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Effect of hydrogen bonding on the spectroscopic properties of molecular complexes with aromatic rings as acceptors

Hailiang Zhao, Jiamin Chang, Lin Du *

Environment Research Institute, Shandong University, Shanda South Road 27, 250100 Shandong, China

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ABSTRACT

We carried out a detailed investigation on the spectroscopic properties of hydrogen bonded molecular complexes of water and methanol (MeOH) with aromatic rings as acceptors, including benzene (BZ), melamine (MA), 1,3,5-triazine (TA) and 1,3,5-triaminobenzene (TAB). The optimized geometries of the complexes have been obtained with four DFT functionals B3LYP, M06-2X, ωB97X-D and B3LYP-D3. Both O—H···π and O—H···N hydrogen bond interactions were found in the complexes. The binding energies, spectroscopic and thermodynamics properties of the complexes were calculated. The calculated IR spectra show large red shifts of the symmetric OH-stretching transitions of the H_2O-complexes and the MeOH-complexes, together with large intensity enhancement. On the other hand, small red shifts of the antisymmetric OH-stretching transitions of the H_2O-complexes were discovered and their corresponding intensities are only slightly increased. Ultraviolet–visible absorption spectra of all the monomers and complexes were computed with time-dependent DFT (TD-DFT). The peak absorption wavelengths show small blue shifts upon complex formation and the intensities are only slightly changed as compared with the monomers.

1. Introduction

Hydrogen bonds play an important role in chemical and biological systems, mainly because of their importance for structure stabilization and reaction catalysis [1,2]. Aromatic compounds are the constituents of many common organic substances, such as proteins and nucleic acids. Their biological activity is largely determined by the molecular structure, which has a great relationship with hydrogen bonds. On the other hand, aromatic compounds are widely used as chemical products, and most of them become environmental pollutants. 1,3,5-triazine (TA) is a nitrogen-containing heterocyclic aromatic compounds and one of the most common derivatives of TA is 2,4,6-triamino-1,3,5-triazine (melamine, MA). MA was used as food additive, which caused serious harm to human health [3]. It became headline news after the occurrence of an outbreak of urinary stones in infants and children consuming melamine-tainted milk in China. Besides, aromatic compounds can be efficiently excited by ultraviolet (UV) radiation in the environment [4,5].

Water is one of the most common components in natural environment and it is recognized as a strong proton donor. The interaction of aromatic molecules with water and its role to determine the physical and chemical properties of such systems is an area of particular interest for many theoretical and experimental studies [6,7]. The geometrical parameters, vibrational frequencies and binding energies of the $(H_2O)_n$–benzene ($n = 1–7$) clusters have been characterized by means of second-order Møller-Plesset perturbation theory (MP2) and density functional theory (DFT) [8,9]. The $(H_2O)_n$ clusters were found to be hydrogen bonded to the benzene ring, and the intensity of the OH-stretching transition increased significantly because of the hydrogen bonding. The infrared (IR) frequency red shifts of the OH-stretching transition from $(H_2O)_n$ to $(H_2O)_n$–benzene were in the range of 40–60 cm^{-1} [9].

Vibrational spectroscopy is an effective technique to study hydrogen bonded complexes. The red shift with respect to the free stretching transition in the monomer is a typical feature of a hydrogen bonded complex [10–12]. The IR intensity may change significantly upon complexation, which has also been considered to be the criterion for hydrogen bonding. Many investigations have been performed with methanol (MeOH) as the hydrogen bond donor [13–15]. A combination of vapor phase IR spectroscopy and *ab initio* calculations has been performed for the MeOH–dimethylether (DME) and MeOH–dimethylsulfide (DMS) complexes [16]. The experimental red shifts were measured to be 103 and 113 cm^{-1} for MeOH–DME and MeOH–DMS, respectively. The effect of fluorine substitution in alcohol–dimethylamine (DMA) complexes was studied with both experimental and

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* Corresponding author.
E-mail address: lindu@sdu.edu.cn (L. Du).

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theoretical methods [17]. The observed red shifts of the OH-stretching transition were 301, 296 and 460 cm^{-1} for MeOH–DMA, EtOH–DMA and 2,2,2-trifluoroethanol (TFE)–DMA, respectively. The replacement of an H atom by a methyl group has limited effect on the hydrogen bonding interaction, but the replacement by a CF_3 group has a significant effect. Moreover, Bloom and coworkers performed a computational study of substituent effects in noncovalent interaction involving 22 substituted benzenes, and they found that substituents can have a dramatic impact on the X–H···π interactions [18]. The nature of the X atom could primarily determine the magnitude of these effects. In particular, increased polarity of the XH bond is accompanied by a substantial increase in the magnitude of substituent effects.

In the present study, we choose four molecules with aromatic rings, benzene (BZ), 1,3,5-triazine (TA), melamine (MA) and 1,3,5-triaminobenzene (TAB) as the hydrogen bond acceptors, water and MeOH as the hydrogen bond donors to study the relationship between spectroscopic properties and the hydrogen bonding interactions. The geometric parameters, binding energies, IR and Raman vibrational frequencies have been calculated using DFT. In addition, the UV–vis spectra have also been calculated by time-dependent DFT (TD-DFT) to investigate the electronic properties of the hydrogen bonded complexes.

2. Computational methods

All DFT calculations were performed with Gaussian 09 program using the aug-cc-pVTZ basis set, which has been proven to give reasonable geometries and interaction energies of the hydrogen bonded complexes [10,11]. Four functionals were selected: B3LYP, M06-2X, ωB97X-D and B3LYP-D3. Frequencies were calculated with DFT methods for each stable conformer to ensure that a true minimum had been found. The zero-point vibrational energy (*ZPVE*) was corrected for binding energies (*BEs*), however, the basis set superposition error (*BSSE*) was not considered for the correction of *BEs*, because the typical counterpoise (CP) correction may overestimate basis set related errors for large basis set such as aug-cc-pVTZ [19,20]. The IR and Raman spectra were calculated on the basis of the optimized structures. The UV–vis spectra were computed using the TD-DFT method at the B3LYP/aug-cc-pVTZ level.

3. Results and discussion

3.1. Molecular geometries

The geometry optimization of the aromatic rings, H_2O, MeOH and the complexes was conducted with the four functionals using the aug-cc-pVTZ basis set. The optimized structures of the aromatic rings and the complexes at the B3LYP-D3/aug-cc-pVTZ level are shown in Fig. 1. There are two possible types of hydrogen bond interactions in the complexes, O–H···π and O–H···N. Both types can be found in the TAB-complexes and only O–H···π type presents in the BZ-complexes. The TA-complexes and MA-complexes have only O–H···N type of interaction. Selected geometric parameters obtained at the B3LYP-D3/aug-cc-pVTZ level are listed in Table 1. The results with the other functionals are provided in supplementary material.

The water–BZ complex has two stable conformers (Fig. S1 in supplementary material). Engdahl and Nelander identified the complex to exist as conformer (b) with C_{2v} symmetry in an Ar matrix [21], whereas conformer (a) with C_s symmetry was found to be present in the gas phase [22,23]. However, conformer (a) is predicted to be the global minimum for the water–BZ complex with both MP2 and B3LYP methods [24,25]. We focus on the more stable conformer in the following discussion. Interestingly, water molecule is bound on one side instead of the center of the BZ ring [6,23,26]. The similar bonding pattern was also found for MeOH–BZ and the O–H···π bonded conformers of the MeOH/H_2O–TAB complexes.

In the O–H···π bonded conformers of the BZ-complexes and TAB-complexes, the hydrogen bond donor strength of H_2O and MeOH is almost the same based on the change in the OH bond length upon complexation (Table 1). However, as compared with BZ, TAB has three amino (–NH_2) groups, which make the π system of TAB more nucleophilic. As a result, the changes in the OH bond length of TAB-complexes are much larger (0.004–0.005 Å) than the BZ-complexes (0.002 Å), which indicates that TAB is much stronger than BZ as a hydrogen bond acceptor.

In the TA/MA-complexes, the O–H···N type of hydrogen bonding interaction was found between the N atoms on the aromatic rings and H_2O or MeOH. In a previous study, the water–TA complex was found to have a hydrogen bonded structure with the O–H···N hydrogen bond angle of 156.6° and the H···N distance of 2.008 Å (B3LYP/6-31++G**) [27]. On the other hand, the structural difference between MA and TA is that the three H atoms on the TA ring are replaced by three –NH_2 groups. The O–H···N hydrogen bonds in the MA-complexes are stronger than those in the TA-complexes as seen from the geometric parameters: shorter H···N distances, larger O–H···N angles and greater changes in the OH bond length upon complexation. Besides, the calculations show that there is not only O–H···N hydrogen bonding interaction but also N–H···O interaction between MA and H_2O or MeOH. The –NH_2 group in MA could also act as a hydrogen bond donor to form a N–H···O hydrogen bond with the O atom of either H_2O or MeOH to form a six-membered ring (Fig. 1). For MeOH–MA, the NH bond length is enlarged by 0.007 Å (B3LYP-D3/aug-cc-pVTZ). Similar N–H···O interaction was found in MeOH–$PhNH_2$, and the N–H···O angle is about 30° larger than the value of MeOH–MA in our study [28].

In the TAB-complexes, both O–H···π and O–H···N bonded conformers could be formed. The O–H···N bonded conformer of H_2O–TAB is relatively more stable (relative energy: 0.9 kJ mol^{-1} (B3LYP-D3/aug-cc-pVTZ)) than the O–H···π bonded conformer. In the MeOH–$PhNH_2$ complex, the N···O distance was calculated to be 2.06 Å and the N–H···O angle was 166° (B3LYP/6-311++G(2df,2pd)) [28]. As compared with $PhNH_2$, TAB has two more –NH_2 groups. In MeOH–TAB, the N···O distance is shorter by ~0.05 Å and the N–H···O angle is increased by ~4° with respect to MeOH–$PhNH_2$.

3.2. Binding energies

An assessment of binding energies of 107 atmospherically relevant clusters containing H_2SO_4, H_2O, NH_3 and DMA was performed using several different DFT functionals (B3LYP, CAM-B3LYP, M06-2X, PW91, LC-PW91, PBE0 and ωB97X-D) against the benchmark high level explicitly correlated coupled cluster methods [29]. In general, the ωB97X-D functional gives the best estimate of the binding energies over the large test set of clusters. In the study of the MeOH–DMA and MeOH–TMA complexes, the absolute binding energy differences obtained with M06-2X and ωB97X-D are less than 2 kJ mol^{-1} as compared with the CCSD(T)-F12a values [12].

We calculated the binding energy (*BE*), enthalpy of formation (ΔH^{θ}_{298K}) and Gibbs free energy of formation (ΔG^{θ}_{298K}) at 298 K, and the results obtained at the B3LYP-D3/aug-cc-pVTZ level are given in Table 2. The results of other methods are provided in Table S2 (supplementary material). Comparing to *BE*s of the other three functionals, the B3LYP *BEs* are significantly underestimated.