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Red-shifted and improper blue-shifted hydrogen bonds in dimethyl ether (DME)$_n$ ($n=1$–4) and hydrated (DME)$_n$ ($n=1$–4) clusters. A theoretical study

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Abstract

In the present study, dimethyl ether (DME), dimethyl ether dimer (DME)$_2$, trimer (DME)$_3$, tetramer (DME)$_4$ and hydration of these clusters have been investigated using the ab initio and density functional theory methods. The formation of (DME)$_n$ ($n=2$–4) complexes lead to the contraction of methyl C–H bond and elongation of C–O bond, when these two bonds form the hydrogen bonding. The contraction of C–H bond gives a blue shift in the C–H stretching frequency. The interaction of water molecules with the (DME)$_n$ ($n=1$–4) complexes lead to the elongation of O–H bonds. The elongation of O–H bond gives the red shift in the O–H stretching frequency. The length of the C–H⋯O hydrogen bond is longer than the length of the R(O⋯H) hydrogen bond, which gives the standard O–H⋯O H-bond interaction. Interaction energies were calculated after eliminating basis set superposition error by using full counterpoise correction method. Interaction energy for the C–H⋯O hydrogen bond is less than that for the O–H⋯O hydrogen bond. Natural bond orbital analysis reveals that the increase of electron density in the σ* antibonding orbitals of the O–H bond in water yield its weakening. The contractions of C–H bond in the (DME) clusters have been analyzed using the concept of charge density transfer and rehybridization mechanisms. The charge density (ρ), and Laplacian of charge density ($\nabla^2\rho$), were also calculated for both C–H⋯O and O–H⋯O interactions, which are used for the classification of improper (blue shifted) and proper (red shifted) hydrogen bonds.
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1. Introduction

The importance of hydrogen-bonded complex has been felt in the last two decades. Hydrogen bond interaction plays an important role in determining the structure of molecular crystals [1] and biological systems [2]. The identification of hydrogen bonding has attracted the attention of experimental [3,4] and theoretical [5–8] scientists. Numerous high-level ab initio molecular orbital and density functional theory (DFT) calculations have been reported for hydrogen-bonded systems [5–8].

Conventional H-bond interaction is X–H⋯Y type, where X is an electronegative atom (F, O, N, Cl) and Y is either electronegative atom having one or more lone pair of electrons or a region of excess electron (π electron of aromatic systems). Using natural bond orbital analysis (NBO), Weinhold et al. [9] have demonstrated that the charge transfer from lone pair of an electron donor is directed to the σ* antibonding orbital of the proton donor, i.e. X–H bond. The increase of electron density (ED) in the antibonding orbitals weakens the X–H bond, which leads to elongation and concomitant lowering of the X–H stretching frequency (red shift). The red shift represents the most important, easily detectable manifestation of the formation of the hydrogen bond, which is the basis for experimental detection of hydrogen bonding [10]. The red shift has also been correlated with the strength of the hydrogen bond [11], the proton donor–acceptor distance [12], and the ionization potential of the proton acceptor. Few of the experiments

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have found that the X–H stretching frequency is shifted towards the higher frequency side (blue shift) in a X–H$\cdots$Y hydrogen bonded systems [12–24], where X is CF_3, CCl_3 and dimethyl ether and Y is triformylmethane, benzene, ethylene oxide, and dimethyl ether. In this type of hydrogen bonding, less electron density is transferred to the σ^* antibonding orbital of the X–H bond. The major part of the electron density is transferred to a remote part of the proton donor molecule. A number of theoretical studies have also been demonstrated for the blue-shifted hydrogen bonds [22–37].

In 1980, Trudeau et al. [32] have measured the C–H vibrational frequency for fluoroparaffines, which contains –CHF_2 group, having interaction with various proton acceptors and reported the shift of the C–H stretching frequency to higher frequency side. In 1983 Barnes and Beech [38] have beautifully calculated the dimethyl ether–water complex trapped in argon matrices, which shows an upward shift of the C–H stretching frequencies. Hobza and co-workers [21–26] have proposed that blue-shifted hydrogen bonding can be explained by charge transfer from proton acceptor Y to remote (highly electronegative) atoms in X (e.g. F in CF_3) instead of the σ^* antibonding orbitals of the X–H bond followed by a structural reorganization of the proton donor framework resulting in contraction of the C–H bond. A sharp contrast to this theory, Scheiner et al. [27,30] have made a thorough study and proposed that improper and proper H-bond formation lead to a similar change in the remote parts of the hydrogen bond donor, and that there are no fundamental differences between the mechanisms of the formation of improper and proper hydrogen bonds. This is consistent with the results of 'atoms-in molecules' (AIM) [39] analysis of Cubero et al. [21] who have observed that there is no fundamental difference between electron density distributions for the red- and blue-shifted hydrogen bonds. Weinhold et al. [33] have made an extensive study on the nature of hydrogen bonding (blue or red shift) employing the electrostatic and rehybridization schemes.

So far, all the blue-shifted hydrogen bonds have been studied only for smaller systems; it has not yet been completely studied for the hydrogen bonds in clusters. Recently Tatamitani et al. [34] have studied the weak, improper C–O$\cdots$H–C hydrogen bonds in the dimethyl ether dimer using the molecular beam Fourier transform microwave spectra, and identified three weak C–H$\cdots$O hydrogen bonds. They have used the experimental and ab initio result for the determination of interaction energy and hydrogen bond length. Subsequently Hobza et al. [35] have also studied the hydration of sulfo and methyl groups in dimethyl sulfoxide using the quantum chemical methods. They have again confirmed the elongation of the S=O bond and contraction of methyl C–H bond using molecular dynamics (MD) simulations also. Recently, we have studied the proper and improper hydrogen bonds using AIM and NBO analyses [36]. In order to extend these studies to clusters, the present study has been initiated.

The aim of the present investigation is twofold: (1) to study $(DME)_n$ ($n = 2$–4) clusters and their hydration using the ab initio and DFT methods, and (2) to study the proper and improper hydrogen bonds in the clusters and their hydration. Since, more numbers of improper hydrogen bonds are present in these systems, one can get broad explanations for the above concepts. In addition to this, the hydration of dimethyl ether (DME) clusters has also been studied for the proper hydrogen bond, since the DME clusters have been stabilized largely by the improper hydrogen bonds. By considering the above facts into account we have made an extensive study for improper and proper hydrogen bonds using the ab initio and DFT methods. In addition to the geometry optimization, natural bond orbital analysis, electron density, and Laplacian of electron density analysis have also been performed for the above clusters and their hydrated form. The conformation of $(DME)_n$ and HOH$\cdots(DME)_n$ ($n = 1$–4) are shown in Fig. 1 using Molden package [40].

2. Method of calculations

The ab initio and density functional theory (DFT) methods have been used to optimize the geometry of the $(DME)_n$ as well as HOH$\cdots(DME)_n$ ($n = 1$–4) complexes. The changes in the electronic properties of blue and red shifting H-bonds for $(DME)_n$ ($n = 2$–4) clusters and hydration of the clusters have been studied. The second order Moller–Plesset perturbation (MP2) theory [41] of ab initio method, Becke's three parameter exact exchange functional (B3) [42] combined with gradient corrected functional of Lee–Yang–Parr (LYP) [43], Perdew and Wang's 1991 gradient corrected function (PW91) [44] and Vein, Adamo and Barone [45] introduced a hybrid one-parameter functional (mPW1PW91), which mixes the exact-exchange into the mPWPW91 of DFT methods have been employed to optimize the molecules by implementing 6-31G* basis set. The latter functional (mPW1PW91) was tested for all the above structures. All of the H-bonded complexes are found to be at local minima, which have been confirmed by the frequency analysis. The interaction energy, after correcting the basis set superposition error by the counterpoise procedure of Boys and Bernardi [46], has been calculated by using the following equation

$$E_{int}(corr) = E_{AB} - [E_A(AB) + E_B(AB)]$$

where E_{AB} is the energy of the complex with the basis set of monomers A and B and $E_A(AB)$ is the energy of monomer A with the full dimer basis set by setting the appropriate nuclear charges to zero which is located at the same intermolecular configuration as the complex, with similar to the other. Vibrational frequencies, charge transfer, and topological properties such as charge density (ρ) and Laplacian of charge