A CNDO STUDY OF THE SPECTRAL EFFECTS OF 
B-BONDING IN COMPLEXES

I. V. Sokolova and L. V. Orlovskaya

CNDO has been used with spectroscopic parameterization and configuration interaction for the
1:1 and 1:2 complexes between acetone and water; the H-bonded complex produces a blue
shift in the long-wave absorption of the acetone, and the shifts combine additively as the com-
plex enlarges. Additivity occurs also in the properties of the ground states in the 1:1 and
1:2 complexes, with the charge transferred to the acceptor increased by a factor 2 on pas-
sing from the 1:1 complex to the 1:2 complex.

Although there is now very much research on hydrogen bonds by quantum-chemistry methods, the
calculations relate mainly to the ground state, while very little is known about H bonds in the excited state.
Particular interest attaches to the case where the electron donor can participate in two H bonds, e.g., via
the nonbonding pairs on O, S, and Se.

For instance, IR spectroscopy indicates that the carbonyl group can form complexes with electron ac-
ceptors [1, 2]. If the acceptor concentration is low, one gets a 1:1 complex, but there is a shift to 1:2 as
the acceptor concentration increases. Acetone forms 1:1 and 1:2 complexes with H2O [1] and I2 [3].
The changes observed in the UV region on going from one complex to the other for acetone + I2 are quite
clear [3]: the charge-transfer band shifts 48 nm towards the red side, while the absorption band of I2 shifts
95 nm towards the blue side. The acetone—H2O complexes show a shift in λmax(S0 → Sπ*) towards higher
energies as the composition changes [14].

Complexes of n—σ type between a carbonyl group and halogens resemble hydrogen bonds [4]; if the
complex has a 1:1 composition, the nonbonding electron pair pσ on the oxygen is involved together with
the σ orbital of the acceptor. When the acceptor concentration is such to produce the 1:2 effect, both the
nonbonding pairs of O are involved [2, 5]. There is no coordination to a second acceptor molecule at low
acceptor concentrations because [6] there are strong steric factors, and also a reduction in the scope for
complexing of the second nonbonding pair when the first pair is involved in an H bond.

Here we consider the spectral features for the acetone—H2O system when the composition changes
from 1:1 to 1:2.

We use the optimized geometry derived by Morokuma [7] for the 1:1 formaldehyde—H2O complex and
also the 1:2 one (Fig. 1). The 1:2 complex has a structure [7] close to that found from IR spectroscopy
for carboxyl compounds [1, 5]. The 1:1 complex was considered in two forms: the angular (I), which is
most likely on the basis of Morokuma's calculation [7], and the linear (II), which is the most likely from
structural data [1].

CNDO with appropriate parameterization is quite suitable for describing the spectra; the method can
be used to predict the equilibrium geometry of H-bonded complexes with less success, since the equilibrium
distance is shortened on account of overestimation of the bonding in the CNDO method. The optimized
geometry for the complex [7], which we used here, is close to the observed one [9].

We have previously [10] considered the spectral features of the acetone molecule. The long-wave
absorption is ascribed to a transition localized on the carbonyl group, and its intensity is due, in particular,
A blue shift occurs in the long-wave absorption of acetone when each bond is formed to H$_2$O (Table 1).

The difference $\Delta \varepsilon$ between the one-electron energies of the n molecular orbital and the $\pi^*$ orbital is reduced when the 1:1 complex is formed and is reduced still further for the 1:2 one (Table 1). This occurs because the energy of the $\pi^*$ molecular orbital is reduced more than that of the n molecular orbital. The nature of the $\pi$ molecular orbitals (whether excited or unexcited) is not affected by the complexing; the reason is probably that the acetone $\pi$ electrons are involved in the bond with H$_2$O. It may be that somewhat different conclusions would be obtained [11] by incorporating the polarized 2p functions for the H atom. The $\Delta \varepsilon$ is reduced by complexing, which does not explain the cause of the blue shift in the long-wave absorption of acetone on interaction with H$_2$O.

The configuration—interaction matrix indicates the $S_0$ -- $S_{n\pi^*}$ blue shift for acetone with H$_2$O arises from the different degrees of mixing with higher-lying states in configuration interaction (Table 1).

The blue shift in the 1:1 complex is dependent on the structure of the latter; the shift is less for the linear structure than for the nonlinear one.

It is usual to ascribe the $S_0$ -- $S_{n\pi^*}$ blue shift in H bonding to destabilization of the nonequilibrium excited state (Frank—Condon effect), this being the state reached directly by absorption. Various reasons have been given for destabilization of the Frank—Condon state: effective reduction in the size of the n orbital on excitation, change in the O—H...O distance of excitation, oriented stretching of the solvent shell, and geometrical change in the solute on excitation. However, the shift in the solvent molecules occurs after the electronic transition, as does the change in the nuclear configuration within the module itself, and this can make itself felt only in fluorescence. Our calculation indicates that the Frank—Condon state is destabilized mainly on account of the altered mixing of the higher-lying states with the $S_{n\pi^*}$ state. When one compares the calculation with observed shifts, one must bear in mind that it is usual to detect H bonds from the peaks in electronic absorption bands, but the bond may substantially alter the potential energy surfaces for both electronic states, and hence may produce a considerable redistribution of the intensity between the individual vibrational peaks within the electronic band. Then the shift $\delta \nu_{\max}$ in the peak may differ substantially from the shift $\delta \nu_0$ in the purely electronic transition.

R. M. Fofonova has determined the latter shift for acetone in the $S_0$ -- $S_{n\pi^*}$ transition when the solvent is changed from nonpolar to hydroxyl-bearing at 990 cm$^{-1}$, while $\delta \nu_{\max} = 1080$ cm$^{-1}$; consequently, there is only a small vibrational effect in the electronic spectra when the H bond is formed in this system. Theoretical estimates by Anderson and Lippincott also show that in general the vibrational effect is not more than 20–30% of the total H-bond energy [12].

The calculated strength of the $S_0$ -- $S_{n\pi^*}$ transition for the acetone + H$_2$O complex is higher than that for acetone itself, evidently due to change in the hybridization of the $p_y$ orbital and to change in the configuration mixing of the $S_{n\pi^*}$ state. Experiment also indicates an increase in the strength of the long-wave absorption of the acetone on going from a nonpolar solvent to a more polar one or to a solvent capable of forming H bonds [13].