Computational Study of σ- and π-type Hydrogen Bonding in Acetonitrile-Water Clusters

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Clusters are of fundamental interest, because studying them may shed considerable light on the effects of "microsolvation" on the properties of the solute on molecular scale. Although considerable amount of information has been accumulated for the structures of the clusters, most of the investigations were focused either on "pure" clusters, consisting of identical solvent molecules such as water, methanol, ammonia, or "microsolvated" solute[1-12] consisting of solute molecule and a number of solvent molecules. More intriguing and complicated "mixed" clusters may consist of different kinds of molecules of more or less equal molar ratio. Since one cannot simply use the weighted average of the dielectric constants of the constituent solvents to employ the PCM[13] type methods in this situation, the cluster model will be more useful.

In this work, we study the water-acetonitrile clusters to examine the nature of interactions in the mixed clusters by using the GAUSSIAN 94 set of programs.[14] Our focus in this work is on the interactions between different kinds of "solvent" molecules in the mixed clusters. We investigate the acetonitrile-(water)$_n$ (n=1-4) system to elucidate the property of the clusters as a function of the number of the binding water molecules. We first investigate the acetonitrile – (water)$_1$ cluster, and find two isomers as shown in Figure 1. There exists a noticeable difference in the structures of the two isomers, p1-1A and s1-1B, in the sense that the hydrogen bonding in the first isomer in Figure 1 is approximately perpendicular to the axis of the acetonitrile moiety, while it is almost parallel in the second isomer. We call the first isomer as "π-type" and the second one as "σ-type", following the nomenclature of Mikami *et al.*[12] and by Kim and co-workers.[15-17] The energies of the two isomers are calculated to be very similar, depending on the method and the basis set employed. At MP2/6-31G+(d,p) level of approximation. isomer p1-1A (including ZPE) is calculated to be slightly (by only 0.11 kcal/mole) lower, while s1-1B is of lower (by 0.09 kcal/mol) energy when the aug-cc-pVDZ basis set is employed. Similarly, the σ-type isomer s-1-1B is predicted to be slightly of lower energy when 6-31G+(d,p) method is employed. Thus, the σ-type and the π-type hydrogen bonding are equally favorable in 1 : 1 water – acetonitrile complex. These results are listed in (Table 1), along with the binding energies of the clusters.

We also calculate the harmonic frequencies of the clusters,

and find very interesting pattern concerning the structures of the clusters: The clusters p1-1A and s1-1B exhibit the opposite tendency for the frequency shifts of the C-N stretching modes from that of the free acetonitrile molecule. For the σ-type isomer (s1-1B) the CN stretching is *blue-shifted* (by 13.4 cm^{-1}), while for the π-type cluster (p1-1A) it is *red-shifted* (by −6.7 cm^{-1}) from that of the bare acetonitrile. Considering that the effects of microsolvation of molecules usually produce red-shifted[15,16] frequency for the stretching motion of hydrogen bond acceptor and donator, the origin of this latter observation (blue shift of the CN stretching mode in the σ-type bonding isomer) is highly intriguing.

To further corroborate our latter findings, we now calculate the CN stretching frequencies in acetonitrile – (H$_2$O)$_n$ (n = 2-4) clusters so that the effects of the π-type and the σ-type hydrogen bonding may "accumulate". In the first series of calculations, water molecules are added one by one to the isomer p1-1A so that the effects of the σ-bonding character may increase. As shown in Figure 2, the water molecule directly binding to the CN group lies more and more parallel to the molecular axis of the acetonitrile moiety, thus increasing the σ-bonding character. We notice that the harmonic frequency of the C-N stretching mode *increases* (2347.4, 2354.0, and 2359.3 cm^{-1} for s1-2, s1-3 and s1-4, respectively). The effects of the π-and σ-type character breaks even for the s1-3 isomer, yielding the C-N stretching frequency that is identical to that of the bare acetonitrile. For s1-4, the effects of the σ-type character prevail, and the C-N stretching frequency blue-shifts with respect to free acetonitrile.

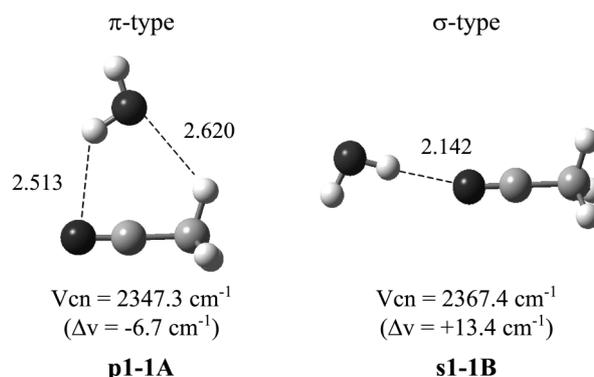In the second series of calculations, we add water molecules

π-type   σ-type

2.620

2.513

2.142

Vcn = 2347.3 cm^{-1} Vcn = 2367.4 cm^{-1}
(Δv = -6.7 cm^{-1})   (Δv = +13.4 cm^{-1})

p1-1A   **s1-1B**

Figure 1. The structures and C-N stretching harmonic frequencies of (CH$_3$CN)-(H$_2$O) complexes.
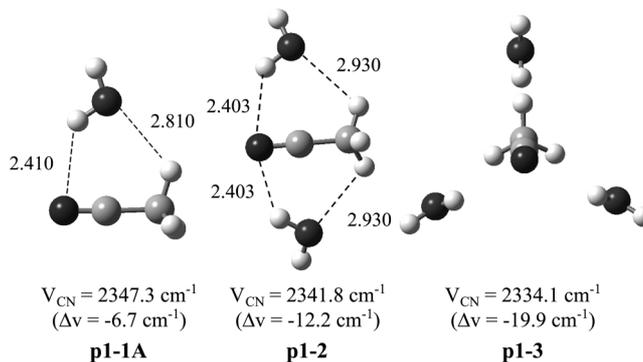
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Table 1. Calculated energies (hatree), ZPEs (kcal/mol) and binding energy (BE) of $(CH_3CN)_1$-$(H_2O)_1$ complex

	p1-1A			s1-1B			E(A)-E(B)[a]
	Energy	ZPE	BE	Energy	ZPE	BE	
MP4SDQ/6-31+G(d,p)	−208.63645	43.84	–	−208.63661	43.92	–	0.017(s1-1B)[b]
MP2/6-31+g(d,p)	−208.60990	43.65	3.91	−208.60988	43.74	3.80	−0.11(p1-1A)
/aug-CC-pVDZ	−208.65274	42.93	3.81	−208.65293	42.96	3.90	0.091(s1-1B)
B3LYP/6-31+G(d,p)	−209.20632	43.09	2.74	−209.20752	43.15	3.43	0.69(s1-1B)
/aug-CC-pVDZ	−209.22153	42.80	2.41	−209.22285	43.89	3.14	0.74(s1-1B)
HF/6-31+G(d,p)	−207.97330	46.25	2.45	−207.97388	46.23	2.82	0.379(s1-1B)

[a]The energy difference (kcal/mole) (ZPE included), between the energy E(A) of p1-1A, and the energy E(B) of p1-1B. [b]isomer of lower energy.
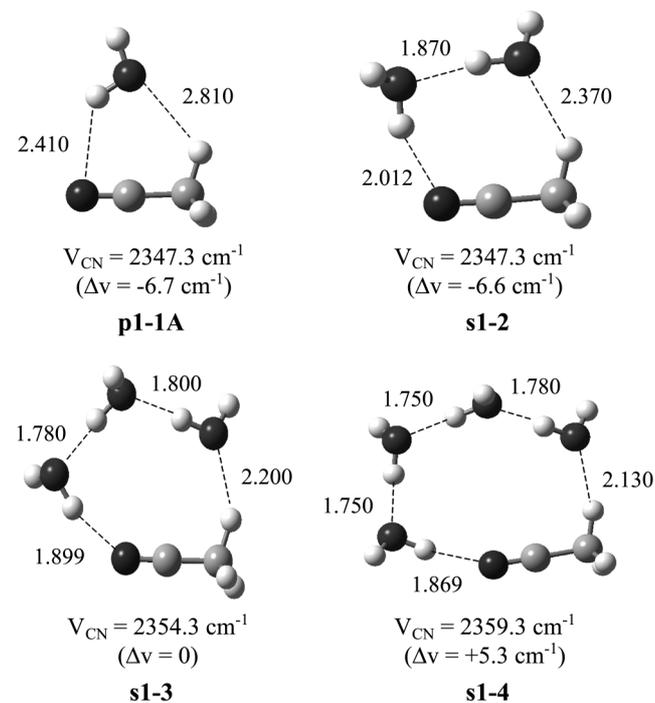
Figure 2. The structures of (CH_3CN)-$(H_2O)_n$ (n = 1-4) clusters with increasing σ-type bonding character.

Figure 3. The structures of (CH_3CN)-$(H_2O)_n$ (n = 1-3) clusters with increasing π-type bonding character.

in approximately perpendicular position, as depicted in Figure 3, increasing the π-type bonding character. The CN stretching harmonic frequency significantly *decreases* (2347.3, 2341.8 and 2334.1 cm^{-1} for p1-1A, p1-2 and p1-3, respectively), red-shifting more and more (-6.7, -12.2 and -19.9 cm^{-1} for p1-1A, p1-2 and p1-3, respectively) from that of the bare acetonitrile. In other words, the π-type hydrogen bonding reinforces the red-shifting of the infrared frequency. It should be noted that all the water molecules bind in symmetrical fashion in these clusters, the bond lengths, angles and dihedral angles being essentially identical. Therefore, since the hydrogen bonding between each water and acetonitrile moiety are expected to contribute to the C-N stretching vibration frequencies more or less similarly, the amount of red-shifting may be considered as being affected only by the number of water molecules binding in π-type positions. Theoretical elucidation of the origin of these highly interesting observations and more calculations for other types of acetonitrile – water clusters will be presented in the near future.

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