

CNDO/2 Study of $C_2H_2 + H_2O$ System

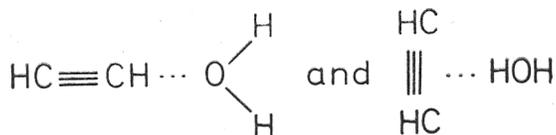
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Different configurations of the $C_2H_2 + H_2O$ system obtained by various translations and rotations of H_2O around the C_2H_2 molecule were studied. The two molecules were found to form not only hydrogen bond but also a charge transfer complex.

Acetylene and water molecule are known to form hydrogen bond of two different types with a bonding energy of 2—4 kcal/mol¹⁻⁷:



In systems like these, where both molecular fragments appear as good electron donors and acceptors, charge transfer complexes have often been found to exist⁸⁻¹⁴.

In this paper the possibility for the existence of such a complex in the $C_2H_2 + H_2O$ system was studied by examining all kinds of intermediates between hydrogen bonded structures. It was also of importance to find how the molecular features change upon different movements of the water molecule around acetylene, and how different is the contribution of charge transfer and electronic rearrangements in the bonding.

The CNDO/2 method¹⁵ was used since it provides good relative values of the main molecular features in such cases. The O—H bond length and HOH bond angle were taken as variables. The examined rotations and translations of H_2O around the C_2H_2 molecule, as well as a number of minimum energy molecular properties, are shown in Figure 1 and Table I.

The linear hydrogen bond was found to be more stable than the four different bent hydrogen bonds (Figure 2). The γ and δ -rotations of the water molecule around the terminal atom of C_2H_2 , however lead, after a small barrier at 60° ($\Delta E \approx 2$ kcal/mol) to a new, deeper energy minimum at the rotation angle of 108° (see also Figure 1.2 and 1.4). This minimum could hardly be caused by hydrogen bonding since the hydrogen in the C—H group turns into an electron acceptor upon a rotation of more than 100° . The charge transfer from

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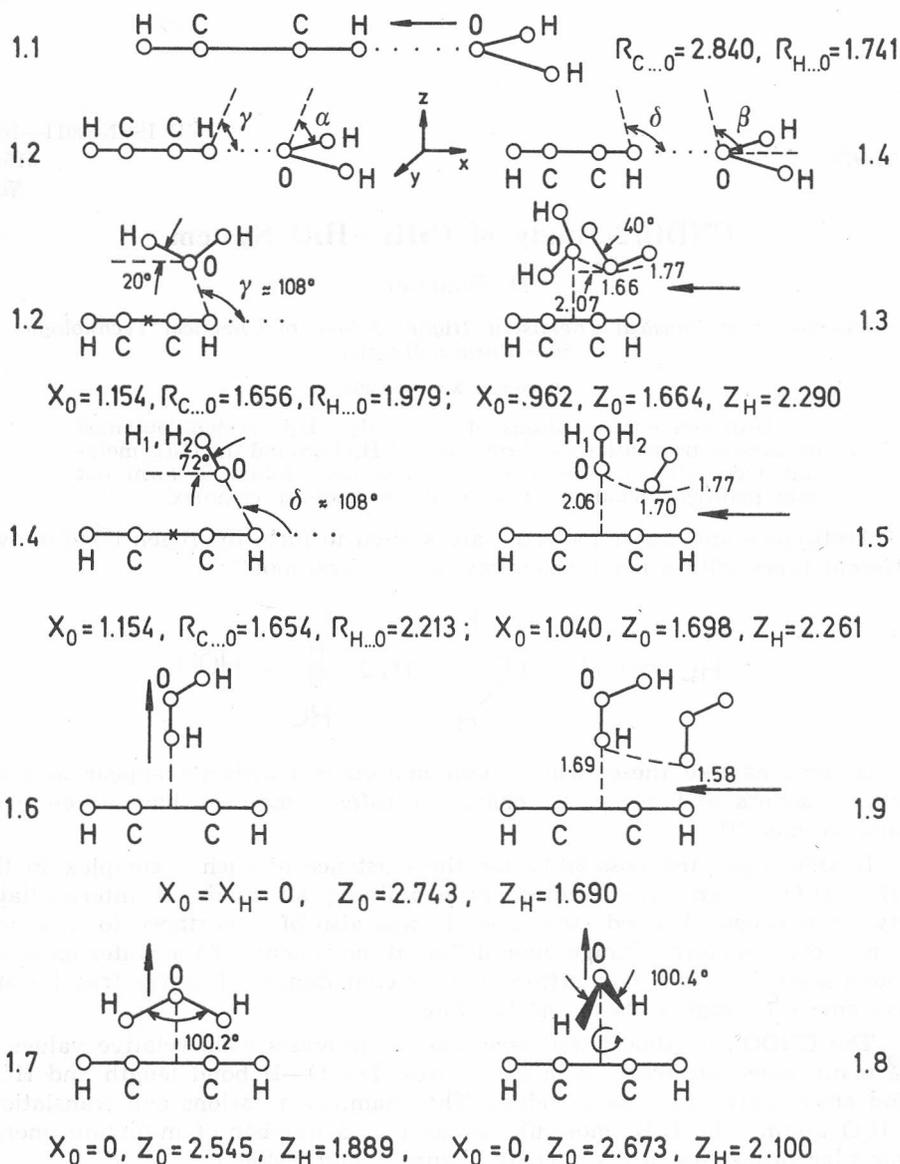


Figure 1. $C_2H_2 + H_2O$ system configurations under study. α, γ -angles of rotation in xy -plane; β, δ -angles of furcated rotation out of xy -plane. Origin of the coordinate system in the centre of the C—C bond; all coordinates and distances in Å. (Classification of configurations is given in Table D).

H_2O to C_2H_2 , as well as the charge shifts in both fragments, decreases to a rotation angle of 75° and then increases rapidly. At the energy minimum the dipole moment and the total charge transferred to π -MO of C_2H_2 both from the water molecule and from the σ -MO of C_2H_2 , have their maximum values. The charge transfer from the σ -MO is twice as large as that from the water

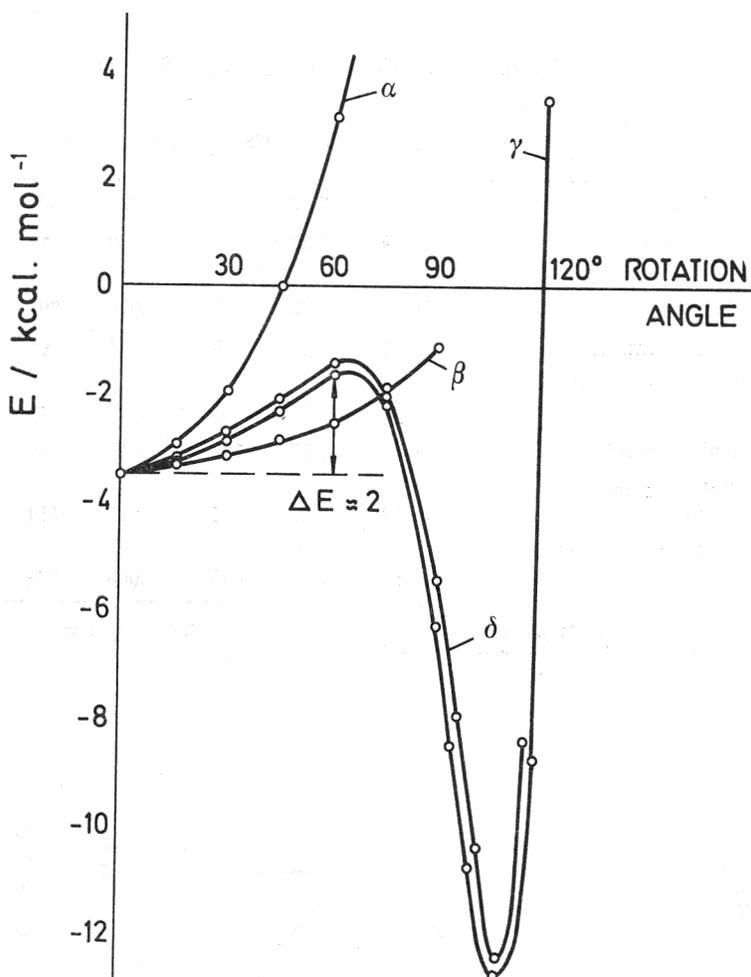


Figure 2. Bonding energy of $C_2H_2 + H_2O$ system as a function of four angles of water molecule rotation.

molecule. One can conclude that probably a charge transfer complex is formed, associated with an inner $\sigma-\pi$ charge transfer in C_2H_2 . The amount of charge transferred (0.04—0.06) is more than twice greater than those found by Schlug and Levinson¹⁶ for the benzene-chlorine complex (CT = 0.02).

We studied further the translations of the water molecule along the acetylene chain, starting from the minimum energy geometries of γ - and δ -rotations (Figure 1.3 and 1.5). The lowest energy configuration was found to be the one with an oxygen atom at 1.66 Å over C—H bond and the H atoms away from C_2H_2 . The energy of the complex, the charge transfer ($H_2O \rightarrow C_2H_2$), the charge shift and the total change in the π -electron charge of acetylene are shown in Figure 3 to vary with translation in nearly the same way. The charge transfer changes its sign near the centre of the the $C\equiv C$ bond where the water molecule turns into an electron acceptor.

TABLE I
Minimum Energy Properties of $C_2H_2 + H_2O$ System

N ^o	Quantities Configurations	E	μ	CS _{ACC}	CS _{DON}	CS	
						CS	CT
1.1	Linear H bond	3.93	2.42	.040	.012	0.52	.009
1.2	Unfurcated rotation	12.69	2.33	.109	.068	.177	.039
1.3	Horizontal unfurcated translation	16.12	2.62	.216	.075	.291	.053
1.4	Furcated rotation	12.61	2.67	.138	.042	.180	0.64
1.5	Horizontal furcated translation	12.48	2.74	.201	.046	.247	.047
1.6	Vertical H bond	18.86	2.57	.168	.014	.182	0.52
1.7	Parallel furcated structure	22.27	2.28	.045	.006	.051	.019
1.8	Perpendicular furcated structure	18.57	2.32	.045	.008	.053	.018

Energy, E , in kcal/mol; dipole moment, μ , in D; charge transfer, CT, and charge shift, CS, in atomic units (See ref. 6 for a definition of a charge shift).

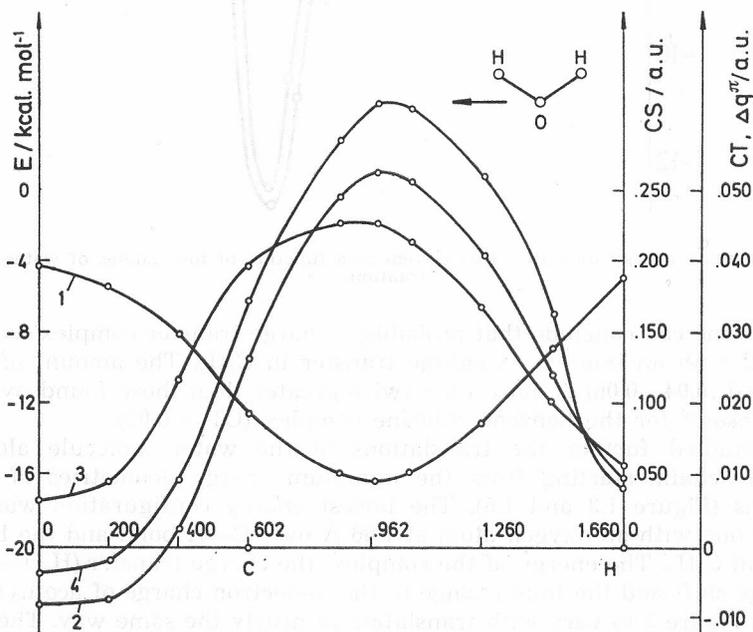


Figure 3. Bonding energy, charge transfer, charge shift and change in π -electron atomic charge in $C_2H_2 + H_2O$ system upon horizontal unfurcated translation of H_2O over C_2H_2 .

In the other four translations, shown in Figures 1.6 to 1.9, one or two of the water hydrogens are closer to the acetylene molecule and the bond should be classified as an $O-H \dots \pi$ hydrogen bond. The bonding energy is greater when oxygen is above the centre of the $C \equiv C$ bond, although in the case of horizontal translation 1.9, it is nearly the same along the whole bond. The parallel furcated structure 1.7 is the most favourable with no energy barrier between structures 1.7 and 1.8. As can be seen in Figure 4, the bonding energy of the structure 1.7 correlates very well with the dipole moment and the π -charge transfer. The charge shift has a minimum at the minimum energy distance between the two molecules, although it remains nearly three times greater than the charge transfer. Comparing these two physical effects in all examined positions of C_2H_2 and H_2O (Table I) one can state that the charge transfer is less important than the charge shift, the latter being 3 to 5 times greater. The ratio between both effects varies from a nearly constant value with rotations 1.2 and 1.4, to a slight relative increase of CT with translations 1.3 and 1.5 and to a greater increase in cases 1.6 to 1.9.

One can summarize that four of the 9 structures studied in this paper (Figures 1.2 to 1.5) may be classified as a charge transfer complex between H_2O and C_2H_2 . This result is in agreement with some findings^{11,12} that for weak complexes probably a wide range of geometries exist having similar binding energy. The $C_2H_2 + H_2O$ complex appears as an intermediate between the linear $C-H \dots O$ (Figure 1.1) and the vertical $O-H \dots \pi$ hydrogen bond structure (Figures 1.6 to 1.9). It has a bonding energy near to that of the $O-H \dots \pi$ bond although the CNDO/2 values of both energies seem to be strongly over-estimated.

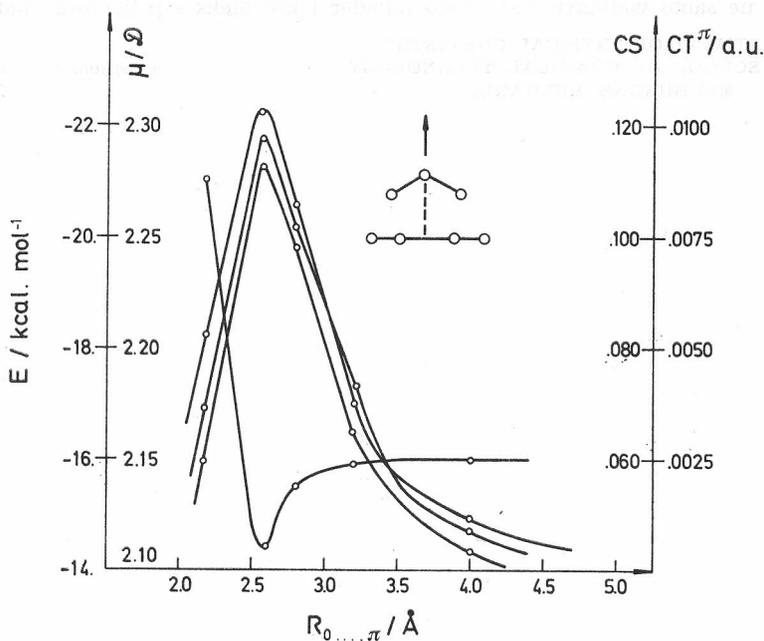


Figure 4. Bonding energy, dipole moment, charge transfer, and charge shift in $C_2H_2 + H_2O$ system upon vertical translation of H_2O over C_2H_2 .

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SAŽETAK

CNDO/2 studij sustava $C_2H_2 + H_2O$

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Istraživane su različite konfiguracije sustava $C_2H_2 + H_2O$ koje su dobivene različitim translacijama i rotacijama H_2O oko molekule C_2H_2 . Nađeno je da dvije molekule stvaraju ne samo vodikovu vezu nego također i kompleks s prijenosom naboja.

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