sigma^*, \pi \rightarrow \pi^*$	23.9
³A₁	2	0	1	1	GVB	
³(π-π*)	0	2	1	1	GVB	15.1
	1	1	2	0	$\sigma \rightarrow \sigma^*, \pi^* \rightarrow \pi$	1.4

B. A₂ and A" States (n-π*)

Configuration						Character	Energy contributions[b] (mh)[c]			
							Geometry A		Geometry B	
σ	σ*	π	π*	CH	n		Singlet	Triplet	Singlet	Triplet
2	0	2	1	2	1	GVB				
0	2	2	1	2	1	GVB	13.2	12.4	16.5	15.2
1	1	1	2	2	1	$\sigma \rightarrow \sigma^*, \pi \rightarrow \pi^*$	7.7	10.4	7.5	11.1
2	0	1	2	1	2	$\pi \rightarrow \pi^*, CH \rightarrow n$	4.9	4.9	2.7	3.4
1	1	2	1	1	2	$\sigma \rightarrow \sigma^*, CH \rightarrow n$	3.7	4.2	3.2	4.0
2	0	2	1	1	2	CH readjustment	2.1	2.1	1.4	1.9
1	1	2	1	2	1	σ readjustment	2.1	0.8	2.6	1.0
2	0	1	2	2	1	π readjustment	1.6	1.6	1.6	2.4

[a] All spatial configurations leading to an energy contribution larger than 1 mhartree are listed. [b] The energy contribution listed here is the increase in the energy that would result from deleting this configuration but without modifying the other CI coefficients. [c] The units here: mhartree (mh) = 10^{-3} hartree = 0.03 eV = 0.6 kcal/mol.

bond. The O 2p lone pair, (n) though, is shifted in the opposite direction giving a contribution of +0.17 au, and the C-H bonds show a shift onto the hydrogens resulting in a contribution of 0.39 au apiece. The net result is a total dipole moment of -1.02 au ($= 2.59$ D), to be compared with an experimental dipole moment of -0.92 au ($=2.34$ D). Note that the contribution of the CO σ and π pairs (-1.25 au) is approximately equal to the total moment (-1.02 au).

Also of interest are the changes in these quantities between the four valence states. The results summarized in Table V indicate that the most significant changes occur in the $b_1(\pi)$ and b_2 orbitals. Both of these contributions actually change direction upon going from the ground state to the n-π^* states. In the b_2 orbitals these components reflect the change from the delocalization of the n orbital into the C-H region to the delocalization of the CH orbitals onto the oxygen as discussed in the previous section.

The change in the b_1 components may be understood as follows. In the ground state where both π orbitals are singly occupied, the delocalization of the carbon p orbital onto the oxygen dominates the b_1 component. In the n-π^* states it is the delocalization of the doubly occupied orbital onto the carbon that dominates. In the limit of the π orbital moving completely onto the carbon, i.e.,
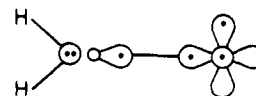
the carbon is negatively charged and the oxygen positively charged. This delocalization, then, results in the reversal of the b_1 components of the dipole moment of the (n $\rightarrow$ π^*) states.

As noted in section IIIB, consideration of the effect of the $K_{n\pi^*}$ exchange integral indicates the π orbitals of the ^{3}(n $\rightarrow$

Table IV. Dipole Moments

State	Character	Type of calculation	Geom	Components, au		Total |μ|	
				μ_x	μ_z	au	Debye
$^1A_1$	G.S.	HF	A	0	−1.22	1.22	3.10
		GVB(2)	A	0	−1.02	1.02	2.59
		GVB(2)-DZd	A	0	−0.93	0.93	2.36
		GVB(4)	A	0	−1.03	1.03	2.62
		GVB-CI	A	0	−1.02	1.02	2.59
		Exptl	A			0.913	2.32[a]
$^3A_1$	$\pi \rightarrow \pi^*$	HF	A	0			
		GVB(2)	A	0	−0.523	0.523	1.33
$^1A_2$	$n \rightarrow \pi^*$	HF	A	0	−0.768	0.768	1.95
		GVB(2)	A	0	−0.665	0.665	1.69
		GVB(2)	B	−0.303	−0.603	0.675	1.71
		GVB-CI	B	−0.352	−0.573	0.673	1.71
		Exptl	B			0.614	1.56[b,d]
$^3A_2$	$n \rightarrow \pi^*$	HF	A	0	0.693	0.693	1.76
		GVB(2)	A	0	0.600	0.600	1.52
		GVB(2)	B	−0.345	−0.548	0.647	1.64
		GVB-CI	B	−0.414	−0.470	0.627	1.59
		Exptl	B			0.508	1.29[c,d]

[a] Reference 25. [b] Reference 26. [c] Reference 18. [d] The observed n → π* dipole moments are averaged over the inversion motion in these states and hence are expected to correspond more closely to the calculated z components.

Table V. Orbital Components of the Dipole Moment (in au) of CH_2O from the GVB(2) Wave Function and the Ground State Geometry

	Components[a]				
	A_1 core	CO	$\pi(B_1)$	B_2	Total
$^1A_1$	−0.194	−0.613	−0.491	+0.280	−1.02
$^3A_1$	−0.229	−0.644	+0.118	+0.232	−0.523
$^1A_2$	−0.242	−0.637	+0.366	−0.148	−0.661
$^3A_2$	−0.257	−0.639	+0.489	−0.193	−0.600
Atomic H	1	0	0	1	
charges[a] C	3	1	1	1	
O	4	1	1 (2)[b]	2 (1)[b]	

[a] In order to obtain meaningful (origin independent) dipole moments, the nuclear contributions are partitioned among the components by assigning charges based on the direction of the orbitals according to the GVB diagrams (3) and (4). The assigned charges are listed at the bottom of the table. [b] Values in parentheses are for the A_2 states.

π*) state to be more delocalized than those of the ^{1}(n → π*) state.

An alternative interpretation of this difference in the dipole moments of the singlet and triplet (n → π*) states was suggested by Buckingham, Ramsay, and Tyrrell.[18] They assume that in going from a singlet state to the corresponding triplet state the electrons move further apart and suggest that in the case of a polar molecule, this movement will be greater toward the positive end of the molecule. The result is a decrease in the dipole moment of the triplet state relative to that of the singlet state.

We find that the decrease in the dipole moment of the ^{3}(π → π*) state relative to the ground state is correctly explained by the interpretation of ref 18. For the (n → π*) states, however, since the n and π* orbitals are orthogonal, we find the explanation to be essentially the reverse of that proposed by Buckingham; the π* orbital of the triplet state moves *toward* the n orbital, rather than away.

C. Comparison with Previous Calculations. 1. Excitation Energies. A summary of previous calculations on the valence excitation energies of formaldehyde is contained in Table II. With the exception of the HF calculations (see section A), there is reasonable agreement between the various calculated n → π* and ^{3}(π → π*) excitation energies. The GVB-CI results, however, consistently lead to slightly higher vertical excitation energies in closer agreement with

the experimental values. It should be noted that all of the other CI calculations listed in Table II employ HF calculations on each of the states as a basis for the CI calculations. (We will denote this HF-CI.) As is well-known, HF calculations lead to much larger errors for the ground state than for the excited states, whereas the GVB method leads to a more balanced description. The low-excitation energies found with HF-CI as compared to GVB-CI are probably just due to this poor initial description of the ground state.

2. Dipole Moments. The results reported here and elsewhere[27,33] indicate sizable errors in the Hartree–Fock dipole moments (on the order of 30%). We find this to be due primarily to the π contribution. The HF π component is calculated to be −0.72 au, as compared with the GVB(2) result of −0.49 au. This indicates the HF wave function overemphasizes the closed shell configuration,
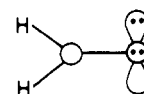

where both π electrons are on the oxygen. The error in the HF $^1A_2$ and $^3A_2$ dipole moments[27] (where the π system is properly described) is found to be much smaller (∼0.1 au).

Using the DZ basis for the ground state, the GVB-CI dipole moment (1.02 au) is found to be in closer agreement with experiment (0.913 au) than previously reported HF-CI dipole moments (1.16 and 1.23 au).[22,29] This then is another indication that the HF-CI ground state calculations contain inaccuracies due to the poor initial description of the ground state.

Comparisons with experiment for the excited state dipole moments calculated with HF-CI are not possible since HF-CI dipole moments were reported only for the ground state geometry.

V. The O_2 Model of H_2CO

An alternative analysis of the states of H_2CO can be based on the isoelectronic molecule O_2, where we consider the H–C bonds to correspond to double-occupied O 2s and 2pπ orbitals of O_2. Thus (3) and (4) become,
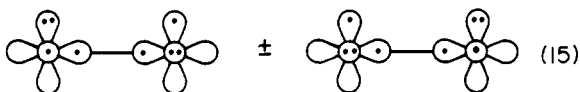

(12)

(13)
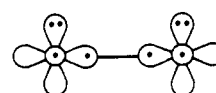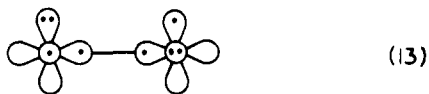
respectively. Coupling the singly occupied orbitals of (12) and (13) gives a total of two singlet states and two triplet states just as in H_2CO; however, neither (12) nor (13) is a satisfactory description of the states of O_2. Combining (13) and (14)
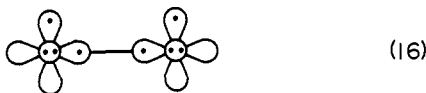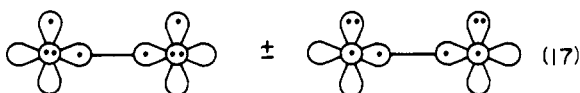

(14)

to obtain

±

(15)

and coupling the singly occupied orbitals appropriately leads to the ground state, $^3\Sigma_g^-$, and one component of the $^1\Delta_g$ state (which lies 1 eV above the ground state).

Similarly combining (12) with (16)

(16)

to obtain

±

(17)

and coupling the orbitals into a singlet leads to the $^1\Delta_g$ and $^1\Sigma_g^+$ states of O_2.

A more useful form of these relationships is to express the energy of configurations 12 and 13 in terms of the states of O_2 and to use the correspondence to (3) and (4) as follows,

$$H_2CO(^1A_1) = \frac{1}{2}[O_2(^1\Delta_g) + O_2(^1\Sigma_g^+)] = 1.40 \text{ eV}$$

$$H_2CO(^3A_2) = \frac{1}{2}[O_2(^3\Sigma_g^-) + O_2(^3\Delta_u)] = 3.0$$

$$H_2CO(^1A_2) = \frac{1}{2}[O_2(^1\Delta_g) + O_2(^1\Sigma_u^-)] = 3.4$$

$$H_2CO(^3A_1) = \frac{1}{2}[O_2(^3\Sigma_u^+) + O_2(^3\Delta_u)] = 6.1$$

where the energies are based on the O_2 energies using the ground state geometry. Comparing these energies with the calculated energies of H_2CO (0.0, 3.6, 4.1, and 5.9) we find reasonable correspondence.

VI. Summary

The GVB wave function leads to a consistent description of the valence states of formaldehyde, and the GVB orbitals provide simple explanations of the character of the states. In addition, these orbitals form a very suitable set for including the additional correlation effects with relatively small CI calculations.

References and Notes

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