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Electron Density Analysis of the n $\rightarrow$ π^* Transition of Formaldehyde

Andrew Streitwieser* and Boris Kohler

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received June 25, 1987*

Abstract: Double-ζ molecular orbital (MO) calculations with configuration interaction including all singles and doubles are reported for formaldehyde in its ground ($^1A_1$) and singlet ($^1A_2$) and triplet ($^3A_2$) n $\rightarrow$ π^* excited states at the ground-state geometry. Analyses of projected electron density functions show that these excited states involve primarily an oxygen p $\rightarrow$ p transition with relatively small leakage of electron density to carbon. The results are compared to a simple MO picture and rationalized. Comparison of the singlet and triplet excited states shows the latter to involve electron transfer both to carbon (greater nucleophilicity) and closer to the oxygen nucleus (greater stability).

Formaldehyde occupies an important position in organic photochemistry. A detailed study has been made of its spectroscopy.[1] Because of the structural simplicity of formaldehyde, a discussion of its molecular orbitals and states form a general introduction to carbonyl photochemistry and especially to n $\rightarrow$ π^* transitions of carbonyl compounds.[2] A large number of molecular orbital calculations have already been carried out at semiempirical,[3] Hartree–Fock,[4] generalized valence bond (GVB),[5] and configuration interaction[6,7] levels. Few of these studies, however, have involved electron-density analyses. Dunning and Winter[4f] have examined in some detail, but only at self consistent field (SCF) level, the electron density of the ground state. Buenker and Peyerimhoff[7b] gave brief consideration to some electronic densities for various states of formaldehyde with SCF including partial configuration interaction (CI). In the present study we present a more detailed electron-density study of formaldehyde and some of its excited states calculated at the double-ζ (DZ) level with configuration interaction including all singles and doubles. The results provide important and heuristic visualization of the electronic changes accompanying excitation and point up some significant limitations in common molecular orbital (MO) interpretations.

MO Calculations. A standard[8] planar structure was adopted for formaldehyde with $r(\mathrm{C{=}O}) = 1.22$ Å, $r(\mathrm{C{-}H}) = 1.08$ Å, $\angle(\mathrm{HCH}) = 120°$ for all of the states considered. The OC bond is taken as the z axis, and the molecule lies in the yz plane. Accordingly, the n $\rightarrow$ π^* transition is $^1A_1 \rightarrow {}^1A_2$, and we made a separate calculation of the $^3A_2$ state. The computations involve SCF, CI, and approximate natural orbitals (NO's) and were performed on a Harris Slash Four minicomputer for theoretical chemistry, operating the Cal Tech–Berkeley–Ohio State Version[9] of the POLYATOM program.[10] In all calculations we used the completely DZ standard basis set of Huzinaga (9s5p/4s),[11] with the (4s2p/2s) contraction and coefficients suggested by Dunning,[12] and a scale factor of 1.2 for the hydrogen 1s functions.

The open-shell A_2 states were calculated by using restricted theory to give for the three states considered the (spinless) electronic configurations:

$$^1A_1 \quad (1a_1)^2 \ldots (4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$$

$$^1A_2 \quad (1a_1)^2 \ldots (5a_1)^2(1b_2)^2(1b_1)^2 2b_2 2b_1$$

$$^3A_2 \quad (1a_1)^2 \ldots (5a_1)^2(1b_2)^2 2b_2 (1b_1)^2 2b_1$$

The CI included all single and double excitations relative to the parent SCF reference configuration of each state involved. This treatment is justified[13] by the fact that the wave functions of all three states are dominated by the Hartree–Fock determinants, which have coefficients in the CI expansion of greater than 0.95 in all cases. In preliminary calculations the core of 1s orbitals on oxygen and carbon were frozen, but all MO's were included at a later stage. In the simplest treatment only 6 (7) occupied MO's were correlated for a total of 1471 (1772) configurations for the $^1A_1$ ($^1A_2$) states, respectively. Correlation through all single and double excitations gave 2749, 3232, and 3283 configurations for the $^1A_1$, $^1A_2$, $^3A_2$ states, respectively. The energies obtained are collected in Table I. The results compare well with the most recent literature values, obtained at same level.[7]

Davidson's approximation was used to estimate the effect of correlation involving higher than double excitations.[14] Siegbahn[15] has suggested that this approximation, although possibly not of

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Table I. Number of Configurations, Calculated Energies, Dipole Moments, and Transition Energies for Formaldehyde

state	observable	DZ SCF	CI[a]	CI[b]	CI + QG[c]	NO[d]
$^1A_1$	no. configs	1	1471	2749	2749	2749
	$-E$, *h*	113.830 385	114.035 072	114.059 853	114.078 020	114.058 852
	μ, calcd	3.199	2.727	2.748		2.640
	expl[e]	2.33				
	IPP(O)[f]	8.82		8.83		8.74
$^1A_2$	No. configs	1	1773	3232	3232	3232
	$-E$, *h*	113.733 871	113.900 451	113.925 386	113.939 541	113.925 175
	ΔE, calcd, eV	2.63		3.66	3.77	
	expl[g]	4.1 (3.50)				
	μ, calcd	1.739	1.748	1.745		1.813
	expl[h]	1.56				
	IPP(O)[f]	8.58		8.57		8.58
$^3A_2$	no. configs	1		3283	3283	3283
	$-E$, *h*	113.747 553		113.939 885	113.957 358	113.939 966
	ΔE, calcd, eV	2.25		3.26	3.28	
	expl[g]	3.5 (3.12)				
	μ, calcd	1.561		1.495		1.511
	expl[h]	1.29				
	IPP(O)[f]	8.51		8.45		8.54

[a] All singles and doubles, frozen core. [b] All singles and doubles. Coefficient of the SCF configuration in the CI expansions are, respectively, 0.959 597, 0.962 336, 0.953 492. [c] With unlinked cluster quadrupoles correction (ref 14). [d] Natural orbital final iteration. [e] Reference 19. [f] Integrated projection population on oxygen. [g] Vertical (adiabatic) excitation energies as given in ref 5. [h] References 20 and 21.

extremely high accuracy, does give the right trend and order of magnitude for even higher than unlinked cluster quadruples corrections. This correction is included in Table I. There is good agreement between the calculated $^1A_1 \rightarrow {}^1A_2$, $^1A_1 \rightarrow {}^3A_2$ transitions and experimental vertical transitions.[16]

Natural orbitals were chosen for studying electron densities since they are known to yield the best one-electron properties.[17] The NO's were approached from the CI expansion through a well-documented iterative procedure.[14b,18] Iterations were stopped when the dipole moment changed by <0.01 D. The difference between the experimental[19] and calculated dipole moments of the $^1A_1$ state is typical of previous results at this level.[4g-i,6c,7g] The NO-calculated dipole moments of the A_2 states are actually further from experiment[17,21] than the CI-based value (Table I). This is at first sight disturbing until we recall that the experimental dipole moments refer to equilibrium (bent) geometries rather than the planar "standard" geometry, which is the only geometry considered in our calculations. Since our emphasis is on electron-density changes from ground to excited states, any change in nuclear positions would add additional complexity from the movement of cores without contributing to insight. A difference in dipole moments of the order of 0.3 D appears reasonable for the difference between Franck–Condon and relaxed geometries.[20,22] For the ground state, the NO dipole moment is closest to the experimental value.

Projection Functions. A few authors have used contour and perspective diagrams of calculated electron-density (or density difference) functions in order to explore the electronic structure of formaldehyde.[4f,7f] Various representations have been presented for electron density difference functions resulting from excitation.[3h,23-28] An important problem is that the electron-density function is a four-dimensional function that is commonly represented as contour levels for individual geometric planes important for a molecule—usually the molecular plane. Excitation can involve large transfers of electron density from one plane to another. Thus, a normal planar contour rendition of the n → π* transition of formaldehyde would show only negative contours for the density difference in the molecular plane and positive contours in the π plane. The "Delta Plots" of Morrison et al.[3h,24] avoid this problem with perspective representations of an individual positive and negative contour as solid shapes. These plots provide

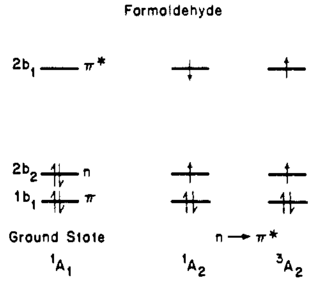

Figure 1. Simple orbital diagram for formaldehyde in its ground and n → π* excited states.

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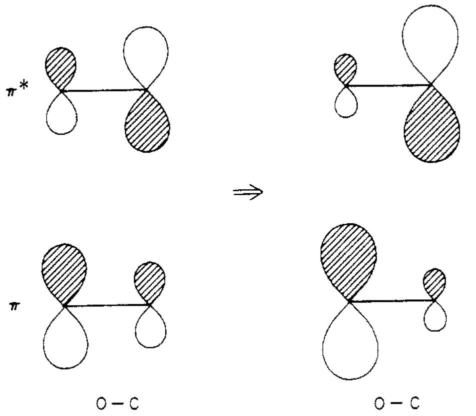

Figure 2. Schematic diagram of the π and π^* MO's of formaldehyde before (left) and after (right) $n \rightarrow \pi^*$ excitation.

excellent visualization of gross functions but can hide some details and are not useful for quantitative evaluation or integration.

For some time we have used contour representations of a *projection function* that is particularly useful for systems described adequately by a plane.[26,27] This function is the integral of the density function[28] along an axis perpendicular to the chosen plane. For Gaussian functions, this integration is analytical and rapid. The program PROJ[27] was modified for the present purpose by allowing noninteger MO occupancies. Integrations were carried out for regions bounded by minima in the projected density functions to give the numerical "integrated projection populations", IPP.[29] The minimum density demarkations of such projected functions are approximations to the virial boundaries of Bader;[30] these boundaries are vertical curtains compared to the true virial curved surfaces. Accordingly, the derived integrated populations are only approximations to the true integrations over Bader "basins"; however, they are expected to be qualitatively correct and are faster to compute. IPP values for oxygen are summarized in Table I. True Bader integrations would involve only the density function of a given state, a physical observable. We also calculated the integrated values by using as demarkation lines the zero contours of the difference projection functions; these therefore give an approximation to the *change* in electron population in a given region. Note that by this definition the integral of the difference function over the entire plane chosen must vanish. This technique has been applied to the $^1A_1 \rightarrow {}^1A_2$ and $^1A_2 \rightarrow {}^3A_2$ transitions of formaldehyde, and the calculated ΔIPP values are given on the figures. Plots were calculated for all three computational levels, SCF, CI, and NO, but the differences are relatively small, and only one is shown.

$n \rightarrow \pi^*$ Transition. The usual simple MO description of the $n \rightarrow \pi^*$ transition of formaldehyde is shown in Figure 1.[2] The singlet excited $n \rightarrow \pi^*$ state is formed by promotion of an electron from the lone pair n ($2b_2$) MO to the π^* ($2b_1$) MO, keeping the two odd electrons of opposite spin. In the π MO the coefficient of the oxygen orbital is greater than that of carbon because of its greater electronegativity (Figure 2). Conversely, to preserve orthogonality the amplitudes are reversed in the π^* MO. The n orbital is localized mostly on oxygen. Thus, the $n \rightarrow \pi^*$ transition involves removing an electron from an orbital mostly on oxygen and putting it in an orbital predominantly on carbon; this implies significant oxygen to carbon charge transfer. These effects are clearly evident in the Delta Plots of Morrison et al.[3h,24]

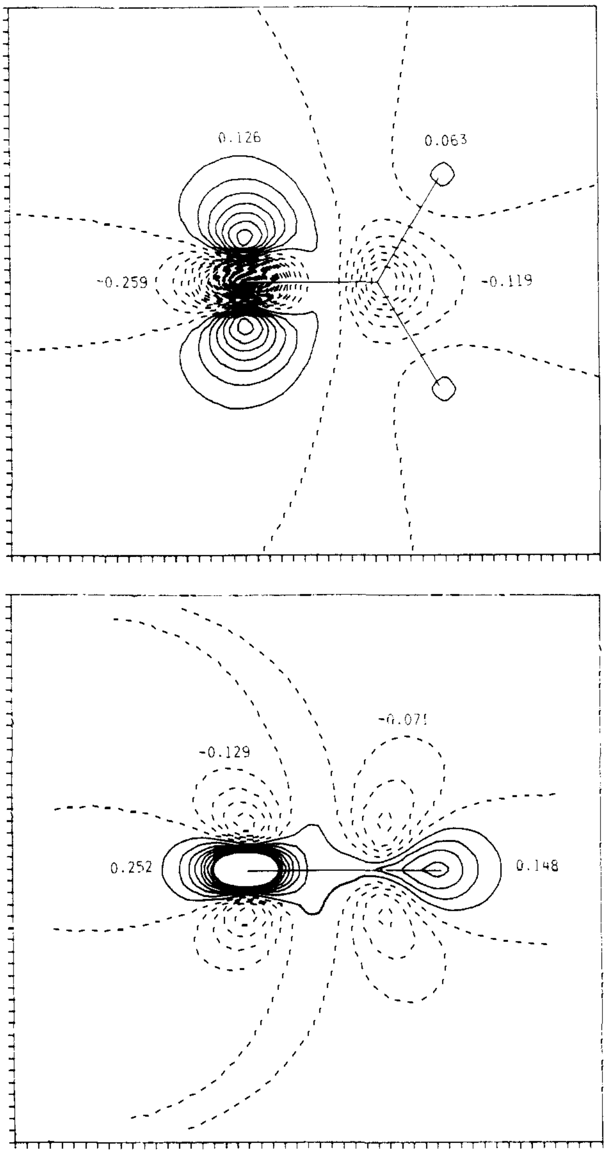

Figure 3. Difference projection function, $^1A_1 \rightarrow {}^1A_2$, for formaldehyde in the molecular plane (top) and the perpendicular plane (edge-on, bottom), NO CI. Contour levels from −0.10 to +0.16 by 0.02 e au^{-2}. Solid contours show where electrons are denser in the ground state.

The dipole moment does show a calculated (final NO, Table I) reduction in magnitude from 2.64 D in $^1A_1$ to 1.81 D in $^1A_2$, but the change is relatively small and the net moment is still in the same direction (C^+O^-). The difference projection plots in Figure 3 show what has happened. The upper plot is for the molecular plane. The solid contours are essentially those of the lone-pair electrons localized in the ground state primarily on oxygen. On excitation they increase the density, as indicated by the dashed lines, of the π-system on which we are looking down. But the contours are much denser at oxygen than on carbon! This point is affirmed by the alternative projection on the bottom of Figure 3. The solid contours show the lone pair of the ground state now edge on. The dashed lines look much like a π^* orbital but with the contours denser at oxygen than on carbon. The numbers show the ΔIPP values for the indicated regions and confirm the qualitative visual impression. In short, the $n \rightarrow \pi^*$ transition of formaldehyde is essentially an oxygen $p \rightarrow p$ transition with some leakage of electrons to carbon.

This result is not completely unexpected because it is inherent in the net dipole moments. Nevertheless, past discussions have emphasized the reversal of dipole moment components,[5] and the changes in total electron densities are different than expected on looking only at the n and π^* orbitals.[24] One rationalization of this apparent dichotomy is shown in Figure 2. Removal of a lone-pair electron from oxygen makes the oxygen effectively more

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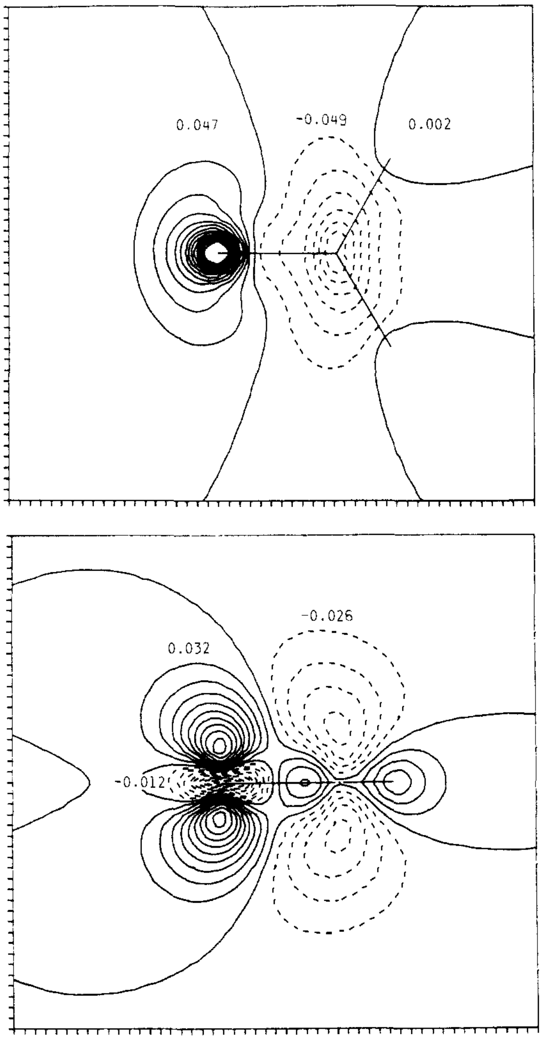

Figure 4. Difference projection function, $^1A_2 \rightarrow {}^3A_2$, for formaldehyde in the molecular plane (top) and the perpendicular plane (edge-on, bottom), NO CI. Contour levels from -0.05 to 0.05 by 0.002 e au^{-2}.

electronegative. The corresponding schematic MO picture is shown on the right of Figure 2. Thus, although an electron is put into the π^* orbital heavily weighted toward carbon, the π MO is still *doubly* occupied and weighted more heavily toward oxygen than in the ground state. The carbon does have greater π--density than in the ground state and should be more π donating; but the present results show that the net change is relatively small.

Finally, some comment should be made concerning the relevance of the electron density changes to photochemistry. The photochemistry of formaldehyde has been studied in extensive detail.[31] Two major pathways are important: formation of molecular hydrogen plus carbon monoxide and Norris Type I cleavage to radicals, but it has been shown that these reactions involve primarily excited vibrational states of the ground electronic state. That is, $^1A_2$ can decompose via a barrier (higher vibrational states) to hydrogen atom and an excited formyl radical, but most reaction occurs by internal conversion to $^1A_1$ having sufficient internal energy to undergo further reaction.[31b] Accordingly, the electron density difference functions in Figure 3 have no relevence to such photochemical reactions. This limitation would not apply to other carbonyl compounds that do undergo reactions in the excited electronic state.

Singlet vs Triplet. The dipole moment calculated for the triplet n → π^* state is significantly less than that of the singlet (Table I) in agreement with previous calculations and with experimental results for the nonplanar relaxed states. There is less agreement, however, about the interpretation of this difference.[32] Interesting insight is obtained from Figure 4 in which the NO projection function of $^3A_2$ is subtracted from that $^1A_2$; that is, this difference between the singlet and triplet n → π^* excited states corresponds to a Franck–Condon intersystem crossing. The top plot for the molecular plane shows transfer of significant density from oxygen to carbon in the $^1A_2 \rightarrow {}^3A_2$ transition, in agreement with the reduction in dipole moment. The more electron rich or nucleophilic carbon of the triplet state is in agreement with mechanistic inferences of oxetane formation in reactions of excited carbonyl compounds with olefins.[33,34] However, the transfer of electron density to the *less* electronegative atom seems inconsistent with the greater stability of the triplet state. The explanation is found in the side view on the bottom of Figure 4. This plot shows a polarization of some oxygen electron density closer to the nucleus accompanied by a greater density transfer from the periphery of the oxygen to carbon. That is, with the change in spin, the Fermi hole about each electron allows increased density close to the nucleus. This small change provides the bulk of the stabilization. As a consequence of the virial theorem an excess of electrons located in the outer periphery of an electronic system is necessary to compensate for the virial of a smaller amount of electrons closer to the nucleus. In other words, a few electrons closer to the oxygen center act as a screen toward a greater number of outside electrons. As far as the outer electrons are concerned, the oxygen is now less electronegative, and some outer density shifts to carbon.

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Registry No. Formaldehyde, 50-00-0.

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[31] For recent reviews, see: (a) Lee, E. K. C.; Lewis, R. S. *Adv. Photochem.* **1980**, *12*, 1. (b) Moore, C. B.; Weisshaar, J. C. *Annu. Rev. Phys. Chem.* **1983**, *34*, 525. (c) Jackson, W. M.; Okabe, H. *Adv. Photochem.* **1986**, *13*, 1.

[32] Compare, for example, ref 5 with ref 21. The interpretation given below shows that both of these sets of authors are correct!

[33] Turro, N. J.; Farrington, G. L. *J. Am. Chem. Soc.* **1980**, *102*, 6051 and 6056.

[34] (a) Herndon, W. *Tetrahedron Lett.* **1971**, 125; *Mol. Photochem.* **1970**, *2*, 277. (b) Epiotis, N. D. *J. Am. Chem. Soc.* **1972**, *94*, 1941 and 1946. (c) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.