

Basicity of some proto-typical carbonyls in the ground and some low lying excited states: Application of the orthogonal gradient method of orbital optimization in an INDO–MC–SCF framework – I

CHITRANI MEDHI and S P BHATTACHARYYA*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

MS received 27 February 1992; revised 8 October 1992

Abstract. Gas phase proton affinities of formaldehyde and fluoroformaldehyde in the ground, $^1\text{}^3n\pi^*$ (lowest) and $^3\pi\pi^*$ (lowest) states have been theoretically studied within the framework of the INDO–MC–SCF orthogonal gradient method developed earlier. Complete geometry optimization has been carried out for both the protonated and unprotonated bases in the ground and relevant excited states. Computed proton affinities (PA) of H_2CO in different electronic states are in the following order:

$$\text{PA}(^1S_0) > \text{PA}(^3\pi\pi^*) \sim \text{PA}(^1n\pi^*) > \text{PA}(^3n\pi^*).$$

In F_2CO , however, the ordering turns out to be different viz. $\text{PA}(^1S_0) > \text{PA}(^1n\pi^*) > \text{PA}(^3n\pi^*) > \text{PA}(^3\pi\pi^*)$ for protonation at the carbonyl oxygen. For protonation at the F atom the ordering is $\text{PA}(^1S_0) > \text{PA}(^3n\pi^*) > \text{PA}(^1n\pi^*) > \text{PA}(^3\pi\pi^*)$. Protonation at the oxygen atom is predicted to be energetically more favourable than protonation at one of the F atoms by approximately 30 kcal/mole in all the states studied. The role of Fermi correlation in shaping the difference in proton affinities of the singlet and triplet $n\pi^*$ states of H_2CO is discussed.

Keywords. Excited state basicities; theoretical proton affinities; orthogonal gradient method; Fermi correlation; $n\pi^*$ states of carbonyl.

1. Introduction

The concept of acidity or basicity of molecules is a very general and useful empirical concept. Despite divergent views, an acid is generally taken to be an electron acceptor and a base to be an electron donor. The very definition implies the possibility of existence of a close connection between the electron density distribution and the acid–base properties of a molecule. Since many electronic transitions are often accompanied by extensive reorganization of molecular electronic charge distribution, acidity or basicity of the same molecule may vary from state to state. The direct measurement of acid–base properties of molecules in excited states in the presence of a solvent mainly utilizes absorption and fluorescence spectral data in conjunction with the Forster cycle (Forster 1950; Ottolenghi 1973; Saeva and Olin 1975; Ireland and Wyatt 1976) to estimate changes in pK in the excited singlet and triplet states. The interpretation of the results requires accounting for the solvation effects. Gas

* For correspondence

phase methods such as flowing afterglow (Bhome *et al* 1973; Beauchamp 1974), high pressure mass spectrometry (Yamadagni and Kebarle 1973; Bhome *et al* 1974), drift tubes (Solomon *et al* 1974; Long and Franklin 1974) and ion cyclotron resonance (ICR) spectroscopy (Brauman and Blair 1970; Weiting *et al* 1974; Staley and Beauchamp 1975) have the advantage of determining the intrinsic ground state acid–base properties in the absence of complicating effects of solvation. ICR spectroscopy has been very successfully applied to the determination of the gas phase acid–base properties of molecules in excited states as well (Frieiser and Beauchamp 1977).

For molecules containing the carbonyl or other “lone-pair” chromophores, protonation and hydrogen bonding are of importance in a variety of contexts. Being a small molecule, the basicity of formaldehyde, the simplest carbonyl chromophore, has naturally been the target of a number of theoretical and experimental investigations. These studies are mainly confined to the formaldehyde molecule in its ground electronic state (Harrison *et al* 1966). Similar studies on excited states of the species are rather scarce. Strausz *et al* (1978) performed *ab-initio* SCF–MO studies on proton affinities (vertical) of H₂CO in the ground (¹S₀), ³nπ* and ³ππ* states and concluded that the basicity order is ¹S₀ > ³nπ* > ³ππ*. Several other studies have appeared since then, both at the semiempirical (Bhattacharyya *et al* 1983; Dekock *et al* 1983), and *ab-initio* levels (Strausz *et al* 1982) which stressed on the state and geometry dependence of the basicity of the formaldehyde molecule.

Ab-initio calculation of excited state PA being difficult, we have undertaken elaborate investigations on the basicity of some small carbonyl chromophores in a number of low-lying excited states within the framework of our INDO–(MC)–SCF orthogonal gradient method of orbital and geometry optimization (INDO–MC–SCF–OGM). The reason for selecting this particular methodology lies in its success in the calculation of structural features of small carbonyl and thiocarbonyl systems in excited states (Das *et al* 1986, 1989). Our investigations aim at covering broadly the following aspects: (i) The variations in proton affinities of X₂C=O type of carbonyls (X=H, F) from state to state. (ii) The types and extents of electronic and structural reorganizations following protonation. Of special interest in this connection is the effect of protonation on the C=O bond. (iii) The kind and extent of spectral shift caused by protonation. (iv) The relative importance of the initial (before protonation) or the final (after protonation) state electron density distribution in shaping the proton affinity in a particular state, etc. (v) The role, if any, played by Fermi correlation in determining the difference in PA of the singlet and triplet nπ* states.

2. The method

The variational trial function ($\tilde{\psi}$) for the lowest nπ* states (^{1,3}A'') is chosen in the following form:

$$\tilde{\psi} = 1/\sqrt{2}[|\phi_1 \bar{\phi}_1 \cdots \phi_i \phi_j \cdots \phi_n \phi_n| + (-1)^s |\phi_1 \bar{\phi}_1 \cdots \phi_i \bar{\phi}_j \cdots \phi_n \bar{\phi}_n|],$$

where ϕ_i represents the relevant non-bonding orbital and ϕ_j , the π* orbital involved in the excitation; s is equal to zero for the singlet and 1 for the triplet coupling of the spins. For the ³ππ*(³A') state, ϕ_i would represent the π orbital and ϕ_j the π*

orbital involved in the transition. We have not included any more configurations in $\tilde{\psi}$ since protonation is expected to be dominated by relaxation effects which the present form of $\tilde{\psi}$ can adequately account for. The variational optimization of $\tilde{\psi}$ therefore boils down to the solution of the MC-SCF orbital equation (Mcweeny 1968; Mcweeny and Sutcliffe 1969)

$$V = ST\lambda. \quad (1)$$

S represents the overlap matrix in the n -dimensional AO (x) basis set of expansion and T , the matrix of the LCAO expansion coefficients of the m -occupied MOs (ϕ) ($n \gg m$): viz.

$$\Phi(|\phi\rangle, |\phi_2\rangle \cdots |\phi_m\rangle) = x(|x\rangle \cdots |x_n\rangle) T(n \times m),$$

λ represents the matrix of Lagrangian multipliers which must be Hermitian ($\lambda^+ = \lambda$) at the stationary point of the energy functional. The MC-SCF energy matrix V in (1) has been represented in a mixed (AO-MO) basis and is given by

$$V = hTP_1 + Z(P_2). \quad (2)$$

In (2) h represents the one-electron part of the Hamiltonian in the x -basis and P_1 is the one-electron density matrix in the ϕ -basis. Z in (3) represents the two-electron part of the Hamiltonian formed in a mixed AO-MO basis and is defined as follows:

$$Z_{pi} = \sum_{jkl} \sum_{qrs}^{MO \ AO} T_{js}^\dagger \langle ps|qr \rangle T_{kq} T_{lr} P_{2kl,ij}. \quad (4)$$

P_2 represents the two-electron density matrix in the ϕ -basis. The matrix elements of Z and h have been, in the present context, evaluated under the standard sets of INDO approximations and parametrized accordingly. Equation (1) has been solved iteratively by a variant of the orthogonal gradient method (OGM) of orbital optimization (Mukherjee 1978; Golebiewski *et al* 1979; Bhattacharyya and Mukherjee 1979, 1981; Das *et al* 1986, 1989). OGM involves the construction of the following iterative sequence:

$$T_i \rightarrow T_{i+1} = S^{-1} V_i [(V_i^\dagger S^{-1} V_i)]^{-1/2}.$$

The geometry optimization has been carried out by a pattern search method and interpolation involving the use of cubic splines. Occasionally we encountered convergence difficulties which were tackled by invoking a "root-shifting" procedure recently suggested by us (Sarkar *et al* 1989; Das and Bhattacharyya 1991; Medhi *et al* 1993).

3. Results and discussion

3.1 Protonation of H_2CO

(a) Table 1 summarizes fully optimized geometrical parameters of a free and protonated formaldehyde molecule in the ground state and some low-lying excited states in the gas phase. Both H_2CO and $H_2COH^{(+)}$ turn out to be planar species

Table 1. Geometrical features of H_2CO and H_2COH^+ in the ground and low-lying excited states computed by the INDO-MC-SCF orthogonal gradient method.

Species	State	$r_{\text{O-H}}$ (Å)	r_{CH} (Å)	r_{CH_2} (Å)	r_{CO} (Å)	$\text{H}_1\text{-C-H}_2$ (deg)	$\text{H}_1\text{-C-O}$ (deg)	C-O-H^+ (deg)	(in degrees)
H_2CO	Ground	1.117	1.117	1.117	1.249(1.22) ^a	115.8	122.1	--	0
H_2COH^+		1.115	1.117	1.117	1.266(1.27) ^a	121.7	121.2	122.1	0
H_2CO	$(^3n\pi^*)^3A''$	1.107	1.107	1.107	1.315	125.2	117.2	(117.1) ^b	36.5
H_2COH^+	$(^3n\pi^*)^3A''$	1.112	1.112	1.112	1.323	130.2	114.9	180.0	0
H_2CO	$(^1n\pi^*)^1A''$	1.107	1.107	1.107	1.320	124.4	117.8	--	28.2
H_2COH^+	$(^1n\pi^*)^1A''$	1.112	1.112	1.112	1.337	130.8	114.6	180.0	0
H_2CO	$(^3\pi\pi^*)^3A'$	--	1.107	1.107	1.384	121.2	119.4	--	35.5
H_2COH^+	$(^3\pi\pi^*)^3A'$	1.051	1.110	1.111	1.4170	125.7	118.3	116.3	0
							(116.0) ^b		

(a) For definition of various geometrical parameters see figures 1a, b.

(b) H_2CO angle in the protonated species.

(c) Dekock *et al* (1983).

in the ground state with the C=O-H⁽⁺⁾ fragment having an angular disposition, the proton making an angle $\sim 120^\circ$ with the C=O bond axis. The C=O bond itself is seen to have become considerably elongated following protonation at the carbonyl oxygen atom. These features compare favourably with the available *ab-initio* data (Strausz *et al* 1982). The same table also displays data on the structural features of a free and protonated formaldehyde molecule in the $^1,^3n\pi^*$ and $^3\pi\pi^*$ states. While the unprotonated species are rigidly non-planar, the protonated counterparts have planar disposition. The C=O-H⁺ fragment is linear in the $n\pi^*$ states and has a nonlinear ground state-like arrangement in the $^3\pi\pi^*$ states. The orientation of the added proton therefore seems to be controlled by the magnitude and disposition of the non-bonded electron-density on the carbonyl oxygen atom. These findings are in agreement with the available *ab-initio* theoretical data (Strausz *et al* 1982).

(b) Since we find (table 1) that the C=O bond is considerably elongated following $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ excitation and further elongated after protonation we can anticipate that considerable π -electron density must have migrated away from the C=O bond region under the influence of the added proton. We have therefore computed generalized quantum chemical bond order (see appendix-A) for the C=O bond in different electronic states before and after the protonation. Table 2 summarizes the computed bond lengths and bond orders. A perusal of the entries in table 2 would suggest that the C \leftrightarrow O stretching frequency would systematically fall due to excitation and, further, due to protonation.

(c) Table 3 displays n , π and π^* orbital (scf) energies and the $n - \pi^*$ and $\pi - \pi^*$ orbital energy gaps before and after the protonation of H₂CO in the ground state. Each of the orbitals appears to be stabilized in the field of the added proton, the maximum stabilization occurring for the n -orbital and the minimum for the π^* orbital. On the basis of a purely orbital theoretical picture one would therefore tend to conclude that the $n - \pi^*$ transition would have a large blue shift due to protonation and a much smaller blue shift for the $\pi - \pi^*$ transition (assuming the complete absence of any solvent). This picture, however, ignores the fact that the orbitals are expected to undergo extensive relaxation upon excitation which may bring about significant structural reorganization in the molecule, thereby completely obliterating the validity of conclusions derived from the simple orbital picture. We have therefore carried out complete geometry optimization in each state before and after protonation and

Table 2. Computed C=O and -O-H⁺ bond lengths (Å) and bond orders in the ground state and a number of low-lying excited states of a free and a protonated formaldehyde molecule.

Species and state	C=O	C=O	-O-H ⁺	-O-H ⁺
	Bond order	Bond length	Bond order	Bond length
H ₂ CO(ground)	2.03	1.250	—	—
H ₂ COH ⁺ (ground)	1.74	1.266	0.860	1.028
H ₂ CO($^1n\pi^*$)	1.15	1.320	—	—
H ₂ COH ⁺ ($^1n\pi^*$)	0.96	1.337	0.786	1.048
H ₂ CO($^3n\pi^*$)	1.19	1.315	—	—
H ₂ COH ⁺ ($^3n\pi^*$)	1.00	1.328	0.787	1.047
H ₂ CO($^3\pi\pi^*$)	0.99	1.384	—	—
H ₂ COH ⁺ ($^3\pi\pi^*$)	0.83	1.410	0.848	1.048

Table 3. Protonation-induced changes in the computed orbital gaps and transition energies in H₂CO and F₂CO.

Molecule	Orbital	Orbital energy (a.u.) in		Orbital energy gaps (a.u.) in		Transition energies (a.u.) in			Shift (a.u.)
		Free	Protonated molecule	Free	Protonated molecule	Free	Protonated molecule	Protonated molecule	
H ₂ CO	π^*	0.1440	-0.2785	0.654($n\pi^*$)	0.680	0.085($^3n\pi^*$)	0.158	0.073	
	n	-0.5106	-0.9588			[0.105]	[0.195]	[0.092]	
	π	-0.6537	-0.9588	0.797($\pi\pi^*$)	0.828	0.109($^1n\pi^*$)	0.170	0.061	
F ₂ CO	π^*	0.1120	-0.2770	0.719($n\pi^*$)	0.761	[0.124]	[0.210]	[0.068]	
	n	-0.6070	-1.0380			0.165($^3\pi\pi^*$)	0.232	0.067	
	π	-0.619	-1.0400	0.731($\pi\pi^*$)	0.763	[0.223]	[0.273]	[0.05]	
					0.095($^3n\pi^*$)	0.213	0.128		
					[0.148]	[0.271]	[0.123]		
					0.109($^1n\pi^*$)	0.217	0.108		
					[0.162]	[0.280]	[0.118]		
					0.122($^3\pi\pi^*$)	0.223	0.101		
					[0.195]	[0.262]	[0.067]		

Quantities in [] refer to vertical transition energies or shifts in vertical transition energies.

computed the transition energies and shifts caused by protonation as state energy differences. The vertical transition energies are also included in table 3 for comparison. The proton-induced (blue) shifts (PIS) in the adiabatic transition energies (ATE) are in the following order:

$$({}^3n\pi^*)_{\text{shift}} > ({}^3\pi\pi^*)_{\text{shift}} \sim ({}^1n\pi^*)_{\text{shift}}$$

The shifts in the VTE, on the other hand, are in the following order:

$$({}^3n\pi^*)_{\text{shift}} > ({}^1n\pi^*)_{\text{shift}} > ({}^3\pi\pi^*)_{\text{shift}}$$

However, these conclusions refer to the gas phase protonation of an isolated H_2CO molecule without any additional effects caused by solvation. Experimental ICR data would therefore be required to confirm these predictions. Surprisingly, no such experimental data are available, to the best of our knowledge.

Along with the computation of PIS in transition energies we have also calculated the vertical and adiabatic protonation energies (or proton affinities) of formaldehyde in the ground state and some excited states. These quantities are reported in table 4 together with the computed net charge densities on the carbonyl oxygen atom (q_{O}) in unprotonated H_2CO and on the added proton (q_{H^+}) in H_2COH^+ . The calculated adiabatic proton affinities (APA) decrease in the following order $\text{PA}({}^1S_0) > \text{PA}({}^3\pi\pi^*) > \text{PA}({}^1n\pi^*) > \text{PA}({}^3n\pi^*)$. The ordering predicted by us is consistent with the findings of Strausz *et al* (1978) for VPA. Interestingly, this is also the sequence along which

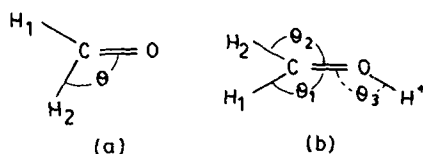


Figure 1. a. Geometrical parameters of H_2CO and atom numberings; b. Geometrical parameters of H_2COH^+ and atom numberings.

Table 4. Computed proton affinities of H_2CO and F_2CO in the ground and several excited states and their correlations, with net charge on the carbonyl oxygen or that on the added proton.

Molecule	Electronic state	Charge on oxygen atom (q_{O})	Proton affinity (a.u.)		Charge on the added proton (q_{H^+})
			Adiabatic	Vertical	
H_2CO	${}^1n\pi^*({}^1A'')$	-0.1157	-0.372	-0.352	0.4309
	${}^3n\pi^*({}^3A'')$	-0.0797	-0.365	-0.346[-0.181] ^b	0.4307
	${}^3\pi\pi^*({}^3A')$	-0.1415	-0.392	-0.389[-0.222] ^b	0.3740
	Ground (${}^1A'$)	-0.2370	-0.439	-[0.350] ^a -[0.286] ^b	0.3425
F_2CO	Ground (${}^1A'$)	-0.3364	-0.421	-[0.250] ^c	0.3697
	${}^1n\pi^*({}^1A'')$	-0.1524	-0.335	-0.303	0.4532
	${}^3n\pi^*({}^3A'')$	-0.1517	-0.326	-0.298	0.4534
	${}^3\pi\pi^*({}^3A')$	-0.1551	-0.322	-0.355	0.4029

a: Ros (1968), b: Strausz *et al* (1978) and c: Dekock *et al* (1983)

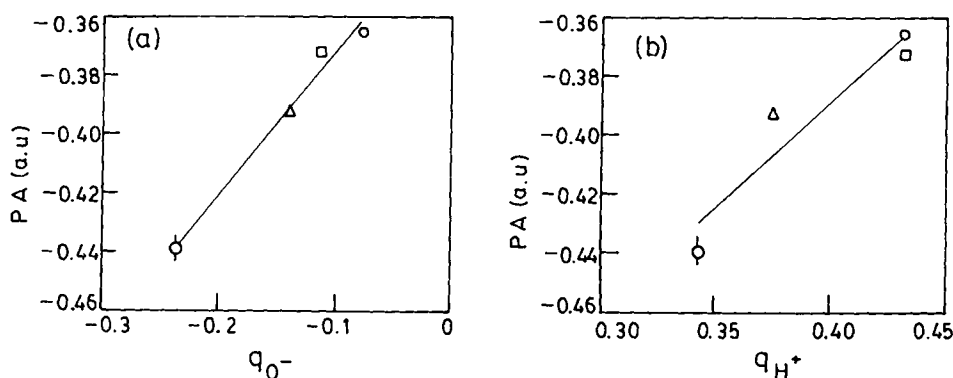


Figure 2. a. Correlation of computed proton affinities of formaldehyde in the ground and excited states with net charge on the carbonyl oxygen atom (q_{O^-}); b. With net charge on the added proton (q_{H^+}): \circ \equiv ground state; \triangle \equiv $3\pi\pi^*$; \square \equiv $1n\pi^*$ and \diamond \equiv $3n\pi^*$ state.

q_{O^-} decreases. The adiabatic proton affinities of H_2CO may therefore appear to be primarily controlled by the net electron density (q_{O^-}) on the C=O oxygen atom in a particular electronic state, the relaxation caused by the addition of a proton having apparently no discernible role in shaping the proton affinity of the species. To analyse this point a bit more closely we have plotted PA versus q_{O^-} and q_{H^+} (figures 2a and b respectively). These plots reveal approximate linear correlation between PA and q_{O^-} as well as between PA and q_{H^+} . Probably, the PA of H_2CO in a given state is ultimately shaped by complex interplay of factors originating from the net electron density on different atoms, the lone pair density on the basic centre and relaxation caused by the addition of a proton. Vertical proton affinities also reveal a more or less similar pattern.

3.2 Protonation of F_2CO

F_2CO has an important difference with H_2CO as far as protonation is concerned. This concerns the possibility of protonation either at the carbonyl oxygen atom or at the fluorine centre. The σ -electron withdrawing effect of the F-atom is expected to distort the electron density distribution within the C=O group strongly. However, the fluorine atoms can participate in π bonding with the C and O atoms in the $>C=O$ group which could have a counterbalancing effect. We have therefore studied protonation both at the carbonyl oxygen and at the fluorine centre in F_2CO .

3.2a Protonation at the oxygen atom ($>C=O \rightarrow >C=O-H^+$): A look at table 3 clearly shows that the fluorine substitution stabilizes the n and π^* orbital systems relative to similar orbitals in H_2CO , the π (bonding) orbital being destabilized a little simultaneously. The highest stabilization occurs for the n -orbital. The net effect is that a pure orbital theoretical picture would suggest that F_2CO will have a blue-shifted $n\pi^*$ band and a red-shifted $\pi\pi^*$ band compared to identical bands in H_2CO . Protonation is expected to bring about additional (almost uniform) stabilization of the n and π^* orbital systems (of H_2CO) and is not expected to outweigh or modify the effects of fluorine substitution. This expectation is seen to be confirmed by the orbital energies of F_2CO and F_2COH^+ reported in table 3. The question of orbital

relaxation caused by excitation and/or protonation, however, requires to be seen. We have therefore computed vertical and adiabatic transition energies of F_2CO and F_2COH^+ which are also reported in table 3. The transition energies confirm that (i) the lowest $n\pi^*$ band in F_2CO is blue-shifted relative to the same band in H_2CO , (ii) the lowest $\pi\pi^*$ band is red-shifted compared to its counterpart in H_2CO , and (iii) protonation causes large blue-shift in the $n\pi^*$ and $\pi\pi^*$ bands. Table 4 summarizes the computed vertical and adiabatic proton affinities of F_2CO along with identical quantities for H_2CO for comparison. Fluorine substitution is expectedly seen to reduce the vertical PA in each state, the maximum reduction occurring for the $^3\pi\pi^*$ and the minimum for the ground state. The adiabatic PA are reduced more or less equally. Experimental data on fluorinated acetones indicate (Drummond and McMahan 1981) that each fluorine substitution reduces the ground state PA by approximately 6 kcal/mole. MNDO calculations have been found (Dekock *et al* 1983) to overestimate the effect and predict 9 kcal/mole reduction per fluorine atom. Our calculation predicts ≈ 10 to 11 kcal/mole reduction of PA per fluorine substituent in H_2CO . The adiabatic PAs of F_2CO have been plotted against $q_{O\cdot}$ and q_{H^+} , respectively in figures 3a, b. The plots reveal lack of the same level of correlation as observed in H_2CO . Table 5 reports computed structural parameters (fully optimized) of F_2CO and F_2COH^+ in several states. As found for H_2CO , F_2CO also turns out to be rigidly planar in the ground state and non-planar in the $n\pi^*$ and $\pi\pi^*$ states. The protonated species (F_2COH^+), however, turns out to be planar in the ground as well as in the excited states under consideration. As has been observed in the case of H_2COH^+ , the disposition of $C=O-H^{(+)}$ fragment is linear in the $n\pi^*$ states and angular in the ground and $^3\pi\pi^*$ states. The $C=O$ bond length is found to increase upon excitation, and further upon protonation, essentially mimicking what has been already observed for H_2CO . Table 6 reports the computed $>C=O$ bond lengths and bond orders in a number of states of F_2CO and F_2COH^+ . The $O-H^+$ lengths and bond orders are also included. Higher proton affinity seems to imply shorter $O-H^+$ bond length and higher $O-H^+$ bond order. From the $>C=O$ bond order and length data one can speculate that the $C=O$ stretching frequencies in F_2CO and in different states would show an exactly similar reduction in magnitude due to protonation as suggested for H_2CO .

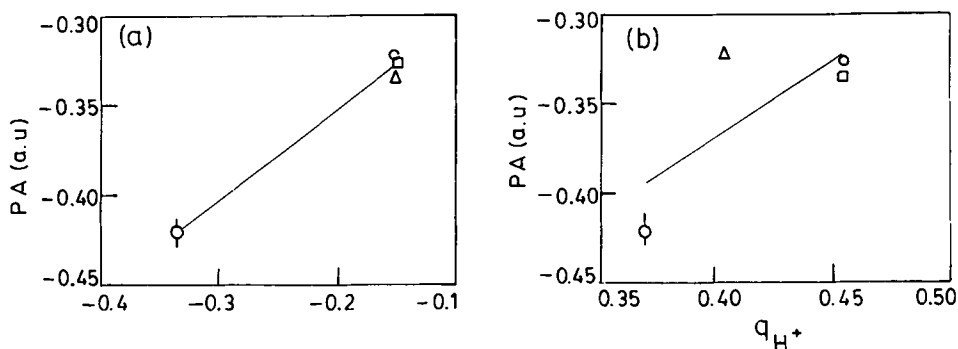


Figure 3. a. Correlation of computed proton affinities of fluoroformaldehyde in the ground and excited states with net charge on carbonyl oxygen atom ($q_{O\cdot}$); b. With net charge on the added proton (q_{H^+}); Explanation of symbols same as in figures 2a, b.

Table 5. Geometrical parameter of O-protonated F₂CO in the ground and several low-lying excited states.

State	r _{CO} (Å)	r _{O-H} (Å)	r _{CF₁} (Å)	r _{CF₂} (Å)	F ₁ CO	F ₂ CO	C=O-H ⁺
¹ A' (ground)	1.27 (1.29) ^a	1.034 (0.96) ^a	1.309	1.305	123.4°	121.0°	121.5° (121°)
¹ A''(¹ nπ*)	1.371	1.053	1.314	1.314	115.9°	115.9°	180.0°
³ A''(³ nπ*)	1.373	1.052	1.312	1.312	115.8°	115.8°	180.0°
³ A'(³ nπ*)	1.401	1.095	1.310	1.306	117.9°	116.2°	118.9°

a: Dekock *et al* (1983). For geometrical parameters of F₂CO in nπ* and ππ* states, see Das *et al* (1986).

Table 6. Computed C=O and O-H⁺ bond lengths and bond orders in the ground and a number of low-lying states of F₂CO and F₂COH⁺.

Species and state	C=O	C=O	O-H ⁺	O-H ⁺
	Bond order	Bond length (Å)	Bond length (Å)	Bond order
F ₂ CO (Ground)	1.8625	1.250	—	—
F ₂ COH ⁺ (Ground)	1.4463	1.279	1.034	0.8390
F ₂ CO (¹ nπ*)	0.9834	1.340	—	—
F ₂ COH ⁺ (¹ nπ*)	0.7797	1.371	1.053	0.7613
F ₂ CO (³ nπ*)	0.9736	1.336	—	—
F ₂ COH ⁺ (³ nπ*)	0.7853	1.373	1.052	0.7614
F ₂ CO (³ ππ*)	0.9575	1.366	—	—
F ₂ COH ⁺ (³ ππ*)	0.8006	1.376	1.050	0.8243

3.2b *Protonation at the fluorine centre:* Complete geometry optimization has been carried out for O=CF₂(H)⁺ in the ground, ^{1,3}nπ* and ππ* states. The optimized geometrical parameters for the F-protonated species in different electronic states are reported in table 7. The difference between the O and F-proton affinities in a particular electronic state is reported in table 8. It is clearly seen that *O-protonation is the energetically more favourable process in all the states*. The difference in the proton affinities is the maximum for the ground state and decreases by ~50% or more in the excited states. The relative ordering of the PA corresponding to F-protonation is, however, quite different from that predicted for O-protonation: viz

$$PA(^1S_0) > PA(^3n\pi^*) > PA(^1n\pi^*) > PA(^3\pi\pi^*)$$

No experimental or *ab-initio* theoretical data are available for comparison. However, exploratory MNDO calculation (Dekock *et al* 1983) on the F-protonation of monofluoro acetone in the ground state shows that O-protonation is energetically more favourable by ~25 kcal/mole.

3.2c *Basicity differences among the singlet and triplet nπ* states in H₂CO and F₂CO:* The nπ* transition in H₂CO involves the transfer of an electron from an orbital (n) that is rather strongly localized on the carbonyl oxygen atom to one (π*) which is more delocalized but has higher amplitude on the carbon atom. The nπ*

Table 7. Structural parameters of F-protonated F₂CO in the ground and a number of low-lying states.

State	r_{CF_1} (Å)	r_{CF_2} (Å)	$r_{C=O}$ (Å)	r_{F_2H} (Å)	F ₁ CO	F ₂ CO	H ⁺ -F-C*
Ground (¹ A')	1.312	1.393	1.231	1.027	119.7°	135.6°	180°
¹ nπ* (¹ A'')	1.311	1.379	1.336	1.031	115.4°	129.9°	180°
³ nπ* (³ A'')	1.326	1.366	1.279	1.034	115.0°	126.1°	120.7°
³ ππ* (³ A')	1.305	1.371	1.359	1.035	127.5°	119.5°	122.1°

* Protonated F₂CO is planar in the ground as well as excited states.

Table 8. Comparison of F and O-protonation energies of F₂CO in the ground and low-lying excited states.

State	F-protonation energy (a.u.)	Difference* between O- and F-protonation energies (a.u.)
Ground (¹ A')	0.329	0.09
(nπ*) ³ A''	0.302	0.02
(nπ*) ¹ A''	0.298	0.04
(ππ*) ³ A'	0.282	0.04

a: Corresponding O-protonation energies are recorded in table 3

transition therefore involves intramolecular transfer of electron density from O → C atom. Being depleted of a part of its electron density relative to what it had in the ground state, the carbonyl oxygen atom in the nπ* states is expected to be less basic. Proton affinities and charge densities computed by us in both the model systems corroborate this expectation. More interestingly, however, H₂CO turns out to have a higher proton affinity in the ¹nπ* state than in the ³nπ* state (table 4). The computed electron density on the oxygen atom also is higher in the ¹nπ* state than in the ³nπ* state (table 4). Since identical orbitals (n and π*) are involved in the transition, the observation requires rationalization. One wonders whether spin-correlation could be operationally responsible for the observed basicity difference in the singlet and triplet nπ* state of H₂CO. This amounts to speculating whether Hund's rule could have observable consequences other than singlet-triplet splittings. Previously we had observed significant differences in the geometrical parameters of H₂CO in the singlet and triplet nπ* states (Das *et al* 1986, 1989).

One recalls that, according to Hund's rule, if two states arise from the same electronic configuration, the state having the higher spin multiplicity will have lower energy. In the early 1960s this phenomenon was rationalized using the perturbative approach (Slater 1960; Strauss 1968), the decreased energy of the higher spin being attributed to the decreased electronic repulsion. Since then, numerous calculations have demonstrated that this explanation is not correct. The average electron-electron repulsion energy often turns out to be higher in the lower energy state (Katriel and Pauncz 1977). Modern explanation for Hund's rule invokes Fermi correlation and shielding arguments (Warner *et al* 1980; Boyd 1984). According to these arguments the following picture can be constructed to rationalize the higher degree of O → C

Table 9. Orbital-wise break-up of electron density on the oxygen atom in the ${}^1n\pi^*({}^1A'')$ and ${}^3n\pi^*({}^3A'')$ states of formaldehyde molecule.

Population in oxygen orbital	State	
	${}^1A''$	${}^3A''$
2s	1.7987	1.7998
2p _x	1.5050	1.5134
2p _y	1.0400	1.0476
2p _z	1.7717	1.7195

transfer of electron density in the ${}^3A_2(n\pi^*)$ state of H_2CO as compared to the ${}^1A_2({}^1n\pi^*)$ state). In the triplet $n - \pi^*$ transition a spin flip occurs and the two unpaired electrons each carrying a Fermi-hole around it polarize some oxygen density closer to the nucleus. This small change (essentially transfer of some electron density from the oxygen 2p orbitals to the 2s) (table 9) accounts for a bulk of the stabilization of the triplet. If there is increased electron density close to the nucleus in the triplet because of Fermi correlation, there must be a corresponding decrease in the outer regions of the molecule. Because of higher screening of the oxygen nucleus in the triplet due to Fermi holes, the effective electronegativity of oxygen atom towards the unpaired (outer valence) electron decreases allowing some additional transfer of peripheral electron density from $O \rightarrow C$ in the triplet. This makes the oxygen atom less basic. Our results are therefore consistent with the recent findings of *ab-initio* calculations carried out in a different context (Darvesh and Boyd 1989). In F_2CO the strong σ -withdrawing effect of the F-atoms apparently smoothens the subtle effect of Fermi correlation so clearly discernible in H_2CO .

4. Conclusion

It appears that the orthogonal gradient MC-SCF method in an INDO framework could be very useful in studying protonation of carbonyl systems in the ground and excited states. The calibrating calculations reported here show that the method overestimates the PA in different states, but reproduces the relative magnitudes fairly well. Encouraged by this success we have undertaken an elaborate study of the PA of acetaldehyde, acetone, acraldehyde, propanal, glyoxal, etc. in different electronic states. The results obtained so far point to the possibility of protonation having a marked and systematic influence on the $C \leftrightarrow O$ stretching frequency, its reactivity, etc. We hope to return to these aspects shortly.

Acknowledgement

One of us (SPB) is indebted to the Council of Scientific and Industrial Research, New Delhi, for a research grant which enabled him to procure a SIRIUS-32 minicomputing system on which all computations were carried out.

Appendix A

The key quantity involved in the definition of quantum chemical valence parameters is the so-called one-electron density matrix (P) in the atomic orbital (AO) basis (x),

$$P = TP_1 T^\dagger.$$

In the most general case, P_1 is the natural spin orbital density in the MO basis. With the specific form of $\tilde{\psi}$ used by us, P_1 can be partitioned into \bar{P}_1 and P_1^s where \bar{P}_1 represents one-electron density due to the core (or doubly-occupied orbitals) and P^s that due to the singly occupied manifold. P then splits into $P^d + P^s$. We have followed Mayer (1983, 1985) and defined the quantum chemical bond-order between a pair of atoms (A and B) as follows: (Maity *et al* 1989; Maity and Bhattacharyya 1990)

$$B = \sum_{\mu \in A} \sum_{\nu \in B} \{ (P^d S)_{\mu\nu} (P^d S)_{\nu\mu} \} + \sum_{\mu \in A} \sum_{\nu \in B} (P^s S)_{\mu\nu} (P^s S)_{\nu\mu}.$$

At the INDO level of approximation $S = 1$, leading to further obvious simplifications in the expression for B_{AB} . A similar definition has also been used recently by Villar and Dupis (1987).

References

- Beauchamp J L 1974 in *Interactions between ions and molecules* (New York: Plenum) pp. 413, 459, 489
- Bhattacharyya S P and Mukherjee D 1979 *Chem. Phys. Lett.* **66** 511
- Bhattacharyya S P and Mukherjee D 1981 *Int. J. Quantum Chem.* **20** 1165
- Bhattacharyya S P, Rakshit S C and Banerjee M 1983 *J. Mol. Struct. (Theochem)* **91** 253
- Bhome D K, Hemsworth R S, Rundle H I and Schiff H I 1973 *J. Chem. Phys.* **58** 3504
- Bhome D K, Mackay G I, Schiff H I and Hemsworth R S 1974 *J. Chem. Phys.* **61** 2175
- Boyd R J 1984 *Nature (London)* **310** 480
- Brauman J I and Blair L K 1970 *J. Am. Chem. Soc.* **92** 5968
- Darvesh K V and Boyd R J 1989 *J. Chem. Phys.* **90** 5638
- Das K K and Bhattacharyya S P 1991 in *The method of self-consistent field: Theory and applications* (eds) R Carbo and M Klobukowski (Amsterdam: Elsevier) pp 195–232
- Das K K, Mukherjee D and Bhattacharyya S P 1986 *Int. J. Quantum Chem.* **29** 1745
- Das K K, Mukherjee D and Bhattacharyya S P 1989 *Int. J. Quantum Chem.* **35** 483
- Dekock, Jaserse R L and Konin M S 1983 *J. Mol. Struct. (Theochem)* **94** 343
- Drummond D F and McMahon T B 1981 *J. Phys. Chem.* **85** 3746
- Forster T 1950 *Z. Electrochem.* **54** 42 1929
- Frieiser B S and Beauchamp J L 1977 *J. Am. Chem. Soc.* **99** 3214
- Golebiewski A, Hinze J and Yurtsever Y 1979 *J. Chem. Phys.* **70** 1101
- Harrison A G, Irko A and Van Rattle D 1966 *Can. J. Chem.* **44** 1625
- Ireland J F and Wyatt P A H 1976 in *Adv. Phys. Org. Chem.* **12** 138
- Katriel J and Pauncz R 1977 *Advanced quantum chemistry* 10 (New York: Academic Press) pp 143–185
- Long J W and Franklin J L 1974 *J. Am. Chem. Soc.* **96** 2320
- Maity D K and Bhattacharyya S P 1990 *J. Am. Chem. Soc.* **112** 3223
- Maity D K, Das K K and Bhattacharyya S P 1989 *Proc. Indian Acad. Sci. (Chem. Sci.)* **101** 421
- Mayer I 1983 *Chem. Phys. Lett.* **97** 270
- Mayer I 1985 *Theor. Chim. Acta* **67** 315
- Mcweeny R 1968 *Farad. Symp. Chem. Soc.* **2** 7
- Mcweeny R and Sutcliffe B T 1969 in *The methods of molecular quantum mechanics* (New York: Academic Press)
- Medhi C, Das K K and Bhattacharyya S P 1993 *Pramana – J. Phys.* **40** 65

- Mukherjee D 1978 *Proc. Indian Acad. Sci.* **A87** 37
Ottolenghi M 1973 *Acc. Chem. Res.* **6** 153
Ros P 1968 *J. Chem. Phys.* **49** 4902
Saeva F D and Olin G R 1975 *J. Am. Chem. Soc.* **97** 5630
Sarkar B, Bhattacharyya K and Bhattacharyya S P 1989 *Chem. Phys. Lett.* **162** 61
Slater J C 1960 in *Quantum theory of atomic structure* (New York: McGraw Hill) Vol. I
Solomon J J, Meot Ner M and Field F M 1974 *J. Am. Chem. Soc.* **96** 3727
Staley R H and Beauchamp J L 1975 *J. Am. Chem. Soc.* **96** 3727
Strauss H L 1968 in *Quantum mechanics: An introduction* (Englewood Cliffs, NJ: Prentice-Hall) p. 168
Strausz O P, Kapuy E, Kosmutza C, Robb M A and Ciszmadia I G 1982 *J. Mol. Struct. (Theochem)* **89** 235
Strausz O P, Kosmutza C, Kapuy E, Robb M A, Theodorakopoulos G and Ciszmadia I G 1978 *Theor. Chim. Acta* **48** 215
Villar H O and Dupis M 1987 *Chem. Phys. Lett.* **142** 59
Warner J M, Bartell L S and Blinder S M 1980 *Int. J. Quantum Chem.* **18** 921
Wieting R D, Staley R H and Beauchamp J L 1974 *J. Am. Chem. Soc.* **96** 7552
Yamadagni R and Kebarle P J 1973 *J. Am. Chem. Soc.* **96** 3727