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Relationes

Hydrogen Bonding in Electronically Excited States of Molecules

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CNDO/2 calculations show that hydrogen bonds in the electronically excited states of $>C=O + H_2O$ and $>C=O + HOCH_3$ systems are slightly weaker than in the ground states. The $n \rightarrow \pi^*$ transition energies as well as solvent blue-shifts are predicted fairly satisfactorily.

Although extensive molecular orbital calculations have been reported in the literature [1, 2] on a variety of hydrogen bonded systems, studies of hydrogen bonding in the electronically excited states have been limited. Pimentel [3] pointed out that hydrogen bonding in the excited state may be considerable, but also cautioned that one should not minimize the importance of the Franck-Condon principle in determining the solvent blue-shifts of $n \rightarrow \pi^*$ transitions of chromophores. There is some spectroscopic evidence [4, 5] to indicate that hydrogen bonds are weaker in the excited state compared to the ground state. On the basis of extended Hückel calculations, Hoffmann and coworkers [6] showed that the hydrogen bond energy in the pyridine-water system is lower by 0.8 kcal in the excited state.

We have carried out CNDO/2 calculations [7, 8] on the hydrogen bonds in the lowest electronically excited states of formaldehyde-water, formaldehyde-methanol, acetone-water and acetone-methanol systems; hydrogen bonding in the ground states of some of these systems have already been reported in the literature [1, 2]. Although it would be necessary to investigate such systems by the INDO and *ab initio* methods to obtain more reliable results, we felt that it was desirable to report our CNDO/2 studies[1] at this stage since the results are encouraging[2]. We should note here that the CNDO method is readily extended to open-shell calculations if a single-determinant wave function is used with different molecular orbitals of α and β spins [7]; the LCAO coefficients $C_{i\mu}^{\alpha}$ and $C_{i\mu}^{\beta}$ are eigen vectors of separate F matrices for which general expressions are available [8]. The CNDO/2 method satisfactorily predicts the known non-planar geo-

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[1] We have employed the QCPE programme for our calculations.

[2] After we completed out studies, we have noticed that De Jeu (Chem. Physics Letters 7, 153 (1970)) has carried out some CNDO/2 calculations on the lowest excited state of formaldehyde-water and our results are in general agreement with those of De Jeu. Our calculations are, however, more extensive and are on a larger number of systems.

Table 1. *Properties of hydrogen bonds formed by molecules in ground and excited states*[a]

	$r_{C=O}$, Å[b] (Calcd.)	Ø[c]	E_T, a.u.	D_e (kcal. mole^{-1})	$R_{O...O}$ Å	Dipole moment (in D)	$n \rightarrow \pi^*$ Energy[d] (a.u.)
HCHO (G)	1.25 (1.21)	0°	−26.8383	—	—	2.1	0.106
HCHO (E)	1.31 (1.32)	30°	−26.7321	—	—	1.4	
H_2O + HCHO (G)	1.25	0°	−46.7409	7.1	2.6	4.3	0.109
H_2O + HCHO (E)	1.31	30°	−46.6324	6.1	2.6	3.8	(660)
CH_3OH + HCHO (G)	1.25	0°	−55.4145	7.4	2.6	4.0	0.109
CH_3OH + HCHO (E)	1.31	30°	−55.3059	6.2	2.6	3.7	(660)
CH_3COCH_3 (G)	1.27 (1.22)	0°	−44.2378	—	—	3.5	0.111
CH_3COCH_3 (E)	1.33	10°	−44.1264	—	—	1.7	
$H_2O + CH_3COCH_3$ (G)	1.27	0°	−64.7482	7.2	2.5	5.2	0.115
$H_2O + CH_3COCH_3$ (E)	1.33	10°	−64.6333	6.1	2.5	3.9	(880)
$CH_3OH + CH_3COCH_3$ (G)	1.27	0°	−72.8027	7.0	2.5	4.9	0.115
$CH_3OH + CH_3COCH_3$ (E)	1.33	10°	−72.6882	5.1	2.6	3.4	(880)

[a] G and E refer to the ground and excited states respectively. The $n \rightarrow \pi^*$ transition energies in the free (or the hydrogen bonded) state of the molecule is the difference between the E_T values of the corresponding G and E states. The blue-shift is the difference between the $n \rightarrow \pi^*$ transition energies of the free and the hydrogen bonded states.

[b] The C–H distance in HCHO and the C–C distance in acetone in the G and E states were the same as in free molecules. The values in parantheses are the experimental distances.

[c] Out-of-plane deformation. In HCHO, Ø is the angle between the CH_2 plane and the C = O bond.

[d] These values do not truly represent the transition energies since we have taken different geometries for the ground and excited states; according to the Franck-Condon principle, the absorption maximum is determined by the ground state geometry. The values in parentheses are the calculated blue-shifts in cm^{-1}; experimental values are between 1000 and 1700 cm^{-1} [4].

metries of the excited states of formaldehyde [9] as well as of acetone [10]; in this approximation, there is, however, no clear separation between the singlet and triplet states [11]. Since both the triplet and singlet states of such carbonyl compounds possess similar geometry [12], we do not expect any serious difficulty.

We have employed the minimized geometries [9, 10] of formaldehyde and acetone in the excited and ground states (Table 1) in our calculation. The calculated values of the excited state dipole moments of formaldehyde and acetone (Table 1) are in agreement with the experimental values of 1.5 and 1.8 D respectively [4, 13]. The calculated electronic transition energies of formaldehyde and acetone correspond to those of $n \rightarrow \pi^*$ transitions, the transition energy in acetone being higher in formaldehyde in agreement with experimental observations [14]. In the water molecule, we have used 1.03 Å and 1.04 Å respectively for the free and bonded O–H bond distances [15]; in methanol, we have used the distances reported in an earlier publication from this laboratory [1a]. In the hydrogen bonded species, the O–H bond of H_2O (or CH_3OH) was along the direction of the sp^2 lone pair orbital of the carbonyl group.

The total energies, E_T, of all the four hydrogen bonded systems, were calculated as functions of the O...O distance in both the ground and excited states. The potential energy curves thus obtained for the two states were quite similar in shape. The potential energy curves directly yield the hydrogen bond dissociation energies, D_e, and the equilibrium O...O distances. While the equilibrium O...O

Table 2. CNDO/2 *charges on different atoms of the hydrogen bonded systems in ground and excited states*[a]

	O_D[b]	C[c]	H[d]	O_A[b]
$H_2O + HCHO$ (*G*)	6.196 (6.194)	3.777 (3.790)	0.831 (0.865)	6.314 (6.270)
$H_2O + HCHO$ (*E*)	6.067 (6.072)	4.006 (4.014)	0.840	6.304
$CH_3OH + HCHO$ (*G*)	6.177	3.741	0.831 (0.857)	6.277 (6.271)
$CH_3OH + HCHO$ (*E*)	6.067	4.004	0.840	6.271
$H_2O + CH_3COCH_3$ (*G*)	6.295 (6.296)	3.723 (3.737)	0.808	6.335 (6.270)
$H_2O + CH_3COCH_3$ (*E*)	6.113 (6.122)	3.931 (3.937)	0.826	6.321 (6.270)

[a] Charges on the atoms in the parent donors (*D*) and acceptors (*A*) are shown in parentheses.

[b] O_D and O_A are the donor and the acceptor oxygen atoms respectively.

[c] Carbon of the donor carbonyl group.

[d] Hydrogen taking part in hydrogen bonding.

distances are the same in the ground and excited states of all the systems studied, D_e values are generally lower by about 1 kcal in the excited states (Table 1). The largest decrease in D_e in the excited state is in the case of the acetone-methanol system, where we also notice a longer equilibrium $R_{O...O}$ distance in the excited state. The dipole moments are considerably lower in the excited states than in the ground states as expected in $n \rightarrow \pi^*$ transitions [4, 14, 16]. Further, the calculated solvent blue-shifts of the $n \rightarrow \pi^*$ transitions [4] of formaldehyde and acetone in H_2O and CH_3OH are reasonable, the blue-shift being larger for acetone than for formaldehyde. It appears that Franck-Condon principle does not play a very important role in determining the blue-shifts [3].

The CNDO charges in the ground and excited state hydrogen bonded complexes of three systems are shown in Table 2. There is more definitive decrease in the electron density on the donor oxygen atom in the electronic excited states than in the ground states. The electron density on the acceptor oxygen atom increases in both the ground and the excited states, the increase being greater in the former. The carbon atom (of the C=O group) as well as the hydrogen atom involved in hydrogen bonding lose charge to a greater extent in the ground state. All these changes in charges are consistent with the properties of hydrogen bonds summarized in Table 1.

We have calculated the proton potential functions [1] of the ground and excited states and found them to be quite similar. This is not entirely surprising since the $R_{O...O}$ in the ground and excited states are about the same. The proton potential curves do not show clear evidence for a barrier as expected in a double minimum potential curve.

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