

A CNDO CALCULATION OF THE HYDROGEN BOND AND THE BLUE SHIFT IN FORMALDEHYDE-WATER

W. H. DE JEU

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Received 6 July 1970

A CNDO calculation is performed on formaldehyde and formaldehyde-water in the ground state and in the lowest excited state. The H bonds in the ground state and in the excited state are very similar although the latter is a little weaker. This difference corresponds to the blue shift in the $n \rightarrow \pi^*$ transition in which the Franck-Condon principle seems to play only a minor role.

The last few years have brought an increasing production of semi-empirical MO calculations using all valence electrons. Without attaching too much value to the quantitative aspects, we can say that these calculations provide interesting comparisons with older purely qualitative ideas. E.g. calculations on simple carbonyl compounds show that the carbonyl σ bond is about as polar as the π bond [1], while in earlier calculations often a non-polar σ bond is assumed. Polar σ bond is also found in abinitio calculations [2]. The CNDO method [3, 4] has been applied to several H bonded systems [5], and comparison with ab initio results shows that it is rather successful in this respect [6]. As this method also works reasonably well for excited state [7, 8], it seems that an application to H bonding in an excited state would be meaningful. The system we have chosen is formaldehyde-water, for which an extensive ground-state calculation has already been published by Schuster [5]. As is well known the blue shift in the carbonyl $n \rightarrow \pi^*$ transition in going from aprotic to H bonding solvents is attributed to a weakening of the H bond in the excited state compared with the ground state [2, 9].

We use the original parametrisation known as CNDO/2 [4]. The ground state is treated in a closed-shell calculation. From the different ways of treating an excited state we choose the unrestricted open-shell method, which can be applied to the $\alpha\alpha$ -component of the lowest triplet state [4]. However, at the level of the CNDO approximation there is no separation between singlet and triplet states [8] because the relevant integrals are omitted. Therefore we shall not attempt to distinguish between the two. For the

Table 1
Geometries used in the calculations

H ₂ O	$r_{\text{OH}} = 0.96 \text{ \AA}$	$\angle \text{HOH} = 105^\circ$
H ₂ CO, ground state	$r_{\text{CH}} = 1.12 \text{ \AA}$	$\angle \text{HCH} = 120^\circ$
	$r_{\text{CO}} = 1.21 \text{ \AA}$	planar
H ₂ CO, triplet state	$r_{\text{CH}} = 1.093 \text{ \AA}$	$\angle \text{HCH} = 120^\circ$
	$r_{\text{CO}} = 1.312 \text{ \AA}$	$\alpha = 27.5^\circ$

ground state we use the same experimental bond lengths as Schuster [5] while those for the excited state are taken from Herzberg [10] (see table 1). We assume in both cases an HCH-angle of 120° , which is very close to the experimental value. The ground state is planar. For the excited state we varied the angle α between the

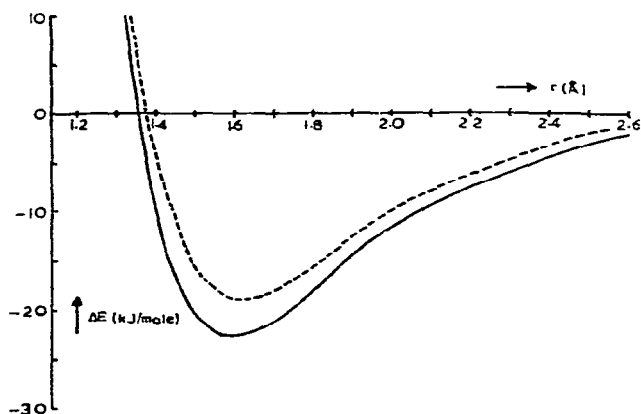


Fig. 1. Energy curves for H bonding between formaldehyde and water (configuration I); full line: ground state; broken line: excited state.

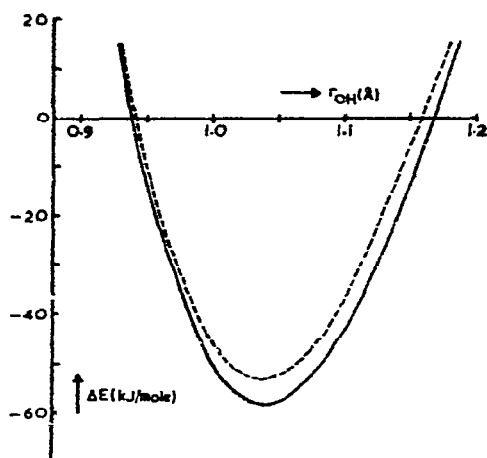
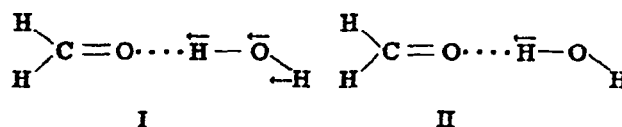


Fig. 2. Energy curves for motion of the H atom (configuration II; $r_{OO} = 2.56 \text{ \AA}$); full line: ground state; broken line: excited state.

CO bond and the CH_2 plane, which gives a minimum for the total energy of H_2CO for $\alpha = 27.5^\circ$ (experiment: 35°). As shown by Kroto and Santry [7] this value is very sensitive to the value chosen for the HCH-angle. However, as the energy differences are rather small this will probably not affect the H bonding properties. From the results of Schuster [5] we know that within limits of about $\pm 75^\circ$ the ground state H bond energy is rather insensitive to the angle between the CO bond and the water OH. We found the same for the excited state. Therefore, we shall take the carbonyl bond and the H bond on a straight line. Rotation of the water OH not involved in the H bond is found to be unimportant.



Energy curves for the two remaining configurations I and II are given in figs. 1 and 2. For II the OO-distance is fixed on the energy minimum of I.

The most striking feature of figs. 1 and 2 is that the H bonds in the ground state and the excited state are very similar. There is very little difference in the configuration that gives optimal stabilisation, while the H bond in the excited state is only slightly weaker. The ground state H bond is too strong (as is the case in most CNDO calculations [5]) while the OO-distance is about 0.2 \AA too short [11]. The charge distributions are given in table 2. We see that in the ground state both the carbonyl π and the σ bond are polar in the direction C^+O^- . For H bonding the π bond becomes more polar, accompanied by a back donation of electrons in the σ plane. The water molecule gains a net charge of about 0.03 electrons, mainly at the cost of the carbon and the hydrogens. The excited state calculation shows qualitatively the same features for H bonding except that we now start with a much less polar carbonyl bond due to the $n \rightarrow \pi^*$ transition. It is interesting that this greatly reduced polarity does not affect the H bond more seriously.

Finally we give the $n \rightarrow \pi^*$ transition energies in table 3. Looking first at formaldehyde we see that ΔE calculated with the experimental geometries is a little too small. According to the Franck-Condon principle [9] the maximum of the

Table 2
Charge distributions for formaldehyde-water. H bonded refers to minimum of II ($r_{OO} = 2.56 \text{ \AA}$, $r_{OH} = 1.04 \text{ \AA}$)

atom	ground state		excited state			
	$\text{H}_2\text{CO} + \text{H}_2\text{O}$	$\text{H}_2\text{CO} \cdots \text{HOH}$	$\text{H}_2\text{CO} + \text{H}_2\text{O}$	$\text{H}_2\text{CO} \cdots \text{HOH}$		
H_2CO :	H	1.016	1.008	0.955	0.948	
	C	σ	2.947	2.959	2.917	2.918
		π	0.834	0.807	1.103	1.093
	tot.	3.781	3.766	4.020	4.011	
O	σ	5.021	4.994	4.254	4.234	
	π	1.166	1.193	1.816	1.830	
	tot.	6.188	6.187	6.070	6.064	
H_2O :	H _{bridge}	0.857	0.830	0.857	0.838	
	O	σ	4.946	5.005	4.946	4.995
		π	1.339	1.319	1.339	1.322
		tot.	6.285	6.324	6.285	6.317
	H	0.857	0.878	0.857	0.874	

Table 3
Energy differences between ground state and lowest excited state of formaldehyde. H bonded refers to the minimum of II

		exp. geom.	ΔE (eV) ground-state geom.	exc. state geom.
theoretical:	H ₂ CO	2.71	3.69	2.19
	H ₂ CO...HOH	2.76	3.75	2.25
experimental ^{a)} :	H ₂ CO	3.12	(3.12 - 3.44)	
			4.20	
		3.51	(3.51 - 5.39)	(2.07 - 5.39)
	H ₂ CO...HOH	S-S	4.30	

a) Ref. [10].

absorption band is determined by the ground state geometry, because there is no time for nuclear rearrangement during the transition. The ΔE value calculated in this way is again of the right order of magnitude. In emission the S-S band extends to higher wave length than in absorption [10] which is consistent with the smaller ΔE value we find using the excited state geometry. In all cases a blue shift of about 0.06 eV is predicted on H bonding. This compares reasonably well with the shift in the maximum of the S-S absorption band. It has been assumed earlier that the Franck-Condon principle is important in determining the blue shift [12], and in the case of acetone this is supported by some experimental evidence [9]. Our calculations on formaldehyde-water, where the geometries giving maximum stability in the ground state and in the excited state are about the same, do not conform to this idea. Apart from this last feature we can conclude that the CNDO calculations are in general consistent with the older purely qualitative picture of the blue shift.

The author wishes to express his gratitude to the Royal Society for the award of a fellowship in the European exchange programme, and to Professor J. N. Murrell for his hospitality at Sussex University.

REFERENCES

- [1] W. H. de Jeu, *J. Phys. Chem.* 74 (1970) 822.
- [2] G. Berthier and J. Serré, in: *The chemistry of the carbonyl group*, ed. S. Patai, (Interscience, New York, 1966) p. 1.
- [3] J. A. Pople and G. A. Segal, *J. Chem. Phys.* 43 (1965) S 136.
- [4] J. A. Pople and G. A. Segal, *J. Chem. Phys.* 44 (1966) 3289.
- [5] A. Ocvirik, A. Ažman and D. Hadzi, *Theoret. Chim. Acta* 10 (1968) 187;
A. Pullman and H. Berthod, *Theoret. Chim. Acta* 10 (1968) 461;
A. S. N. Murthy and C. N. R. Rao, *Chem. Phys. Letters* 2 (1968) 123;
P. Schuster and Th. Funck, *Chem. Phys. Letters* 2 (1968) 587;
A. S. N. Murthy, R. E. Davis and C. N. R. Rao, *Theoret. Chim. Acta* 13 (1969) 81;
P. Schuster, *Intern. J. Quantum Chem.* 3 (1969) 851;
J. R. Hoyland and L. B. Kier, *Theoret. Chim. Acta* 15 (1969) 1.
K. Morokuma, *Chem. Phys. Letters* 4 (1969) 358.
- [6] P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.* 92 (1970) 753.
- [7] H. W. Kroto and D. P. Santry, *J. Chem. Phys.* 47 (1967) 2736.
- [8] C. Giessner-Prettre and A. Pullman, *Theoret. Chim. Acta* 13 (1969) 265.
- [9] J. N. Murrell, *The theory of electronic spectra of organic molecules* (Methuen, London, 1963) ch. 8.
- [10] G. Herzberg, *Molecular spectra and molecular structure*, Vol. 3 (Van Nostrand, Princeton, 1966) p. 612.
- [11] G. C. Pimental and A. L. McClellan, *The hydrogen bond* (Freeman, San Francisco, 1960).
- [12] G. C. Pimental, *J. Am. Chem. Soc.* 79 (1957) 3323.