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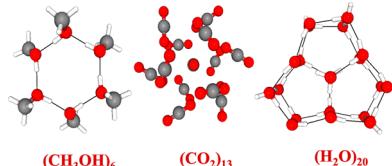
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Quantum Chemical Investigations on Molecular Clusters

Shridhar R. Gadre,^{*,†} Sachin D. Yeole,^{†,‡} and Nityananda Sahu[†]

[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208 016, India

[‡]Department of Chemistry, University of Pune, Pune 411 007, India



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1. INTRODUCTION

A cluster is an aggregate of bound atoms or molecules, intermediate in size between a molecule and a bulk solid. Clusters of a variety of molecules are receiving increasing attention due to their size-dependent physicochemical properties which may be totally different from those of the bulk.^{1–4} The evolution from molecules to bulk can be traced by probing the properties of clusters. Larger clusters, viz. nanoclusters, of some specific materials are of intense scientific interest due to a wide variety of applications in biomedical, electronics, and materials science. Thus, clusters offer an attractive field for

interdisciplinary studies, comprising experimental as well as theoretical investigations of interest to physicists and chemists alike.^{1–4}

Based on the nature and type of the forces that exist between the molecules, molecular clusters may be broadly classified as metallic,⁵ ionic,⁶ and weakly bonded molecular clusters.^{7–10} Aggregates such as Al₇₇, Ga₈₄, Pd₁₄₅, etc. belong to the former category, wherein the atoms are held together by long-range forces originating from valence electron sharing over many adjacent atoms.⁵ Similarly, the electrostatic interaction between the positively and negatively charged species is responsible for binding of the constituents in ionic clusters.⁶ On the other hand, the weakly bonded molecular aggregates involve noncovalent interactions, originating from the interaction between induced or permanent dipoles. These may be dominated by the electrostatic, induction, or dispersion interactions. Such weakly bonded molecular assemblies can be further classified according to the nature of interactions involved. For example, in water clusters, the individual water molecules are held together by hydrogen bonds (HB), whereas aggregates of acetylene and benzene are bound by $\pi\cdots\pi$ and CH $\cdots\pi$ interactions with a significant contribution from the dispersion interactions. Other clusters, such as ZnS, CdSe, CdS, AlN, etc., held together through covalent bonds are endowed with semiconducting properties and are used in modern electronic devices including transistors, diodes, solar cells, etc. The nature of these intermolecular interactions, including cooperativity effects in larger assemblies, govern the stability, structure, and properties of molecular clusters, and hence, the investigations on them have gained importance in many physical, chemical, and biological sciences.^{1–4,7,8} Since the individual molecules in the weakly bound molecular clusters are held together by weak intermolecular forces, the geometries of these units of the clusters generally closely resemble those of the isolated ones.

In the study of molecular clusters, there are unresolved mysteries of structural transitions, extra stability of cages, appearance of solvated atoms or molecules, and many more. Furthermore, understanding the phenomenon of magic numbers^{11,12} in clusters has been a subject of intense theoretical investigations. Therefore, several reviews addressing these aspects are available in the literature summarizing the experimental and theoretical studies on clusters during the last three decades.^{7–10,13–37} Some of the recent ones include experimental studies on gas phase clusters,¹⁰ high resolution spectroscopy of neutral and ionic clusters,²⁵ theoretical studies on clusters of π -systems,²⁶ and the excellent review on water trimer by Saykally and co-workers.³¹ More recently, Jena and

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Castleman³³ summarized studies on clusters with an emphasis on nuclear and condensed matter physics including some examples in chemistry. On the theoretical front, in 1994 and 2000, Chałasiński and Szczęśniak^{9,34} reviewed the ab initio studies of some dimeric complexes. Recently, Mahadevi and Sastry³⁶ presented a review on the cation–π interactions in host–guest complexes, focusing on their energetics and properties. This review³⁶ provides a summary of experimental spectroscopic methods and some of the recent notable theoretical investigations employing the symmetry adapted perturbation theory (SAPT) and density functionals. The recent review on water clusters by Yoo and Xantheas³⁸ gives a detailed discussion on the structures, energetics, and spectroscopy of water cluster containing up to 24 water molecules explored at a high-level of theory. Another recent review by Howard and Tschumper³⁹ provides an overview of the popular strategies present in the literature for estimating the accurate properties and energetics of water clusters employing wave function-based correlated methods. It may be noted that most of the reviews cited above are published prior to 2005, and also to date there are no general review articles on the quantum chemical investigations on molecular clusters, especially on large-sized weakly bonded clusters.

With the recent advents in experimental techniques and powerful computational tools, studies on molecular clusters have grown rapidly in the past decade. However, as noted above, there is no comprehensive general review available on this topic, giving a flavor of current research. Attempting to fill this void, the current article is aimed at presenting a review of the ab initio quantum chemical studies on molecular clusters. Given the vast amount of available literature on molecular clusters, it would be very cumbersome to cover all the topics in a single review. Hence, this review restricts itself to the ab initio quantum chemical investigations on the weakly bound molecular clusters with a special emphasis on large-sized ones. A brief outline of the review is as follows.

In section 2, we discuss the experimental techniques which are being employed for investigating molecular clusters. A short description of jet expansion methods and the matrix isolation techniques is given. It is followed by a summary of Fourier transform infrared (FTIR) and microwave spectroscopy (MW) as well as mass spectroscopy for the characterization and investigation of different aspects of various molecular clusters. The second part of this section summarizes the theoretical methods employed for studying molecular clusters. Here mainly the application of electronic structure methods and various strategies present in the literature for getting the accurate geometries, energetics, and properties of molecular clusters are discussed. This is followed by a short review of fragmentation-based approaches for the treatment of large molecular clusters.

Sections 3 and 4 offer a detailed review of various quantum chemical investigations on different molecular clusters, especially highlighting the works in this area after 2000. Section 3 summarizes the theoretical investigations on the hydrogen-bonded (H-bonded) clusters, e.g., water, ammonia, methanol, and hydrogen peroxide, whereas the other weakly bonded clusters of carbon dioxide, benzene, and acetylene are discussed in section 4. A brief discussion on small clusters of hydrogen, nitrous oxide, and ethylene is also included in this section.

Although this review mainly deals with homoclusters, some representative works on the heteroclusters of water are also

included in section 5. This is because the heteroclusters of water with other substrates represent the phenomenon of hydration at the molecular level. Such explicit hydration studies may offer valuable insights on properties of the solute molecules such as solubility, hydrophobicity, etc. Perspectives on the studies of molecular clusters are given in section 6.

2. METHODS FOR STUDYING MOLECULAR CLUSTERS

2.1. Experimental Methods

Recent advances in experimental techniques have accelerated the exploration of molecular clusters. The gas phase molecular clusters are experimentally generated by pulsed supersonic jet expansion techniques. A dilute mixture of the gas under study with an inert gas (such as argon or helium) is allowed to expand through a slit-jet source, leading to the formation of molecular clusters of variable sizes.^{40–43} This gas expansion is coupled with a variety of experimental techniques, such as infrared (IR), microwave (MW), and photoelectron spectroscopy for probing the molecular clusters thus generated. The powerful tool of mass spectrometry is often used in conjunction with the above experimental methods for determining the sizes of the clusters.

IR spectroscopy is the most popular and powerful technique employed for studying molecular clusters. There are several variants of this technique, providing specific ways to probe molecular clusters. One such method is the direct absorption spectroscopy where broad spectral coverage and accurate intensity information associated with FTIR spectroscopy allow the observation of all the fundamental bands.^{44–47} IR cavity ring-down spectroscopy, another technique popularized by Saykally and co-workers,^{48–50} has emerged as a simple, yet very powerful method of probing clusters with high sensitivity and resolution. The typical setup of this technique consists of a laser that is used to illuminate a high-finesse optical cavity, in the form of two highly reflective mirrors. The cavity mirrors are pressed to seal the vacuum chamber within which the ring-down pulse intersects a pulsed slit jet expansion. Later, the sample is seeded into the expansion by bubbling helium carrier gas through the room temperature liquid. The spectral signals within this ring-down spectroscopy can be directly related to the absorption spectrum of the sample without a knowledge of the pulse characteristics. Due to the ability to probe gaseous samples with extremely high sensitivity and to provide quantitative absorption intensity information, this technique has emerged as one of the popular and useful spectroscopic tool. This group has also devised another variant, named as terahertz laser vibration–rotation–tunneling (VRT) spectroscopy⁵¹ for studying water clusters, wherein the absorption signal is detected through a liquid-helium-cooled stress Ga:Ge photoconductor.^{49,52} Another IR-based method is matrix isolation IR spectroscopy,^{53–55} wherein the molecules of interest are trapped in a solid inert gas matrix, such as Ar or N₂ at low temperatures. The concentration of the sample is kept sufficiently low to ensure that the molecules or their small clusters are surrounded only by the inert gas species, resulting in molecular isolation. The small line-width and spectral sharpening features of the matrix-isolation technique extend its applicability to the study of H-bonded and van der Waals complexes as well as for the identification and quantitation of polycyclic aromatic hydrocarbons. The above-mentioned IR techniques have been extensively applied for exploring molecular clusters of water, alcohol, carbon dioxide, nitrous oxide, benzene, etc.^{44–64}

In a supersonic jet expansion, the expansion of gas at a high pressure results into the separation of vibrational–rotational energy levels.^{42,43} This is the ideal condition for studying MW spectra.⁶⁵ The Fourier transform (FT) microwave spectroscopy has been widely employed for investigating rotational spectra of small-sized weakly bound complexes.^{66,67} A brief summary of the broadband FT rotational spectroscopy from 1953 to 2013 is described in a very recent work from Pate and co-workers.^{68,69} This technique has been extensively used by Legon and co-workers^{70–78} for studying many weakly bound dimeric and trimeric molecular complexes. In the recent years, electron attachment and photoelectron spectroscopies have become popular and important tools for studying weakly bonded complexes.^{79–81} These methods provide information about the electron affinity and ionization energy. Besides this, these are important tools for the study of molecules and clusters concerning the production and identification of the corresponding ions in mass spectrometry and determination of cross sections, fragmentation patterns, reactivity, etc. The electron ionization technique is more useful where photoionization studies are not feasible, for instance for large organic molecules. It has been extensively applied to clusters of a variety of molecules such as water, benzene, carbon dioxide, nitrous oxide etc.^{79–87} Very recently, Harnes and co-workers⁸⁸ have used photoelectron spectroscopy to determine the sizes of CO₂ clusters. Neutral free CO₂ clusters produced in a free-jet condensation source are expanded from a stagnation chamber. The beam of molecules and clusters is led through a skimmer that extracts the cluster-rich part of the beam. The cluster beam contains clusters of various sizes as well as uncondensed monomers, all of which show up in the recorded C_{1s} photoelectron spectra as two distinct peaks. The peaks are convoluted by Gaussian distribution to account for the distribution of ionization energies within each cluster and the distribution of cluster sizes present in the beam and also the excitations of intermolecular vibrational modes.

Since the current review mainly deals with the quantum chemical investigations on molecular clusters, only a brief summary of the experimental methods is given here. Further details of these methods can be found in the respective original refs 48–55, 70–78, and 88.

2.2. Theoretical Methods

Contemporary ab initio theory of electronic structure offers several methodologies for accurate treatment of molecular clusters. The early ab initio level calculations on small water clusters were reported by Clementi and co-workers⁸⁹ in 1974. Although the HF results were not accurate enough, it mainly remained the only choice of level of theory until the end of the 80s, owing to the limited computational resources. However, due to the advancement in computational resources, ab initio calculations at MP2 level on some of the dimers and trimers of small molecules became feasible during the 90s. As time progressed, this level of theory was applied to clusters containing a larger number of atoms. There are MP2 level studies reported by Xantheas^{90,91} for water clusters up to hexamer, MP2 and CCSD(T) level investigations on dimers of carbon dioxide, naphthalene, and benzene by Tsuzuki and co-workers^{92,93} and Hobza et al.^{94,95} and many others. The results obtained from the MP2 level were in better agreement with the experimental ones than those at HF for water, carbon dioxide, and benzene clusters.

In the past decade, with the recent advances in computer technology, the application of MP2 theory has grown to larger-sized clusters. Benchmark calculations for the geometry optimization of (H₂O)₁₆ and (H₂O)₁₇ clusters at MP2 level were reported by Xantheas,⁹⁶ using huge computational power. However, the inherent $O(N^5)$ scaling^{87–99} of the theory still restricted the geometry optimization of clusters to small size, say to less than typically 60 first row atoms. In the meanwhile, density functional theory (DFT)-based methods have become more popular for the theoretical treatment of molecular clusters. Several functionals such as BLYP, BP86, X3LYP, B3LYP, PBE0, etc. (see the list of acronyms and abbreviations at the end of this review) have been applied for the investigations on water clusters.^{90,100–102} It was found⁹⁰ that the structures and energetics obtained by BLYP and BP86 functionals with correlated consistent basis sets, match well their MP2 counterparts for water clusters with sizes up to $n = 4$. However, for larger water clusters, the MP2 theory remained the choice of level of theory over the DFT, probably due the parametric nature of the latter.

In clusters of molecules such as carbon dioxide, benzene, etc. dispersion interactions are found to play an important role in the stability and energetics of the aggregates.^{92,94} This restricts the use of conventional density functionals for studying these systems and the only option left is to employ correlated methods such as MP2, CI, or CCSD(T).^{92,94} For the accurate treatment of long-range dispersion interactions, Grimme and co-workers^{103–108} have devised a set of dispersion-corrected functionals abbreviated by them as vdW-DF, TPSS-D3(BJ), B97D, B2PLYPD, etc. These functionals are now being tested out for investigating the weakly bound complexes. For instance, a very recent study¹⁰⁹ from our group has shown that the results obtained by B2PLYPD functional provide the correct rank ordering of the structures for N₂O clusters with those suggested by the experiments whereas MP2 theory shows different trends. However, the scaling of this functional (B2PLYPD) is somewhat higher than that of the MP2 level, which restricts its use for only smaller-sized clusters.^{103,104,108}

Even with the availability of large computational resources today, HF, DFT, and MP2 have mostly remained the preferred levels of theory for geometry optimization of medium/large-sized molecular clusters in the literature. Accurate energies and correct rank ordering may be obtained by a single point treatment at higher levels such as MP4, CISD, and CCSD(T), the latter being the contemporary gold standard of quantum chemistry. The energy of a molecular cluster obtained by any ab initio method that normally employs a finite basis set is susceptible to basis set superposition error (BSSE).^{98,99,110–113} In the studies of weakly bound clusters, one often encounters artificial shortening of intermolecular distances and concomitant artificial strengthening of the intermolecular interactions. For example, in the description of a dimeric system containing monomers A and B, the basis functions of the two monomers overlap as they tend to approach each other. As a result, at a lower intermonomeric distance, each monomer can borrow the functions from the other monomer to expand its basis set and yield lower energy, whereas at a larger distance, the superposition of the basis sets does not occur. This inconsistent treatment of the basis set for each monomer as the intermolecular distances vary, is the origin of the BSSE.^{114–116} There are two ways of correcting the final energy of the molecular cluster, viz. counterpoise (CP) correction proposed by Boys and Bernardi¹¹⁴ and extrapolation to the

complete basis set (CBS) limit.^{117–122} However, CP correction calculation is computationally much more expensive and always overestimates the BSSE.¹²³ Hence, finding the CBS limit is a widely used technique for extrapolation of the energies. Dunning and co-workers have devised correlated consistent basis sets which are especially suited for such extrapolation procedures.^{124–126}

In addition to obtaining the total intermolecular interaction energy correctly, it is important to explore the physical origin of the interaction energy and to obtain its components such as electrostatic, exchange repulsion, polarization, and charge transfer etc. This information is especially useful for the development of force field methods and pseudopotentials which are used for modeling the different types of interactions. One such early, and the most popular method, is the energy decomposition analysis (EDA) proposed by Morokuma et al.^{127,128} In this method, the total interaction energy is separated into various contributions such as electrostatic, exchange repulsion, polarization, and charge transfer thereby providing information about the intermolecular interactions and their contribution toward the total energy.^{129,130} However, the energy decomposition analysis for molecular clusters at MP2 or other correlated theories is not possible since this method has been designed only at the HF level. On the other hand, methods based on intermolecular perturbation such as SAPT^{131–135} are extensively used because they can be applied to calculations employing MP2 and CCSD(T) levels of theory.

In the case of molecular clusters, tracing the origin of many-body interactions is of immense utility, because it provides insights about the strengths of two-, three-body interactions and the cooperativity effects.^{136,137} Such an analysis is termed as many-body interaction analysis (MBIA) wherein the total energy E_n of the n -body cluster is calculated as the sum of the one-, two-, three-, four-, ..., n -body terms (cf. eq 1):

$$\begin{aligned} E_n = & \sum_{i=1}^n E(i) + \sum_{i=1}^{n-1} \sum_{j>i}^n \Delta^2 E(ij) + \sum_{i=1}^{n-2} \sum_{j>i}^{n-1} \sum_{k>j}^n \Delta^3 E(ijk) \\ & + \sum_{i=1}^{n-3} \sum_{j>i}^{n-2} \sum_{k>j}^{n-1} \sum_{l>k}^n \Delta^4 E(ijkl) + \dots + \Delta^n E(1234\dots n) \end{aligned} \quad (1)$$

where $E(i)$, $E(ij)$, and $E(ijk)$ denote the energies of monomers, dimers, trimers, etc. The individual two-, three-, and hence the four-, ..., n -body terms can be defined as follows:

$$\Delta^2 E(ij) = E(ij) - E(i) - E(j) \quad (2)$$

$$\begin{aligned} \Delta^3 E(ijk) = & E(ijk) - \Delta^2 E(ij) - \Delta^2 E(jk) - \Delta^2 E(ki) \\ & - E(i) - E(j) - E(k) \end{aligned} \quad (3)$$

Numerous studies on MBIA have been reported in the literature, e.g., those by Hankins et al.,¹³⁸ White and Davidson,¹³⁹ Xantheas,^{140,141} Kulkarni et al.,¹⁴² Christie and Gordon,¹⁴³ to name a few. For all the cases examined by them, the two-body interaction energies were found to be the major contributor, with more than 90% of the total interaction energy coming from them. There are clusters, such as benzene clusters, wherein three-body interactions in short-range contribute significantly toward the stability of the clusters. Further, the many-body energy terms obtained through MBIA are prone to BSSE, restricting the application of the former to small-sized clusters. It may be noted that the aforementioned methods are

only for the analysis of energetics of an optimized geometry of a molecular cluster, while getting the low energy structures is the most crucial step in studying molecular clusters.

In spite of the availability of fast computers, the geometry optimization of large molecular clusters at a high-level of theory still remains a formidable task due to the nonlinear scaling involved. A solution to this problem is partly provided by the fragment-based methods.^{144–158} In these methods, a large molecular problem is divided into two or more subproblems until the latter become simple enough to be solved directly. One of the very early attempts for such methods was reported by Christoffersen and Sprangler¹⁴⁵ followed by the divide-and-conquer (DC) approach by Yang¹⁴⁶ and the molecular tailoring approach (MTA) by Gadre and co-workers.^{147,150} Though the above methods provide a solution to the nonlinear scaling, still the first two of these were not extensively applied to molecular clusters. The former¹⁴⁵ was introduced only within HF level with sub minimal basis sets, whereas the latter¹⁴⁶ was attempted only within the DFT framework. The other fragmentation methods include the DC method devised by Nakai and co-workers,^{151,152} the fragment molecular orbital (FMO) method by Kitaura and co-workers,^{153,154} and the generalized energy-based fragmentation approach (GEBF) reported by Li and co-workers,^{155,156} to name a few. All these fragmentation methods seem to work as per the nearsightedness principle of Kohn,¹⁵⁹ and enable the MP2 and CCSD(T) level treatment for large molecular systems. However, for all the fragmentation methods, the estimated energy of the parent system is always in error with respect to that obtained by the conventional full calculation (FC) on the parent system. In the literature, there exist remedies for keeping this error as small as possible by the addition of missing many-body contributions.^{160,161} Also, in the recent years, some new fragmentation methods based purely on many-body expansions^{162–164} are being devised. Recently, Deshmukh and Sakaki reported a two-step approximate evaluation method of binding energy starting from MP2 energy through reasonable approximations at the HF level.¹⁶⁵ Among these fragment-based methods, mainly MTA, FMO, and GEBF have been applied to a variety of large molecular clusters for the estimation of the relative stability of the clusters. MTA has been extensively used, especially for the geometry optimization and vibrational spectra of large-sized clusters during the last five years.

Molecular geometries of clusters are obtained either by fragmentation-based methods or by means of full geometry optimization. Molecular graphics visualization packages are necessary for displaying the geometries and properties of molecular clusters. All the figures in the present review article are generated afresh from the coordinates provided in the Supporting Information files of some of the cited references and are displayed in the present article either by using UNIVIS,¹⁶⁶ MeTA Studio,¹⁶⁷ or Gabedit¹⁶⁸ visualization packages.

3. HYDROGEN-BONDED CLUSTERS

HMs are known to play an important role in directing molecular self-assembly. A HM can be about 10 times as strong as the other intermolecular interactions and plays an important role in the hydration of solutes in aqueous solution, determining the three-dimensional structures adopted by proteins and nucleic bases etc. It is responsible for the existence of water as a liquid at normal temperatures; since water would be expected to be a

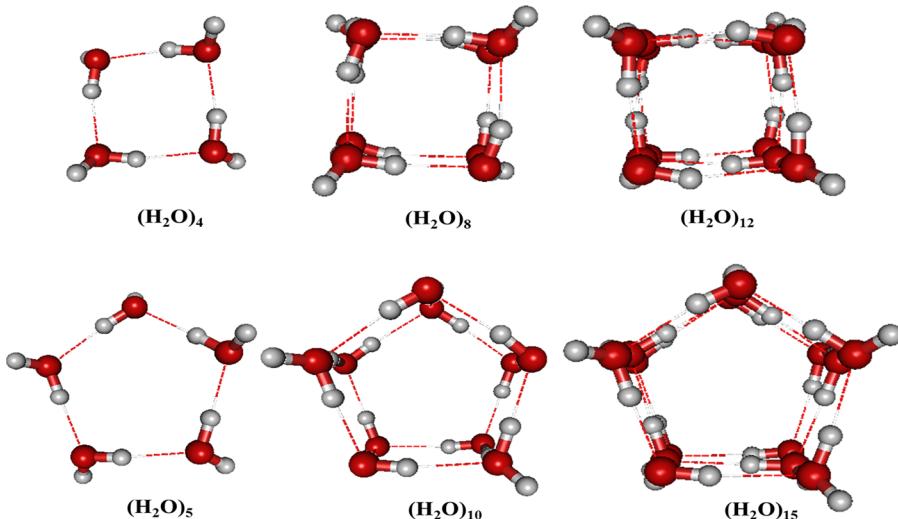


Figure 1. Minimum geometries of $(\text{H}_2\text{O})_n$ clusters for $n = 4, 5, 8, 10, 12$, and 15 at the HF/6-31G** level of theory. Data derived from ref 187.

gas due to its low molar mass. Theoretical investigations on molecular clusters of water, ammonia, methanol, hydrogen peroxide, etc. held together through HBs are summarized in the following subsections.

3.1. Water

Water has received more scientific attention than any other substance due to the vital role it plays in many biological and physicochemical processes. Particularly, the structure of water in bulk as well as in the vicinity of solute molecules is crucial in many disciplines of science.^{169,170} Among molecular clusters, water clusters are of paramount importance due to their unusual properties as well as their applications in solution chemistry. The charges in the water molecule are located on the four arms of a tetrahedron centered on the oxygen atom and are responsible for the directionality of the interaction^{171–174} and for the dissociation of many of the electrolytes. The polar nature and the tendency to form intermolecular HBs make the study of water clusters interesting as well as challenging. Several theoretical investigations based on quantum chemical calculations, Monte Carlo (MC), and molecular dynamics (MD)-based simulations, classical force field studies, etc. have been the core of active research for water clusters in the last few decades. The following subsection summarizes the theoretical studies on small water clusters with a special emphasis on ab initio quantum chemical investigations.

3.1.1. $(\text{H}_2\text{O})_n$ Clusters, $n \leq 10$. Clementi and co-workers pioneered the study of water clusters, in 1974, up to the octamer through HF computations.⁸⁹ For dimer, the open form was found to be more stable over the cyclic configuration, whereas for trimers through hexamers, the cyclic forms were more favorable over their open analogues. Since water clusters possess multiple minima on the potential energy surface (PES) and entropy effects are found to play important role in the relative stability of clusters, the probability distribution based on the Boltzmann distribution was done⁸⁹ instead of the exact energetics of the clusters. This observation was further confirmed through the self-consistent field (SCF) calculations and IR vibrational predissociation spectroscopy.^{175,176} A comparison of theoretical results obtained at MP2 and MP3 levels of theory to the experimental results was reported for water dimers.¹⁷⁷ The calculated O···O equilibrium distance ($r_e = 3.05 \text{ \AA}$) in the dimer was found to be larger than that in liquid

water ($2.96 \pm 0.01 \text{ \AA}$), indicating the intermolecular distances in the gas phase are somewhat larger than that from the liquid water in bulk.¹⁷⁷ For the first time in 1985, vibrational frequency calculations along with the structure and binding energy calculations of dimers were performed at HF and MP levels of theory.¹⁷⁸ Honegger et al.¹⁷⁹ explored the intramolecular vibrations of $(\text{H}_2\text{O})_n$, $n = 1–4$ based on normal coordinate analysis at HF level, employing a variety of basis sets such as n -31G, n -31G*, and n -31G**, with $n = 4$ and 6. With increasing size of the clusters, the computed frequencies for O–H stretch were found to show¹⁷⁹ large red shifts ($\sim 200 \text{ cm}^{-1}$) for each of the added monomers, in agreement with the earlier experimental findings.¹⁸⁰

During the 90s, the studies of water clusters were extended from small sizes to somewhat larger ones employing higher levels of theory with relatively large basis sets.^{90,91,181–186} The vibrational analysis of hexameric clusters was reported at HF and MP2 levels using augmented correlation consistent double- ζ (aug-cc-pVDZ) basis set.⁹⁰ In this study,⁹⁰ water clusters were found to exhibit two types of OH bonds, viz. bridged OH (H-bonded) and free OH (non H-bonded) with the length of the bridged OH bond increasing monotonically with the cluster size. For all of the clusters up to hexamer, the spectra exhibited a blue shift ($\sim 70 \text{ cm}^{-1}$) for intramolecular bending modes whereas red shift was noticed for both types of OH bonds.⁹⁰ The bridged OH bonds were red-shifted by $\sim 500 \text{ cm}^{-1}$ in comparison to the normal stretching frequency in water. The results obtained from the MP2/aug-cc-pVDZ level computation for monomers to trimers, were found to produce accurate structures, energetics and vibrational spectra.⁹⁰ This study⁹⁰ was further extended for exploring the efficiency of some DFT functionals for probing the structure and energetics for small water clusters as compared to the MP2 level employing larger basis sets (aug-cc-pVXZ, X = D, T).⁹¹ The results of the structures and energetics from the use of exchange-correlation (BLYP and BP86) functionals were found to be in better agreement with those at MP2 level than those obtained by HF level calculations. In particular, BLYP/aug-cc-pVDZ level of theory predicted the structures, energetics, and the relative trend in the stability with cluster size as accurately as the MP2 level calculations, indicating that DFT may provide a viable alternative to MP2 for studying the structures and energetics of

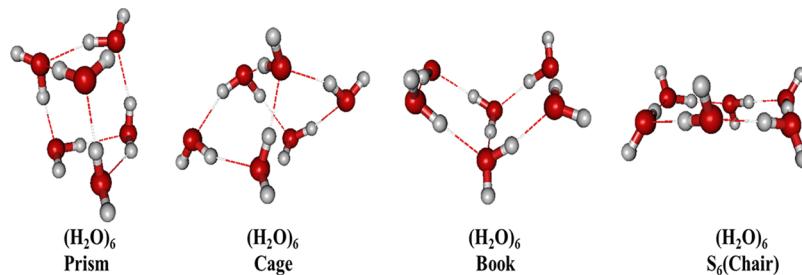


Figure 2. Four low-lying geometries for prism, cage, book, and S_6 (chair) isomers of $(H_2O)_6$ clusters at the CCSD(T)/aug-cc-pVDZ//MP2/6-311+G** level of theory. Data derived from ref 201.

water clusters. The studies were further extended for the structure and spectral intensity of water pentamers at BLYP/DZP level^{181,182} and water hexamers at CCSD(T) level in combination with SAPT.¹⁸³

Later, the thermodynamic properties such as enthalpy, entropy, and free energy as well as the IR and Raman spectra of water heptamer and octamer were investigated up to HF/6-311G** level of theory,^{184,185} wherein the ring and cubic structures were found to be dominant at the room temperature over their acyclic analogues, a fact that later observed from an extensive study by Maheshwary et al.¹⁸⁷ Tetrameric water patterns were found to be common for the cuboid clusters $(H_2O)_n$, $n = 4$ and 8, in agreement with the previous combined study employing force fields and ab initio calculations.^{188,189} For example, the cubic isomers possessing D_{2d} and S_4 symmetry were found to be the two low-lying geometries for the water octamer. To the contrary, pentameric rings were found mainly in $(H_2O)_n$ clusters containing 5, 10 monomers (see Figure 1). Isomers endowed with maximum number of HBs represent the minimum structures on the PES. Besides this, the arrangement of these HBs is expected to play an important role in the energetics and stability in these aggregates, as outlined below.

The water molecules in clusters participate in HB formation either as a proton donor (d) or proton acceptor (a) or a combination of thereof (da). How does the stability of the isomers depend on the arrangement of these HBs? Xantheas¹⁹⁰ examined the cooperativity and HB patterns in small water clusters at the MP2/aug-cc-pVDZ level of theory. Water clusters having maximum number of HBs with donor–acceptor (da) arrangements of water molecules, were found to represent the low energy structure in the range of trimer to hexamer.¹⁹⁰ According to this concept, cyclic isomers of trimer, tetramer and pentamer containing three, four and five da patterns of HBs respectively were found to be the most stable isomers than their respective acyclic analogues. However, due to the structural transition from two- to three-dimensional network, clusters beyond pentamers show a combination of dda and da patterns of water molecules.¹⁹¹ The prism structure was seen to be energetically more favorable over the cage, book and S_6 structures (cf. Figure 2).¹⁹⁰ Thus, both the number and orientation of HBs are seen to determine the energetics and stability of water clusters.

Among the small-sized water clusters, the hexamer is of substantial interest since it represents the transition from monocyclic two-dimensional to multicyclic three-dimensional structure.¹⁹² Much has been discussed in the literature regarding the stability of isomers (see Figure 2) of hexameric water clusters.^{190,193–201} For example, from both HF and MP2 level calculations,^{190,195,196} the prism structure with 9 HBs was found to be more stable by 0.2 kcal/mol than the other cyclic

structures. On the other hand, Clementi and co-workers¹⁹⁷ reported that the chair form turned out to be more stable when the zero-point energy (ZPE) correction is applied for their DFT-based calculations, a fact that was later confirmed by two-electron reduced density matrix method.²⁰² Similarly, according to a combined theoretical and experimental study by Liu et al.¹⁹⁸ the cage structure was observed to be the most stable water hexamer. For the proper estimation of the relative stability among the isomers of water hexamers, an extensive search for local minima was reported at the MP2/aug-cc-pVDZ level of theory.²⁰⁰ Two of the five proposed prismatic frameworks were found to be the lowest energy isomers for the hexamer. More recently, an extensive study on water hexamers was reported by Hincapié et al.²⁰¹ at MP2 and CCSD(T) levels of theory. The overall stability of the isomers was predicted through the attractive electrostatic interactions from the polar nature of the HB networks. The compact structures were energetically more favored over the cyclic frameworks as reported earlier.¹⁹⁷ For trimers, the stability was found to decrease at both MP4 and CCSD(T) level as reported earlier due to Nielsen et al.²⁰³ However, the effects of higher correlation for larger clusters were not available at the time of this work in 1999. At the MP2/CBS level of theory,²⁰⁴ all the isomers (prism, cage, book, and S_6) were found lying within a range of 2 kcal/mol at this level of calculations (cf. Figure 2). The prism isomer was found to be the most stable one among the above structures as discussed in some earlier works.^{195,196,200} For benchmarking the accuracy of MP2 level, further correlation was incorporated through the MP4 and CCSD(T)-level study.

Xantheas and Apra²⁰⁵ extended the studies on small-sized water clusters to medium-sized ones with two distinct isomers of water octamer belonging to D_{2d} and S_4 symmetry at the MP2/CBS level of theory. A “Heuristic Approach” based on the least mean square fittings was employed for the estimation of CBS using the higher angular momentum functions of the correlation basis sets wherein the MP2/CBS binding energies at higher basis sets were estimated using the binding energies at lower basis sets as shown in eq 4.

$$\Delta E = \Delta E_{\text{CBS}} + \frac{\alpha}{(l_{\max} + 1)^4} + \frac{\beta}{(l_{\max} + 1)^5} \quad (4)$$

where ΔE_{CBS} represents the CBS binding energy at higher basis set, ΔE stands for the MP2-level binding energy at lower basis set, l_{\max} is the largest angular quantum number for correlation consistent basis set, and α and β are linear fitting parameters. For instance, the values of l_{\max} for aug-cc-pVTZ and aug-cc-pVQZ are 3 and 4, respectively. Due to the requirement of only lower level calculations for the estimation of CBS binding energies, it would be interesting to extend this methodology²⁰⁸

to large water clusters. Later, in an extensive study, Maeda and Ohno²⁰⁶ reported 164 local minima on the water octamer PES at the MP2/6-311++G(3df,2p)//B3LYP/6-311+G** level of theory. The D_{2d} isomer was found to be energetically the most stable octamer, whereas the S_4 isomer was observed to be the second-most stable one.^{205,206}

Though small-sized water clusters have been extensively studied, there still exists a limited number of investigations on clusters containing odd number of monomers. Water trimer was studied extensively, probably due to its small size, with very few investigations on pentamers and heptamers. An extensive ab initio study was reported by Kim et al.²⁰⁷ exclusively on the energetics and structures of water heptamers. At both HF and MP2 levels of theory, two isomers endowed with three-dimensional cage-like structures were found to be low-lying ones, in agreement with the combined spectroscopic and computational study.²⁰⁸ Compact structures are preferred at low temperatures, however, as temperature increases the high entropy associated with the HB networks results in more open structures.²⁰⁹ Similarly, the structure comprising of two cyclic tetramers bridged through a water monomer was found to be the most stable one, out of 44 nonameric isomers examined at the HF level.²¹⁰ The possibility of getting a number of structures within an energy window of 10 kcal/mol was the highlight of the work. Similar to heptamer and nonamer, the studies on decamer were also limited. In 2010, Shields et al.¹²³ reported an extensive study on water clusters in the range of dimer to decamer with a special emphasis on $(H_2O)_{7,9,10}$. In this study,¹²³ they could reproduce the MP2/CBS values of Xantheas et al.^{204,205} through the extrapolation procedure by least-squares fitting equation as well as through a novel approach (MP2/CBS-e) using the BSSE with CP correction.¹²³ As CP correction is known to overestimate the BSSE, MP2/CBS-e was estimated by taking 1/3 of the CP corrected and 2/3 of the uncorrected MP2/aug-cc-pVDZ (MP2/DZ) binding energies, viz.

$$E_{MP2/CBE-e} = \frac{2}{3}E_{MP2/DZ} + \frac{1}{3}E_{MP2/DZ}^{CP} \quad (5)$$

The calculated CBS binding energies obtained were found to be in better agreement with their MP2/CBS counterparts, implying that the methodology may be employed for the accurate yet inexpensive estimation of binding energy of large clusters. At the MP2/6-31G* level of geometry optimization, the prism conformers with trimer-tetramer (a fact recently confirmed through a combined broadband FT rotational spectroscopy and MP2 level calculation⁶⁹) and tetramer-pentamer stacking pattern of water molecules were found to be the global minima for $(H_2O)_7$ and $(H_2O)_9$, respectively. In the case of decameric water clusters, 30 unique configurations with different HB networks were found to lie within a range of 4 kcal/mol, among which the pentagonal prism isomer was found to be the most stable.¹²⁵ The relative stability of the isomers was predicted based on the hydrogen topology as discussed earlier.^{190,211} In a recent study,²¹² extrapolation of RI-MP2/CBS as well as CCSD(T)/CBS has been performed for small water clusters, viz. dimer through decamer. Since the higher-order electron correlation are very small beyond the cc-pVDZ basis sets, the CCSD(T) level correlation corrections can be calculated²¹³ by taking the difference between the energies at CCSD(T) and MP2 levels of theory and also the CCSD(T)/CBS values from the RI-MP2/CBS and CCSD(T)-level electron correlation. The vibrational bending frequencies

of water clusters in the range of hexamer to decamer are found to be blue-shifted by ~40 to 170 cm⁻¹ with respect to their gaseous analogues.²¹⁴

In summary, the stability of $(H_2O)_n$ clusters for $n \leq 10$ is predominantly governed by the total number of HBs present in the cluster. For clusters having 2-dimensional patterns, structures with maximum number of HBs generated from donor–acceptor (da) arrangements of water molecules are energetically more stable. Therefore, the cyclic isomers up to pentamers are energetically more favorable than their acyclic analogues. Clusters from $(H_2O)_6$ to $(H_2O)_{10}$ contain tetrameric and pentameric patterns. Further, due to the availability of highly parallelizable codes as well as high-end computational architectures, accurate calculations are now routinely feasible for these small-sized clusters. Due to the recent advents in FTMW spectroscopy,^{68,69} the rotational constants and geometries of small water clusters are being determined very accurately. It is with this interplay between experiments and theory, clusters up to $(H_2O)_{10}$ are likely to be probed in the years to come, at the contemporary gold standard in quantum chemistry, viz. CCSD(T)/CBS level of theory. With the availability of advanced computational resources, in 2000s, the MP2 level investigations on water clusters were extended to larger $(H_2O)_n$ clusters.

3.1.2. $(H_2O)_n$ Clusters, $n > 10$. Studies on larger water clusters include the MP2 level investigations on $(H_2O)_{11}$ and $(H_2O)_{12}$ by Lee and co-workers,²¹⁵ followed by $(H_2O)_{11}$ and $(H_2O)_{13}$ due to Bulusu et al.²¹⁶ For $(H_2O)_{11}$, a combination of cyclic pentamer with cyclic hexamer through 16 HBs was found to be energetically more favorable than all the previously suggested structures. The isomer combining a cyclic pentamer with the open-book hexamer with a total of 17 HBs was the next stable isomer.²¹⁵ Similarly for $(H_2O)_{12}$, the isomers formed from the stacking of tetrameric water (D_{2d})₂ or (D_{2d})(S_4) or (S_4)₂ patterns with 20 HBs represent the low-lying structures on the PES (cf. Figure 1), in agreement with the earlier observations.^{187,188} Furthermore, the fusion of two cyclic water hexamers (18 HBs) was also observed to be the next low-lying isomer for $(H_2O)_{12}$. On the other hand, $(H_2O)_{13}$ clusters were found to be formed from by the addition of a monomer unit to the cuboid geometry of the $(H_2O)_{12}$ cluster.

Further studies include the estimation of the dipole polarizability of water clusters ranging from $(H_2O)_2$ to $(H_2O)_{12}$ at CCSD level of theory by Hammond et al.¹⁰⁰ The results were further used for appraising six DFT functionals, viz. PBE, PBE0, B3LYP, BLYP, X3LYP, and PW91, where PBE0 was found to provide accurate estimate of polarizability as compared to the other functionals.¹⁰⁰ This study was further extended for the low-lying geometries of $(H_2O)_{20}$ cluster at DFT level.²¹⁷ Polarizability of these water clusters was found to depend on the number of monomer units and types of HBs rather than their detailed structures and was found to be inversely proportional to the strength of the HBs. Therefore, water molecules having dda patterns of HB network were found to contribute more toward the polarizability of the clusters than the molecules with dda, daa, and da patterns. Consequently, the molecules with maximum number of HBs have a small contribution to the polarizability, and hence, the interior HBs were seen to contribute less to the polarizability of water clusters than the surface HBs.

Are the HB networks in water clusters and their polarizabilities sensitive to external electric field? Several theoretical investigations explaining the stability of different-sized water

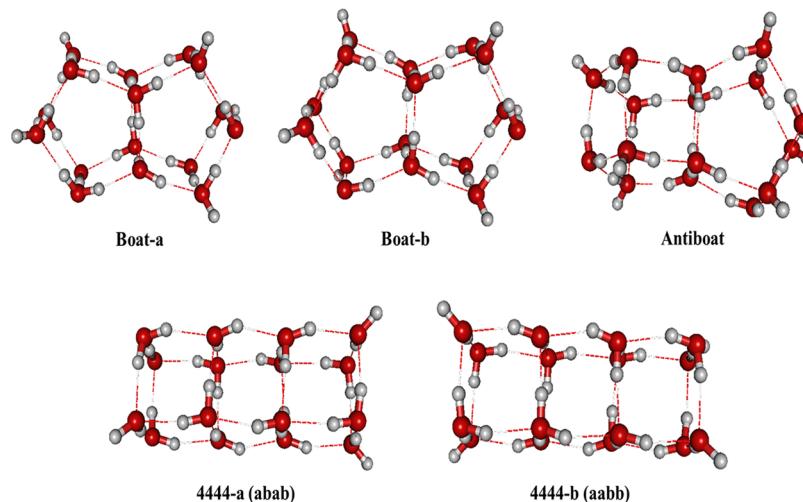


Figure 3. Five lowest energy geometries of $(\text{H}_2\text{O})_{16}$ clusters, at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory. Data derived from ref 96.

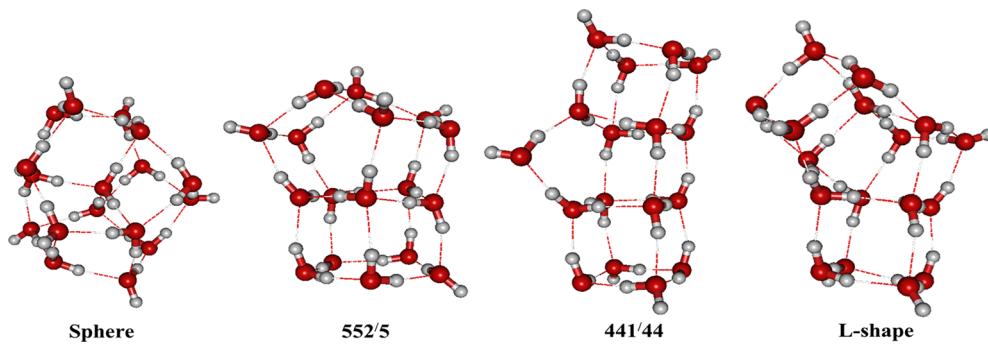


Figure 4. Four lowest energy geometries of $(\text{H}_2\text{O})_{17}$ clusters, at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory. Data derived from ref 96.

clusters have been reported in the literature.^{218–228} A systematic investigation on conformational transitions in $(\text{H}_2\text{O})_n$, ($n = 6$ –8) clusters, in the presence of an external electric field was reported by Pathak and co-workers.²²⁶ The applied field was found to align along the dangling O–H bonds and seen to enhance the H-bonded structure of the water clusters. Furthermore, it results in a partial breaking or reorganization of the H-bonded network with an increasing number of HBs. Similar observation was also made from the B3LYP/cc-pVTZ level calculation²²⁷ viz. that an external electric field may change the number and strength of the HBs. In a very recent work,²²⁸ the effect of an external uniform, dipolar and static electric field on the HB networks of neutral $(\text{H}_2\text{O})_n$ clusters, $n = 9$ to 20, is reported within DFT-framework. With an increase in the strength of the external applied field, the HB network is found to be distorted through elongating and weakening of the HBs. For a given field strength, these effects are more pronounced for larger clusters compared to those for smaller ones, due to enhancement in the cooperativity effects in the HB networks. The HOMO–LUMO gap of the clusters was seen to decrease with the field, approaching zero at the point of structural breakdown of the HB networks. This trend in HOMO–LUMO gap is found to be responsible for the enhancement of the chemical softness and the reactivity of the clusters.

In 2010, high-level ab initio calculations for $(\text{H}_2\text{O})_{16}$ and $(\text{H}_2\text{O})_{17}$ were reported by Xantheas and co-workers⁹⁶ at MP2

and CCSD(T) levels of theory, the latter for the first-ever time. The single-point energies for five low-lying geometries of $(\text{H}_2\text{O})_{16}$ and four low-lying geometries of $(\text{H}_2\text{O})_{17}$ (optimized at MP2/aug-cc-pVTZ) were evaluated at the CCSD(T)/aug-cc-pVTZ level.⁹⁶ Though CCSD(T)/CBS values for water hexamers were reported earlier,²²⁹ still the FC on $(\text{H}_2\text{O})_{16}$ cluster at CCSD(T)/aug-cc-pVTZ level of theory is impossible even on contemporary off-the-shelf high-end parallel hardware due to the high scaling nature of this method. Based on the ring sizes in the HB network, the $(\text{H}_2\text{O})_{16}$ isomers were classified as boat-a, boat-b, antiboat, 4444-a (abab), 4444-b (aabbb) and $(\text{H}_2\text{O})_{17}$ isomers as sphere, 552/5, 441/44 and L-shaped etc. The MP2 optimized geometries for both of the $(\text{H}_2\text{O})_{16}$ and $(\text{H}_2\text{O})_{17}$ clusters are displayed in Figures 3 and 4, respectively. Both boat-a and boat-b isomers are endowed with two laterally placed pentagonal prisms, whereas 4444-a and 4444-b are generated from the stacking of water tetramers (cf. Figure 3). For $(\text{H}_2\text{O})_{16}$, at MP2 level of theory, boat-a isomer was the lowest energy structure whereas for the coupled cluster calculation, the fused cubes isomer 4444-a was found to be the most stable one, in agreement with the recent DFT level computation by Truhlar and co-workers.²³⁰ However, at both MP2 and CCSD(T) levels, the relative energy differences between these isomers were less than 1 kcal/mol, indicating their nearly isoenergetic nature. For $(\text{H}_2\text{O})_{17}$, the spherical isomer (cf. Figure 4) with an interior water molecule was found to be the most stable one at MP2 and CCSD(T) levels of

theory.²³¹ The second most stable isomer for $(\text{H}_2\text{O})_{17}$ was found to be formed through the addition of two monomers to the global minimum structure of the $(\text{H}_2\text{O})_{15}$ cluster. It may be noted that Xantheas et al.⁹⁶ performed the single-point calculation for $(\text{H}_2\text{O})_{16}$ at the CCSD(T)/aug-cc-pVTZ level of theory using 120 000 processors (taking 3.33 h) with a memory usage of 820 MBbytes on each processor. However, the availability of this type of huge hardware is rather scarce and hence such calculations may not be routinely possible in the near future. In a very recent study, Iwata et al.²³² explored the cooperative roles of charge transfer and dispersion terms in the $(\text{H}_2\text{O})_n$ clusters, for $n = 6, 11$, and 16 and later²³³ in $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{25}$ clusters, employing the locally projected molecular orbital (LPMO) and CCSD(T) calculations with correlated consistent basis sets. Besides electrostatic and induction terms, the dispersion interactions originating from the non H-bonded hydrogen pairs are also seen to contribute to the relative stability of the isomers.

It was pointed out by Xantheas and co-workers²³¹ that the $(\text{H}_2\text{O})_{17}$ is the smallest water cluster bearing one internally solvated water molecule, showing a structural transition between “all-surface” and “internally solvated” water molecules. The appearance of internally solvated molecule at $n = 17$ may be regarded as the second structural transition point after hexamers. The stabilization of all surface to internally solvated water clusters from the TTM2-F model^{234–236} was further investigated through MP2 and DFT-based electronic structure calculations.²³¹ Among these, $(\text{H}_2\text{O})_{19}$ and $(\text{H}_2\text{O})_{21}$ were found to have an internally solvated water molecule whereas all the water molecules were of surface type for $(\text{H}_2\text{O})_{18}$ and $(\text{H}_2\text{O})_{20}$ clusters. These thorough investigations due to Xantheas et al.^{96,231} are expected to serve as a guide for the future investigations of structural transitions in water clusters.

Generally, the quantum chemical investigations using MP2 and CCSD(T) levels of theory are feasible only for small water clusters containing a limited number of water molecules. The less-expensive HF and DFT-based calculations are still being performed for large-sized water clusters. Su et al.¹⁰¹ reported, in 2004, the structures and energies of water clusters containing up to 19 monomers employing X3LYP hybrid density functional, which is reported to give accurate estimation of dispersion interaction in water clusters. For a given basis set, X3LYP was found to be typically 100 times faster than MP2, saving both computational power as well as time with a negligible loss of accuracy. Though the X3LYP functional estimates accurate structures and energetics of water clusters containing up to 19 water molecules, still the predictions for the hexamer did not agree with their MP2/CBS counterparts.¹⁰¹ Within this functional, the cyclic (chair) and book forms of water hexamer were found to be the most stable ones whereas it happens to be the prism isomer at MP2/CBS level of calculation. This observation was similar to the recent findings reported by Li and co-workers,¹⁰² where the structures, energies, dipole moments and vibrational frequencies were investigated employing a variety of exchange correlation functionals and benchmarked against MP2 and CCSD(T) methods. Out of these, M05-2X was found to describe the binding energies accurately. X3LYP was found to yield geometries and vibrational spectra for small water clusters akin to those at MP2 level whereas the accurate structural properties were derived employing BLYP functional.¹⁰² In a recent study, another DFT functional, viz. PBE, was found to

provide better binding energies even without dispersion correction.²³⁷

Due to its clathrate structure, the dodecahedral network of $(\text{H}_2\text{O})_{20}$ cluster is important for the explicit hydration of a solute molecule and has been employed for studying solvation of several small molecules. In an extensive study^{238,239} of larger water clusters at MP2/CBS level of theory, four major families of minima of $(\text{H}_2\text{O})_{20}$ clusters were reported based on the previously identified structures by Wales and Hodges²⁴⁰ employing empirical potentials.²⁴¹ They were classified as dodecahedron, fused cubes, face-sharing pentagonal prisms, and edge-sharing pentagonal prisms (cf. Figure 5). The highly

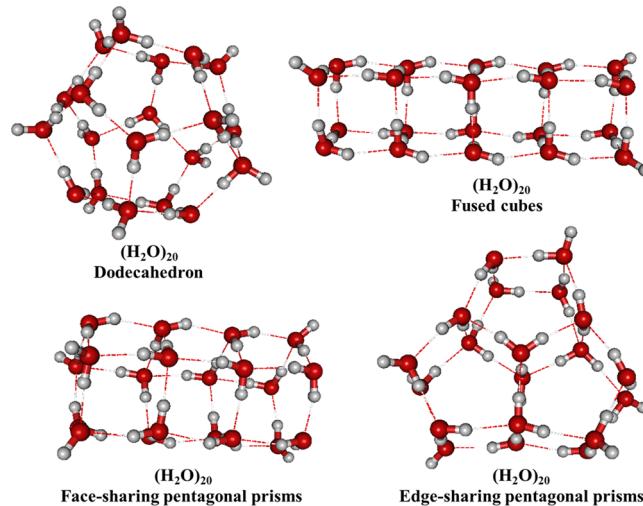


Figure 5. Four (dodecahedron, fused cubes, face-sharing pentagonal prisms, and edge-sharing pentagonal prisms) low-lying minima for $(\text{H}_2\text{O})_{20}$ cluster. Data derived from refs 187, 256, and 258.

symmetrical dodecahedral isomer is endowed²⁴² with a spherical arrangement of pentagonal water rings at the surface whereas the face sharing pentagonal prism isomer consists of water pentamers in a stacked fashion. Fused cubes are found to have tetramers, and the edge sharing cluster contains two layers of pentameric patterns linked through edges. The number of HBs in the dodecahedron, fused cubes, face-sharing pentagonal prisms, and edge-sharing pentagonal prisms is found to be 30, 36, 35, and 34, respectively. The edge-sharing pentagonal prism isomer was found to be the most stable isomer lying 18 kcal/mol below the next stable dodecahedral isomer. The comparison of the vibrational spectra revealed that the dodecahedral network exhibited the largest red shift of $\sim 750 \text{ cm}^{-1}$, whereas the most stable edge-sharing pentagonal prism exhibited a red shift of $\sim 600 \text{ cm}^{-1}$ with respect to the monomer stretch.²³⁹ For each isomer, the O–H stretches associated with a four centered face exhibit more red shift than other O–H stretch modes, since these have relatively stronger HBs than those in other rings. The relative stability of these networks was found to be unaltered, though the energy separation between the most stable and least stable structures is reduced after effecting the ZPE correction.²³⁹

Studies on the HB networks and their effect on the relative stability of the isomers have been extended to large-sized water clusters.^{243–250} The overall stability of the clusters was also found to depend on the relative orientation of the non H-bonded hydrogen atoms.^{244,245} This may be probably due to the dispersion interactions originating from the hydrogen pairs

not participating in HB formation in the water clusters.²³² The interaction energy per water molecule is found to decrease monotonically with the cluster size. Cluster geometries containing triangular faces were found to be less stable, whereas $(\text{H}_2\text{O})_{21}$, considered as a magic cluster, was found to exhibit enhanced stability due to five-membered rings.^{244,245} Qian and co-workers²⁴⁸ further investigated various properties of typical structures of water clusters for $n = 2$ to 34 at HF/6-31G* level of theory and discussed the trends in properties with increasing cluster size. The transition from two- to three-dimension was found at the hexamer region, the next transition from all-surface to one water-centered structures occurred at $(\text{H}_2\text{O})_{17}$, and the third transition from one water-centered to two water-centered structures was observed at $(\text{H}_2\text{O})_{30}$. However, with the present day availability of computational hardware, higher level calculations on these clusters are possible and expected to produce more accurate results. Liu and co-workers²⁴⁹ classified water clusters by employing a different criterion than that used by Xantheas.²³¹ Water clusters were categorized as monoring, multiring, monoring stacking, multiring stacking, and stuffed-cage types where the stability depends upon the strength of the HB networks.^{55,250} As noted earlier, water tetramer ring showed extra stability among the small-sized water clusters $(\text{H}_2\text{O})_{2-5}$ due to the presence of stronger HB network. For $(\text{H}_2\text{O})_{7-16}$, the stability was found to increase due to a large number of HBs for clusters with an even number of monomers, whereas for $(\text{H}_2\text{O})_{17-30}$ the HBs were seen to be stronger for the clusters with an odd number of monomers. On the other hand, $(\text{H}_2\text{O})_n$ clusters for $n > 30$ have relatively larger stabilization energy per monomer. Mainly, the tube-like polar cage of $(\text{H}_2\text{O})_{40}$ fullerene shows an extra stability as compared to other, nearly spherical shaped structures.²⁵¹ Again it may be noted that the theoretical investigations employing the above-mentioned quantum chemical methods such as HF, MP2, and DFT can be performed only up to certain-sized clusters containing typically less than 100 atoms. Furthermore, single-point CCSD(T) level calculations are restricted typically to systems containing up to 50 first row atoms, those too are feasible only on the contemporary high-end hardware.⁹⁶

In summary, large water clusters, due to their 3-dimensional nature, show a combination of daa, dda, and ddaa HB patterns rather than only da one.²¹¹ Hence, the stability and energetics of water clusters seem to be governed by the number as well as the spatial distribution of HBs. Use of DFT enables calculations on large clusters, although the benchmarking and systematic improvisation of the accurate energetics is not often guaranteed, owing to the parametrization involved therein. On the other hand, geometry optimization employing MP2 or CCSD(T) levels is feasible only with the use of huge computational hardware.⁹⁶ In this context, the introduction of fragment-based approaches opens up a possibility for such accurate investigations, especially for the geometry optimization and vibrational spectra of large-sized water clusters (see the following section).

3.1.3. Fragmentation and Many-Body Methods. Due to effective parallelization and the availability of high-end hardware, fragmentation-based approaches have been widely used for the high-level treatment of large water clusters. The studies on large water clusters employing such methods are reviewed below.

One of such calculation for large water clusters (such as $(\text{H}_2\text{O})_{32}$) was attempted by Fedorov and Kitaura²⁵² within

coupled-cluster theory employing the FMO method.^{153,154} Though the computational cost of two-body FMO was found to be linear with cluster size, from the accuracy point of view, three-body FMO was far superior to the two-body FMO. For instance, the two-body FMO-CC calculations took only 13 min, whereas the three-body FMO-CC took 756 min for the CCSD(T)/cc-pVDZ level of calculation on $(\text{H}_2\text{O})_{32}$ cluster on an eight node 3.2 GHz Pentium4 cluster. The gross error in two-body FMO was in the scale of millihartree, whereas it was within a submillihartree range for three-body FMO. In terms of accuracy, about 99.88% and 99.97% of the electron correlation energy was captured in the two- and three-body FMO methods. However, this study was restricted to energetics of the clusters chosen as test examples rather than for the geometry optimization. In another recent study, Gordon and co-workers²⁵³ reported the energetics of $(\text{H}_2\text{O})_n$ clusters for $n = 16, 20, 32$, and 64, employing both FMO and systematic molecular fragmentation method. At the MP2/6-31+G** level of theory, for $n = 16, 20$, and 32, the energies from the two-body FMO calculations are in 2.65, 4.00, and 9.30 kcal/mol error vis-à-vis their FC counterparts. On the other hand, these errors are only 0.72, 0.28, and 1.73 kcal/mol for three-body FMO calculations, indicating the preference of this level for estimation of the energetics of water clusters.

In another study, Li and co-workers²⁵⁴ applied the combined GEBF approach^{155,156} and AMOEBA potential model²⁵⁵ for locating the low-lying geometries of water clusters in the range of 20 to 30 (all containing an internally solvated water molecule) at DFT and MP2 level of theory. They found that $(\text{H}_2\text{O})_{26}$, $(\text{H}_2\text{O})_{29}$, and $(\text{H}_2\text{O})_{30}$ have two internally solvated water molecules, indicating the transition from one-centered to two-centered cage structure in water clusters first occurs at $n = 26$, where all 10 low-lying structural families display various cage structures containing two interior molecules. On the contrary, the low-lying isomers of $(\text{H}_2\text{O})_{27}$ and $(\text{H}_2\text{O})_{28}$ possess only one. As expected for large water clusters, with increasing cluster size, the number of HBs per water molecule in the lowest-energy structures shows a gradually increasing trend along with an increase in number of four-coordinated water molecules. In a very recent work,²⁵⁶ it has been shown that the GEBF-CCSD(T)/HF method at the CBS limit is expected to be a benchmark for DFT and other electron correlation methods for medium- and large-sized systems with complex structures. Although the works²⁵²⁻²⁵⁴ provide a solution to the nonlinear scaling of the quantum chemical methods, these have the limitation that they deal only with the energetics of the water clusters rather than implementing the geometry optimization. Hence, the introduction of gradients for the geometry optimization of large water clusters would certainly be valuable for getting minimum structures.

Yet another fragmentation method, viz. MTA has been successfully applied by Gadre and co-workers¹⁴⁷⁻¹⁴⁹ for studying large molecular clusters. The efficacy of MTA has already been tested and benchmarked on various molecular systems during the past decade. Especially, for geometry optimization at the MP2 level of theory, MTA has shown a great promise over the corresponding FC counterparts. Recently, single-point energy calculations at the MP2/6-31+G**//HF/6-31+G** level were performed for $(\text{H}_2\text{O})_{40}$ and $(\text{H}_2\text{O})_{43}$ clusters employing MTA.²⁵⁷ Initial geometries of $(\text{H}_2\text{O})_{40}$ were generated from the addition of monomers to $(\text{H}_2\text{O})_{37}$ clusters employing the cluster building algorithm which were further used for the generation of $(\text{H}_2\text{O})_{43}$ clusters.

This work provided a proof of concept of systematic addition of water molecules to a parent water cluster, rather than a thorough investigation of energy minima of water clusters.

In a further recent work,²⁵⁸ the level of theory has been extended to the MP2 level with correlation consistent basis sets for exploring the structures and energetics for $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{25}$ clusters employing MTA. The initial geometries were derived from MC-based temperature basin paving (TBP) procedure.²⁵⁹ Geometry optimization has been done at the MP2/aug-cc-pVDZ level of theory using MTA, and the correct estimation of MTA-based energies is effected through grafting procedure. The latter is a two-step calculation, where the error in MTA-based energies at a lower basis is grafted onto a desired higher basis.^{258,260} This is done keeping in view that the error in MTA-energy is not sensitive to basis set and hence may be employed for grafting. For $(\text{H}_2\text{O})_{20}$ cluster, this work²⁵⁸ was able to reproduce the lowest energy structure earlier reported by Xantheas and co-workers^{238,239} and also reported the second most stable isomer that was missed in the earlier literature whereas a new global minimum for the $(\text{H}_2\text{O})_{25}$ cluster, not hitherto noticed in the literature, was reported.²⁵⁸ From the accuracy point of view, this methodology²⁵⁸ showed an excellent agreement with the corresponding FC. Irrespective of the nature of fragmentation scheme, the MTA-based grafted energies were found to lie within 0.5 mH from the respective FC counterparts. The need of carrying out two FCs at lower level of theory may restrict the methodology to clusters containing up to 150 atoms. However, the applicability as well as efficacy of this methodology needs to be further enhanced for studying large molecular assemblies.

Apart from these fragment-based methods, the energetics of water clusters has been investigated based on many-body interaction energies. A procedure termed as "stratified approximation" many-body approach was developed by Góra and co-workers²⁶¹ wherein the calculations were performed at a high-level up to three-bodies, and a low-level of theory was employed for calculations beyond three-bodies. For the energetics of $(\text{H}_2\text{O})_n$ clusters for $n = 6, 16$, and 24 , the CCSD(T)/aug-cc-pVQZ level of theory was employed up to three-bodies and the MP2/aug-cc-pVDZ level of theory was employed for four- or higher-bodies. Similar type of computation on water clusters ranging from trimer to decamer was performed at MP2:HF two-body:many-body fragmentation method employing haTZ basis set.¹⁶² All the two-bodies were treated at the MP2 level of theory, and beyond dimers, the HF level was applied for the estimation of energies of many-body interactions. This study was further modified based on ONIOM techniques, where high-level of theory was applied up to three-bodies again and low-level for higher many-bodies.^{162,262} The computed interaction energies of CCSD(T):MP2 3-body:many-body fragmentation to CCSD(T) full calculation were found to lie within 0.07 kcal/mol, for each cluster from trimer to decamer,²⁶² reflecting the efficiency of such techniques for the estimation of the energetics of $(\text{H}_2\text{O})_n$ clusters.

In yet another recent study,²⁶³ the HB networks as well as the interaction energies of water dimer through pentamer, 13-mer, and 17-mer clusters were investigated through absolutely localized molecular orbital (ALMO) energy decomposition analysis. The overall binding energies of the clusters were found to have large contributions from the geometric distribution, frozen orbital interaction, polarization as well as from charge transfer interactions. For all of the clusters, both polarization, charge transfer, and frozen orbital interactions energies have a

significant contributions toward the two-body as well as the overall interaction energies of the clusters, whereas three-body interaction energies are dominated by the polarization interactions.

In spite of the feasibility of the calculations on large clusters even at high levels of theory, all these methods have some limitations. As approximate methods, energies as well as the geometries derived through these methods are always in error with respect to their FC counterparts, although procedures to alleviate this problems are known. Equipped with these corrections and considering their parallelizability, all these approaches are now poised for taking up new challenges in cluster chemistry. Fragmentation-based methods, notably MTA, are capable of rapid and reliable estimation of the binding energies of clusters in the CBS limit. This is possible due to the basis set insensitivity of the error in MTA methodology. These binding energies at the CBS limit would be useful for the development of interaction potentials or for generating new density functionals.

3.1.4. Charged Water Clusters. Apart from the neutral clusters, investigations on the charged (both cationic and anionic) water clusters are attracting substantial attention due to their wide applications in atmospheric and biological systems.^{264–267} As noted above, due to the clathrate motifs of $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{21}$ clusters and their protonated analogues, they are of great interest in solution chemistry and have been extensively studied.^{241,268–274}

The extra proton was found to distort the HB network of the corresponding neutral clusters and was seen to be located at the surface of the clusters rather than inside the bulk.²⁷⁵ In general, for all of the protonated water clusters containing n monomers, the protonated species possesses a cage-like structure with the proton situated at the surface as the H_3O^+ Eigen form.²⁷⁵ The lowest energy isomers for both $(\text{H}_2\text{O})_{20}\text{H}^+$ and $(\text{H}_2\text{O})_{21}\text{H}^+$ are found to be distorted dodecahedral cage-like structure at HF, MBPT, and coupled cluster (CC) levels.²⁷¹ These global minima for both of the clusters were in agreement with the earlier findings from basin-hopping algorithm,²⁶⁸ MC,²⁶⁹ and empirical valence bond potential-based studies.²⁷⁰ In a further study,²⁴¹ $(\text{H}_2\text{O})_{20}$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ clusters have been studied employing the B3LYP functional as well as the MP2 level of theory. MP2- as well as B3LYP-based studies predict identical structural pattern for the global minimum of $(\text{H}_2\text{O})_{20}$ cluster. However, for the $(\text{H}_2\text{O})_{20}\text{H}_3\text{O}^+$ cluster, MP2 and B3LYP level geometry optimization lead to different isomers with different HB networks. Recently, Bankura and Chandra²⁷³ reported the solvation structures for protonated clusters with 5, 9, 17, and 21 water molecules at both MP2 and B3LYP level calculations by means of ab initio structure calculations and MD-simulation studies. For pentameric cluster, a symmetrical four-membered ring was observed to be dominant over the open chain structure at room temperature whereas it was a distorted cubic geometry for $(\text{H}_2\text{O})_9\text{H}^+$ species.²⁷³ In contrast, though it was earlier observed that the protonated water clusters with 16 or more water molecules favor the clathrate structure, the clathrate cluster of $(\text{H}_2\text{O})_{17}\text{H}^+$ was found to melt at room temperature in order to form a three-dimensional open structure.

The global minimum structure and HB network for the neutral as well as cationic water clusters are generally found to differ from each other. For example, the edge-sharing pentagonal prism isomer is the most stable one for the neutral $(\text{H}_2\text{O})_{20}$ cluster whereas it is the dodecahedron cage like structure for the cationic species. Recently, Parkkinen et al.²⁷⁴

performed MP2 level calculations on $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{20}\text{H}^+$ clusters. The total energy and stability of the cationic water clusters were seen to be dominated by the local geometry of the $(\text{H}_9\text{O}_4)^+$ species rather than the geometry of the H_3O^+ species.^{273,274} The $(\text{H}_9\text{O}_4)^+$ species formed due to the addition of extra proton to the water clusters generally prefers flat geometries, and hence, the formation of the cationic cluster is common in polyhedral cage-like structure of $(\text{H}_2\text{O})_{20}$ than in the prism isomer.²⁷⁴ As a result, the dodecahedral, rather than the edge-sharing pentagonal prism cationic cluster, represents the global minimum for the $(\text{H}_2\text{O})_{20}\text{H}^+$ cluster.²⁷⁴ Further ab initio calculations employing several functionals viz. B3LYP, X3LYP and M06-class, were performed by Bryantsev et al.²⁷⁶ with a purpose of benchmarking binding energies in some neutral as well as protonated and deprotonated water clusters. Clusters of various sizes, $(\text{H}_2\text{O})_n$, $n = 2–20$, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $n = 1–6$, and $\text{OH}^-(\text{H}_2\text{O})_n$, $n = 1–6$ were extensively studied employing these DFT functionals with Dunning's correlation consistent basis sets. The results obtained were compared to the extrapolated values at MP2 and CCSD(T) levels of theory. Both M06 and M06-L functionals with aug-cc-pVTZ and 6-311++G(2d,2p) basis sets were found to give accurate binding energies for neutral structures whereas the B3LYP/6-311+ +G(2d,2p) level of theory was found more suitable for ion hydration.²⁷⁶

On the other hand, the optimized anion geometries have excess electron density at a non H-bonded proton of either one or several water molecules.^{277,278} Estimation of vertical energy of the electron detachment at the MP2 level of theory shows the formation of the trimer anion from the combination of monomer and dimer. Similarly, the octamer species forms a solvation shell around the excess electron. Hence the electron localization in water clusters may be either at the surface or at the interface. In other words, the excess electron density is either found to localize on the nuclei situated outside of the H-bonded clusters or in the faces of two bonded subclusters of the larger system.^{277,278} Later, Kulkarni et al.^{279,280} investigated the structures of some anionic water clusters of various sizes at MP2 and DFT levels. The excess electron localizations were traced through MESP and found that the excess electrons in these clusters were essentially at the surface of the clusters.²⁸⁰ The excess electron density was found to be stabilized by the dangling hydrogens in clusters. Both surface and internal stabilization of an excess electron provide evidence for through space electron transport phenomena.²⁷⁹ Other investigations include the analysis of finite temperature behavior and electron binding motifs of anionic water clusters by Jordan and co-workers.^{281–283} We would like to point out that there are many more investigations on charged, mainly cationic H_2O clusters reported in the literature.^{284–302} However, we have included very few of the recent ones in the present review due to the limitation of space.

3.1.5. MC- and MD-Based Studies on Water Clusters.

Besides these extensive ab initio investigations, several MC- and MD-based studies^{303–327} have been reported for searching putative minima on the PES of water clusters. However, as mentioned in the Introduction, only a brief report on these investigations is provided below. In an earlier work, full CI calculation and MC-based studies were performed on various configurations of water dimers by Clementi and co-workers³⁰⁴ where the total correlation for the entire potential surface was analyzed in terms of inter- and intramolecular effects. Further comparison between MC-based intermolecular potentials and

models such as Bernal-Fowler, SPC, ST2, TIPS2, TIP3P, and TIP4P (see the list of acronyms and abbreviations at the end of this review) for water dimers was reported by Jorgensen et al.³⁰⁶ In another pioneering study, Benson and co-workers³⁰⁸ constructed a model representing the isomerization between small-sized water clusters. Effective fragment potential and MC studies have been employed³¹⁰ for locating lowest energy structures of water clusters containing 6–20 monomers. The interaction energies obtained from this empirical potential were found to be in excellent agreement with those calculated at the ab initio HF level and also those due to Wales et al.²⁴⁰

More recently, an efficient method for the geometry optimization of TIP3P and TIP4P water clusters have been developed by Takeuchi.³²⁰ Although this methodology failed to reproduce global minimum for $(\text{H}_2\text{O})_{24}$, new global minima for $(\text{H}_2\text{O})_n$ clusters, for $n = 24–30$ were found. Kazachenko and Thakkar³²¹ reported TIP4P cluster geometries up to $(\text{H}_2\text{O})_{37}$ and produced new minima for $(\text{H}_2\text{O})_{28}$ and $(\text{H}_2\text{O})_{29}$ and global minima for $(\text{H}_2\text{O})_n$ with $31 \leq n \leq 37$. Recently Li et al.³²⁴ have extended the study of the large water clusters $(\text{H}_2\text{O})_n$, $n = 30–48$, based on the combined use of MC- and DFT-based calculations. In this range, water clusters prefer to have amorphous core–shell structures instead of cage like patterns. The large number of HBs, and the corresponding HOMO–LUMO gaps are expected to contribute to the high stability of such amorphous water clusters. In a very recent work,³²⁸ size-resolved spectroscopy has opened a window for exploring structures of large water clusters. In this work,³²⁸ a single all-surface structure for water cluster of $n = 25$ and mixtures with one or two interior water molecules for $n = 24$ and 32 were identified.³²⁸ Mainly the buckminsterfullerene of the $(\text{H}_2\text{O})_{60}$ cluster represents a minimum energy structure on the PES which is further strengthened through the insertion of small hydrophobic molecules such as methane.³²⁹ This is achieved due to the preferential orientation of water molecules in the hydration shell of a nonpolar solute. Water tries to strengthen its network around the nonpolar solute when the latter placed inside the water cages. Thus, placing a solute molecule in liquid water leads to a rearrangement of the HB network.³²⁹

In a recent study due to Miró and Cramer,³³⁰ the structures and energetics of water clusters containing up to 100 monomers are reported employing the tight-binding density functional theory (DFTB).^{331–333} The DFTB approach is considered to be the bridge between empirical force fields and first-principles methods, mainly meant for the efficient quantum chemical simulation methods. The accuracy of the DFTB methodology is benchmarked against the binding energies from M06-L/aug-cc-pVTZ calculations.³³⁰ The optimized geometry of the $(\text{H}_2\text{O})_{100}$ nanodrop is in quite good agreement with the available experimental data.³³⁴ The generation of such large water clusters is achieved by trapping them in a structurally well-defined, differently sized and functionalized nanocapsule cavities. Muller and co-workers³³⁴ have already demonstrated the formation of water nanodrop $(\text{H}_2\text{O})_{100}$ inside Mo_{132} cavity. The outermost and innermost water shells have extensive HB networks leading to binding energies of 380 and 175 kcal/mol, respectively. However, the intermediate shell is considered as $20(\text{H}_2\text{O})$ instead of $(\text{H}_2\text{O})_{20}$ moiety and holds the key for the interaction of the external and intermediate water shells through a large number of intershell HBs. Although DFTB-based studies underestimate the energy of intermolecular HBs, these are successful for locating minimum energy structures and hence systematically corrected through the contribution from

the energy of intermolecular HBs. More importantly, these are faster than other available methods yet offering accuracy similar to the existing quantum chemical methods. Authors would like to again point out that, due to the limitation of space, very few of the MC- and MD-based investigations on water clusters are presented here.

With the increase of cluster size, the number of minimum energy structures grows exponentially. Thus, finding good starting structures using chemical intuition for large-sized water clusters is indeed difficult. It is here that the MC- or MD-based simulation methods such as basin-hopping, genetic algorithm, and simulated annealing serve usefully for generating several cluster geometries. These have been successfully employed for water clusters, in conjunction with quantum chemical methods.

3.2. Ammonia

Unlike the other weakly bonded clusters, the structure of the ammonia dimer has remained controversial, being sensitive to the level of theory applied.³³⁵ In an earlier study,³³⁶ MP2 calculations with large basis sets including bond functions concluded that the C_{2h} structure was more stable than the C_s one. The trend was unaltered even at higher levels of theory.^{337,338} To the contrary, the stability of these two isomers was reversed at the MP2 level of calculation excluding bond functions.³³⁸ The earlier experimental observations also clearly brought out this dichotomy.^{339–342} For example, molecular beam electric resonance experiments showed the C_{2h} structure as the favorable one,^{339,340} whereas according to the far IR and microwave experiments³⁴¹ and VRT-dynamics study it was the C_s isomer.³⁴² Further investigations on dimers confirmed the eclipsed isomer (C_s) with an almost linear NH···N HB as the global minimum.³⁴³ The minimum energy path connecting these two equivalent C_s structures via the C_{2h} structure was found to be extraordinarily flat³⁴⁴ with a broad region around the C_{2h} structure rising steeply upon approaching the C_s structure.³³⁷ The energy difference between these two structures (cf. Figure 6) was found to be very low (i.e., 0.17 kJ/mol) thereby making it sensitive to the level of theory.^{337,344}

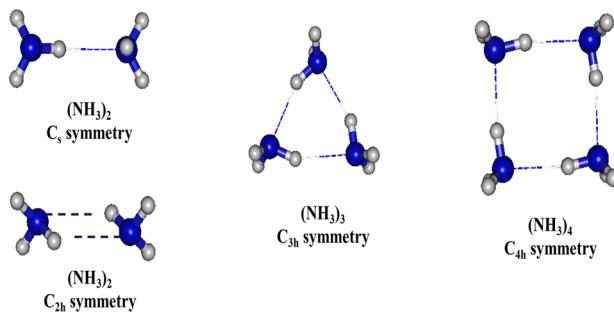


Figure 6. Two-low lying isomers for the ammonia dimer, one each for the trimeric and tetrameric ammonia clusters at MP2/aug-cc-pVTZ level of theory. Data derived from ref 347.

Similar to water clusters, the cyclic trimer with the H-bonded protons pointing away from the N–N lines, was found to be the global minimum at ab initio level of theory.^{336,345} Several studies on medium-sized ammonia clusters from dimers to hexamers have been reported at HF and MP2 levels^{346,347} and also employing DFT with hybrid functionals.³⁴⁸ At the HF level of theory, cyclic clusters beyond dimer were found to be more favorable than their acyclic analogues. Both trimeric and tetrameric ammonia clusters were endowed with perfect

molecular symmetries (C_{3h} and C_{4h}) and found to be nonpolar in nature due to the cancellation of overall dipole moments (cf. Figure 6). However, the pentamers and hexamers showed a slightly asymmetric nature with nonzero dipole moments, in agreement with the earlier findings from pairwise additive potentials.³⁴⁹ Similar observations were made through DFT level investigations.³⁴⁸ Structures from B3LYP and B3P86 calculations showed more relative stability and excellent structural parameters as against those derived from HF and MP2 level calculations.³⁴⁶ These observations were in agreement with those derived from a study³⁴⁷ at MP2 level using large basis sets (aug-cc-pVQZ, X = D, T, Q). Both tetramer (16 kcal/mol) and pentamer (20 kcal/mol) had very similar relative binding energies per molecule, indicating that the PES of ammonia was flat and the presence of small energy different between the isomers revealed the possibility of their fast interconversion.

An extensive work on the accurate geometries of ammonia clusters from trimers to higher-sized clusters containing up to 18 molecules was reported through pairwise additive model potential and molecular perturbation approach^{350,351} followed by an ab initio level study up to 20 molecules.³⁵² The low-lying trimers and tetramers were found to exhibit a cyclic arrangement, in agreement to those from earlier findings.^{346–348} To the contrary, for pentamers and higher clusters, the isomers possessed a 3D structure which converged to an amorphous pattern with further increase in size.^{350,351} The $(\text{NH}_3)_n$ clusters were found to exhibit magic numbers³⁵² at $n = 8, 10, 12, 15$, and 20. The average coordination number (number of HBs per molecule) for the ammonia molecules was seen to increase monotonically with size. For trimer and tetramers, it was 2 and seen to increase to over 4 for $n = 12$ and 4.2 for cluster containing 18 molecules.³⁵⁰ Though this value was quite far from that of the solid ($n = 6$), it was found to be larger than that obtained from simulation of liquid ammonia,³⁵³ indicating that the 18-mer ammonia cluster possesses a behavior similar to that of the liquid ammonia.³⁵³

Several MC- and MD-based studies have also been performed for developing interaction potentials for ammonia and for searching the minima on the PES. In 1981, Turner and David³⁵⁴ reported the minimum structures of ammonia clusters containing up to six monomers using a polarization model. The geometrical parameters for trimers, tetramers, and pentamers were found to agree with those derived from experiments as well as theoretical calculations. Instead of a regular hexagonal configuration, a new chair configuration, similar to that of the cyclohexane was found to be the most stable hexamer. Later, from molecular mechanics (MM) for clusters model study, both trimer and tetramer were found to have symmetric and cyclic structures.³⁵⁵ Recently, from a study³⁵⁶ based on ab initio calculations and fluctuating charge potential model, the cyclic dimer was observed to be a transition state between the interconversion of asymmetric linear isomers, indicating the agreement with the earlier investigation³³⁷ whereas the trimer and tetramer preferred to be cyclic and the pentamer preferred a 3D structure.³⁵⁶

The presence of intermolecular HB plays a major role in determining the properties of ammonia clusters.^{357,358} For cationic or protonated ammonia clusters, the ammonia molecules were found to surround the central core NH_4^+ cation.^{359–361} For $(\text{NH}_3)_5\text{H}^+$, a magic cluster,³⁵⁹ the central ion is surrounded by first-shell ammonia molecules. Both unprotonated $(\text{NH}_3)_n^+$ ($n = 1–6$), protonated $\text{NH}_4^+(\text{NH}_3)_{n-1}$

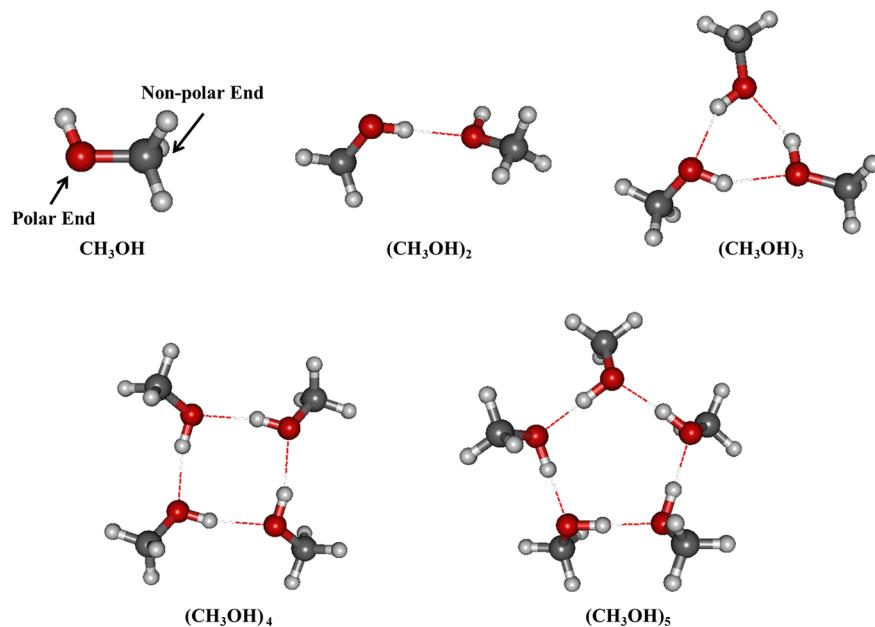


Figure 7. Methanol monomer showing the polar and nonpolar end along with the minimum geometries for $(\text{CH}_3\text{OH})_n$ clusters for $n = 2-5$. Data derived from refs 376 and 382.

($n = 1-6$), and proton-transferred $(\text{NH}_4^+ \cdot \text{NH}_2)(\text{NH}_3)_{n-2}$ ($n = 3-7$) ammonia cluster cations were reported at both HF and MP2 level.³⁶⁰ At both levels, the central core of these cationic clusters was found to be NH_3^+ , NH_4^+ , and $\text{NH}_4^+ \cdot \text{NH}_2$ respectively. The clusters are held through the charge-dipole interactions between the core ion and the neutral ammonia on the surface, wherein this interaction was found to decrease with cluster size. Similar study for $\text{NH}_4^+(\text{NH}_3)_n$ for $n \leq 8$, was extended employing DFT.³⁶¹ Clusters with $n < 5$ were found to be stable below 100 K, whereas $n \geq 5$ were seen to isomerize among each other. The clusters were found to have globular structures where the presence of NH_4^+ was noticed as shown in the earlier observations.^{357,358,360} The small anionic ammonia clusters were found to resemble small water clusters at CC level of theory.³⁶² Ammonia tetramer was observed to be the smallest isomer to form anions with triple acceptor monomer, being a binding motif for large clusters. Unlike cationic water clusters, the excess protons in ammonia clusters are present in the bulk rather than on the surface and stabilized through the charge-dipole interactions. However, in both water and ammonia clusters, the globular or polyhedral cage-like structures favor the formation of cationic clusters.³⁶¹

3.3. Methanol

Ab initio investigations on methanol clusters are rather scanty compared to those of water. However, the study on methanol clusters is of great interest due to the presence of both polar and nonpolar moiety in the monomer. In one of the very earlier studies, Del Bene³⁶³ reported the structures of $(\text{CH}_3\text{OH})_2$ at the HF level of theory. The dimer was found to have no plane of symmetry, and the O···O distance ($\sim 2.74 \text{ \AA}$) was similar to that in water dimer. In the studies of polymeric clusters, the cyclic structures were found to be more stable than the chain structures.^{364,365}

Mó et al.³⁶⁶ studied three conformations, viz. cyclic, bowl, and acyclic open-chain for the methanol trimer at MP2 and DFT (B3LYP) levels of theory. As reported earlier,³⁶⁷ the cyclic trimer with two methyl groups on one side of the O–O–O plane and the third one on the other side was found to be the

global minimum isomer. On the other hand, the bowl conformer was also cyclic in nature containing all the three methyl groups on the same side of the O–O–O plane. The vibrational analysis of these three conformations was reported at MP2 and DFT (B3LYP) levels of theory by Tschumper et al.³⁶⁸ and then at B3LYP level by Mandado et al.³⁶⁹ A new conformer with C–H···O interaction was identified wherein additional stabilization was due to the cooperative effects mainly originating in the charge gained by the oxygen.³⁶⁹ The hydrogens of the methyl group (participating in HB formation) were also found to play a significant role in the stabilization of these clusters. Besides these three distinct isomers, the systematic flipping of the methyl groups resulted into transition states or saddle points of higher-order, being energetically very close to the cyclic global minimum.

For higher clusters such as tetramers and pentamers, the cyclic structures with large number of HBs were found to be more stable as compared to their acyclic counterparts.³⁷⁰⁻³⁷³ Furthermore, due to cooperativity effects, the binding energy per molecule was observed to increase upon aggregation of more methanol monomers.³⁷⁴ The cyclic isomer was composed of planar OH···OH···O rings with methyl groups in an alternating positions, either above or below the plane of the rings. In this configuration, each methanol molecule acts both as an HB acceptor and HB donor to the nearest neighbors. The methanol tetramer was found to exhibit a S_4 symmetry in agreement with the earlier observation.³⁷¹ This can undergo concerted proton transfer by forming a transition structure with D_{2d} symmetry in between two S_4 isomers.³⁷⁵ Similarly, the hexamers and octamers were endowed with S_6 and S_8 symmetry, respectively. Due to the HB network, the O–H frequencies exhibited large red shifts relative to that in methanol monomer³⁷⁰ whereas it was a blue shift for C–O stretching frequencies.³⁷¹ Vener and Sauer³⁷⁵ investigated another tetramer with C_1 -symmetry at MP2 level wherein CH₃ groups were found in an up-up-down-down configuration instead of up-down-up-down arrangement. The relative stability of these two isomers was 360 cm^{-1} with an

interconversion barrier of 470 cm^{-1} . However, the C_i isomer exhibited four asymmetric O–H modes instead of two degenerate pairs shown by the S_4 isomer.

Further extensive search of the minimum energy structures on the PES of methanol clusters containing up to 20 monomers has been reported within the DFT framework.^{376,377} All these clusters were seen to favor ring structures over the acyclic ones. The HB networks in the most stable geometries up to methanol pentamer (see Figure 7) resemble those in small-sized water clusters. For the cuboid octamer, the HB network was found similar to that of the water octamer. However, the larger methanol clusters do not resemble the corresponding water clusters, since the former is stabilized by weak C–H…O bonds.³⁷⁷ The binding energy of the clusters per molecule was seen to increase up to hexamers and remained almost constant at about 6.43 kcal/mol thereafter.³⁷⁶ This suggested that methanol in the bulk may be a mixture of ring and chain structures and dominated by six and eight membered methanol units. Therefore, five to six methanol molecules are considered to be sufficient for mimicking the behavior of liquid methanol.^{378,379} Furthermore, gaseous methanol was found to show a higher vibrational frequency for the O–H stretch than liquid methanol,³⁸⁰ which was seen to decrease with increasing cluster size.³⁷⁰ Such a decrease in the vibrational frequency continued up to pentamer and remained almost constant thereafter. This provided further evidence that five or six H-bonded methanol molecules are sufficient to mimic liquid behavior. In a recent study,³⁸¹ the thermochemistry of methanol clusters was reported at RIMP2 and CCSD(T) levels of theory, predicting the pentamer to be the most important cluster for supersaturated gas densities at low temperature. On the other hand, a combined study at PM3, HF, and DFT levels of theory employing ONIOM technique concluded that cluster properties begin to reach an asymptotic limit after six methanol molecules rather than representing bulk properties.³⁸² The evidence for the presence of cyclic structures in liquid methanol was reported by Ludwig³⁸³ employing both DFT and quantum cluster equilibrium model. The average energy of all cluster HBs was seen to increase significantly with cluster size (e.g., tetramer 36%, pentamer 42%, and hexamer 47% for B3LYP/6-31+G*).³⁸³ It was observed that the cooperative enhancement stabilized the methanol hexamer by about 60.9 kJ/mol, equivalent to adding three new HBs through the pairwise additive dimer HBs, providing the evidence that such cooperative corrections increase the strength of particular HBs and are close to saturation at the largest cluster sizes.³⁸³ Experimental findings, such as heats of vaporization, NMR chemical shifts, and NMR deuteron quadrupole coupling constants can be modeled only if cyclic species are considered.³⁸³

Krishtal and co-workers³⁸⁴ estimated the polarizability of $(\text{CH}_3\text{OH})_n$ clusters for $n = 1\text{--}12$ employing DFT. Since the hydrophilic end involves with HB networks, the polarizability of the hydroxyl group was found to be strongly dependent on the number, type and strength of the HBs as well as on the electric field.^{385,386} On the other hand, the steric factor was found to influence the polarizability of the hydrophobic end. The combined investigation of the hydrophilic end at ab initio (QM) level and the hydrophobic end at MM level, can be used for the study of the structure of the methanol bulk liquid and hence to reproduce the experimental structure with reasonable accuracy.³⁸⁷ Recently, Pathak and co-workers³⁸⁸ reported the structural transition of small methanol clusters containing three

to six molecules employing B3LYP functional. The vibrational frequencies in the cyclic ring structures exhibited a blue shift for the O–H stretch and a red shift for the C–O stretch on the application of an electric field perpendicular to the ring. For similar field orientations, the effect on O–H stretching region of methanol clusters was found to be comparable with that on cyclic water clusters.

Several MD- and MC-based studies on methanol clusters have appeared in the literature.^{389–399} Sarkar and Joarder,³⁸⁹ reported the X-ray and neutron diffraction data of liquid methanol at room temperature. The hexameric methanol cluster was dominant due to the intermolecular HBs, in agreement with the previous observations. The bulk properties of methanol clusters from the MC-based study revealed that the cluster heat capacity attains a maximum for a cluster containing 128 molecules and later converges to the bulk value.³⁹⁰ Very similar to the earlier observations, monocyclic and semiplanar structures were found to be dominant up to about 12 molecules followed by bi- and poly cyclic structures for 13–20 molecules with dense intermolecular HB network, while the clusters containing more than 20 monomer units are found to prefer spherical configurations. In 2003, a Car–Parrinello molecular dynamics (CPMD) study was reported for probing the strength of HBs in methanol clusters.³⁹⁵ The presence of strong intermolecular interaction due to HBs is responsible for the substantial rearrangements of the molecular electron density and hence the overall dipole moment of methanol clusters. The dipole moments of methanol clusters are seen to depend upon the number of HBs and found to increase by 28% due to the aggregation in the liquid. Again, the proton transport in liquid methanol is expected as fast as that of the water due to the extensive HB network. From an ab initio MD-study, it was found that the structure associated with an excess proton in liquid methanol, was a H-bonded cationic chain.³⁹⁶ This chain length generally exceeded the average chain length in pure liquid methanol where the proton transfer reactions took place. Furthermore, the HBs in the first and second solvation shells of the excess proton were found to be shorter and stronger than those of the methanol–methanol HB networks.

3.4. Hydrogen Peroxide

Investigations on peroxides, especially hydrogen peroxide (HP), are of great significance due to the peculiar nature of the O–O bond as well as their applications in biological, atmospheric and medicinal chemistry. HP, an important oxidant in clouds,⁴⁰⁰ is responsible for the oxidation of sulfur dioxide to produce sulfuric acid and is used as a catalyst for many organic and inorganic reactions.^{401–403} Besides this, it is a byproduct of several metabolic processes including the conversion of hypoxanthine to xanthine⁴⁰¹ and in neutrophil phagocytosis,⁴⁰⁴ the important process of engulfing a solid particle by a phagocyte in cell biology.

HP is one of the simplest molecules exhibiting a large-amplitude torsion motion around the O–O bond. The conformations (cf. Figure 8) and geometrical parameters of HP have been investigated through high-level ab initio methods.^{405–407} With increasing number of basis functions, the geometrical parameters from the MP2 level calculations are found to closely resemble their experimental counterparts. Nonlocal density functionals with basis sets containing polarization functions on oxygen are also successful in reproducing the experimental geometrical parameters, especially, the torsion angle. Several studies have been carried out

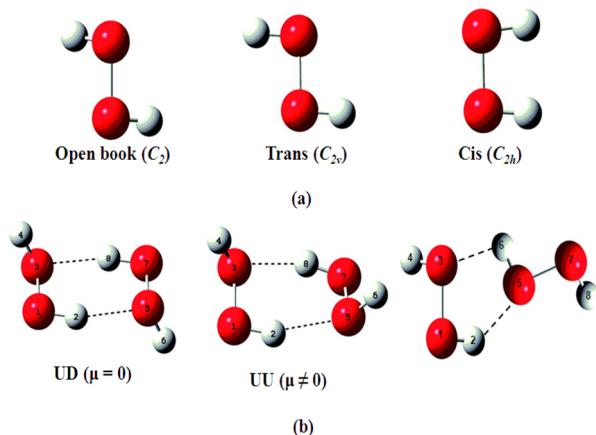


Figure 8. (a) Three conformations of H₂O₂ molecule. (b) 6-membered (up-up and up-down) and 5-membered H₂O₂ dimers. Data derived from refs 411 and 415.

on the barrier for the torsional mode of the H₂O₂ molecule.^{337,408–410} One six-membered and one five-membered ring dimers (see Figure 8) were reported by employing MP2 and QCISD(T) methods with the 6-311++G(2d,2p) basis set.⁴¹¹ The six-membered one (with C_i symmetry) was observed to be the global minimum for the dimer and found to lie 1.1 kcal/mol below the five membered isomer. The linear structure, in which one HP acts as HB donor and the other as an HB acceptor, was a transition state at these levels of theory. However, the strength of the HB in the linear geometry was observed to be greater than the average of the cyclic isomers. This study was further extended employing a variety of nonlocal exchange functionals⁴¹² followed by a combined matrix isolation and ab initio study.⁴¹³ The dimer was found to be in a cyclic form wherein the two monomers act both as proton donor and proton acceptor for the intermolecular HB.⁴¹³

The MP2 level investigation on HP dimers to tetramers revealed two energetically close (energy difference \sim 0.3 kcal/mol) conformational isomers for the dimers.⁴¹⁴ These isomers were categorized as up-up (UU) and up-down (UD) depending upon the arrangement of the hydrogen atoms which are not participating in the HB formation (cf. Figure 8). The lower energy inversion-symmetric isomer, i.e., UD, was in conformity with the earlier observations.⁴¹¹ As expected, the UD isomer has a zero dipole moment ($\mu = 0$) whereas the UU isomer is polar in nature, with a dipole moment value of 3.24 D. For trimers and tetramers, stable cyclic configurations were found.⁴¹⁴ This study was further extended up to hexamers employing MM and MD methods.⁴¹⁵ Similar observations for dimer, trimer and tetramer were reported from HF and MP2 level computations.⁴¹⁶ For both of the tetramer and pentamer, cyclic arrangement of the monomers was observed wherein all hydrogen atoms participated in HB formation. Beyond pentamers, all clusters up to $n = 12$ were found to exhibit cyclic and cage-like conformations.⁴¹⁶

In summary, due to the extended HB networks, cyclic clusters of methanol and ammonia with maximum the number of HBs are generally more stable than the corresponding acyclic ones. The cyclic isomers generally exhibit higher HOMO-LUMO gaps,³⁴⁶ which seem to decrease with increasing size of the cluster. This is responsible for the enhancement of the chemical softness and hence the reactivity of the isomers, in agreement with the HSAB principle.⁴¹⁷ On the contrary, large

H₂O₂ assemblies favor cage-like and helical arrangements of the monomers. Generally dimers and trimers of H₂O₂ have mixed chirality whereas larger clusters favor homochiral cluster. However, in helical structures, all the trimeric patterns assume open book conformation. Extrapolating to the liquid behavior and mimicking the bulk properties of various substances out of the corresponding small-sized clusters is of a great interest in contemporary cluster chemistry. For instance, since aggregation patterns in (NH₃)₁₈ resemble those of the liquid ammonia, this size of the cluster is adequate to mimic the bulk properties of ammonia. A unique feature of bulk methanol is that it contains 6- and 8-membered rings of methanol and it is noted that pentamer or hexamer structures approximate the bulk liquid behavior. For unraveling the mystery of these ring structures, high-level theoretical investigations as well as spectroscopic studies would be immensely beneficial. Very few studies on other hydrogen-bonded clusters viz. ethanol clusters^{392,394,397,398,418–422} and acetone clusters^{423–427} have been reported in the literature and hence are not discussed here in detail.

4. OTHER WEAKLY BONDED CLUSTERS

Besides HBs, other weak intermolecular forces such as dipole-dipole interactions (electrostatic), dipole-induced-dipole interactions (polarization), and dispersion interactions are found to play a major role in the stability of some molecular assemblies. Molecular aggregates of carbon dioxide, benzene, acetylene, etc. are mainly stabilized by such interactions. For instance, clusters of benzene and acetylene incorporating CH \cdots π and $\pi\cdots\pi$ interactions are mainly dominated through dispersion forces. The following subsections summarize the quantum chemical investigations on such clusters.

4.1. Carbon Dioxide

Among molecular clusters, CO₂ clusters rank second in terms of their importance, next only to the water clusters. From both atmospheric and industrial chemistry point of view, CO₂ clusters are of great contemporary interest.^{7,428} Next to the water vapor, CO₂ gas is one of the major greenhouse gases and plays a significant role in global warming.^{429,430} It is also vital in the processes of respiration and photosynthesis. In many of the chemical reactions at supercritical conditions, it acts as a drycleaning agent.^{429,430} Besides this, CO₂ gas is useful for the recovery of oil from wells and is used for enhanced coal bed methane recovery.^{431,432} Due to these diverse applications, both theoretical and experimental investigations on CO₂ clusters are receiving substantial attention during the last two decades.

In a combined MD and quantum chemical study in 1977, Brigot et al.^{431,432} reported two possible low energy structures, viz. parallel and T-shaped for CO₂ dimers, with the former being more stable. The results also suggested that the T-shaped isomer to be a transition state between two slipped parallel isomers, a fact later confirmed by experiments.^{433,434} Many similar theoretical investigations were carried out on CO₂ dimers at various levels of theory such as HF, MP2, MP3, MP4(SDTQ), and CCSD(T).^{92,435–437} Tsuzuki et al.⁹² reported the MP2 level interaction energies to be close to those at CCSD(T) level when large triple- ζ quality basis set is used. In a recent CCSD(T) level investigation, McMahon and Lane,⁴³⁸ have shown that the slipped parallel structure is lower in energy than T-shaped one by 0.26 kcal/mol, in agreement with the previous investigations.^{433,434}

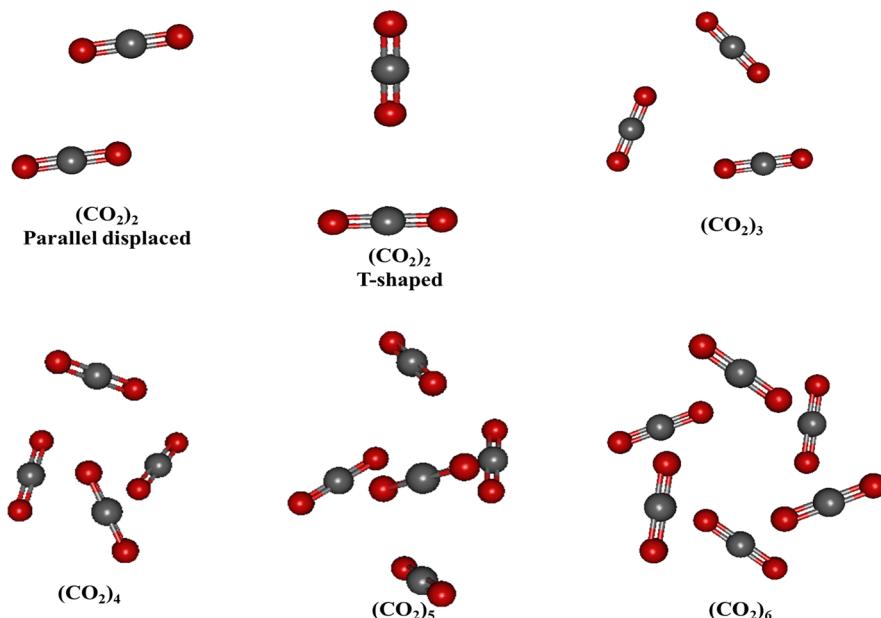


Figure 9. Low-lying parallel displaced and T-shaped CO₂ dimer and planar (C_{3h}) CO₂ trimer. Low-lying structures for (CO₂)₄, (CO₂)₅, and (CO₂)₆ clusters. Data derived from refs 443 and 450.

Earlier, Bukowski and co-workers⁴³⁹ employed SAPT to obtain PES of CO₂ dimers and trimers. In contrast to the earlier observations, the T-shaped isomer was found to be a saddle point rather than a minimum. This may be due to the quality and limitation of the potential used therein. Three minima and two saddle points were observed for the trimer structures. The nonplanar structure (C₂ symmetry) was energetically more stable by 48.8 cm⁻¹ than the planar (C_{3h} symmetry) one, not in agreement with the experimental findings.^{440,441} This led to a conclusion that only the pairwise treatment of the potentials is not sufficient for estimating the relative stability of CO₂ clusters. In investigations on trimers at MP2 and CCSD(T) levels of theory,⁴⁴² the cyclic and noncyclic CO₂ trimers had rather similar interaction energies, viz. -4.02 and -4.11 kcal/mol. It was pointed out⁴⁴² that CCSD level underestimates the interaction energy as compared to CCSD(T) method, due to the inadequate treatment of dispersion interaction by the former. On the other hand, MP2 results are comparable to those at CCSD(T) as previously reported by Tsuzuki et al.⁹² Hence, for accurate estimation of structures and energetics of large CO₂ clusters, methods such as MP2 or CCSD(T) with sufficiently large basis sets were recommended.

Thus, before the advent of relatively less expensive dispersion-corrected DFT functionals, the geometry optimization and vibrational analysis for large CO₂ clusters at high-level correlated methods was not possible with contemporary off-the-shelf hardware. Hence, the quantum chemical literature on them is not so rich although CO₂ clusters of various sizes are extensively studied through experimental techniques. However, the introduction of dispersion-corrected hybrid DFT functionals such as MPWB1K, mPW1PW91, HSES1PBE, etc. has enabled studies of large CO₂ clusters, since 2000.

One such double-hybrid meta-GGA functional, MPWB1K, was applied for investigating the geometries and vibrational frequency of (CO₂)_n clusters.⁴⁴³ Initial geometries of various (CO₂)_n clusters generated by the electrostatics potential for intermolecular complexation (EPIC) model.^{444–446} For benchmarking the efficiency and accuracy of the functional, small

clusters up to n = 5 were also optimized at MP2 level of theory (see Figure 9). The results derived from MP2 and MPWB1K levels were found comparable to each other, confirming the utility of MPWB1K functional for the investigations of large CO₂ clusters. For the minimum structures, two-body interaction energy was found to contribute substantially (>96%) to the overall binding energy of the clusters.¹⁴² This study was further extended to large (CO₂)_n clusters containing 13, 20, and 25 monomers.⁴⁴⁷ An MESP- and MTA-based algorithm was applied for the generation of initial geometries of these clusters. For each of the (CO₂)₁₃ and (CO₂)₂₀ clusters, two new structures lying below those reported in the earlier investigations^{448,449} were observed at this level of theory. Both of them were found to contain triangular motifs of CO₂ monomers. On the other hand, in the case of the (CO₂)₂₅ cluster, the isomer with regular arrangement of monomers was found to be more stable than other isomers with more number of pentagonal pyramidal and triangular motifs. MTA-based vibrational frequency analysis revealed asymmetric C–O stretch showing blue shift with respect to the monomers, in good agreement with experiments. The study was further extended by carrying out the ab initio treatment at HF/6-31+G* level of theory⁴⁵⁰ merely as a test case on three isomers of the (CO₂)₃₀ cluster obtained from molecular dynamics simulation.⁴⁵¹ This size of 30 was chosen since it was previously identified as a magic number for CO₂ clusters. It was seen that these three isomers exhibit the zigzag pattern shown by the CO₂ crystal.

In an extensive study, the present authors⁴⁵² have reported the structures, energetics and vibrational spectra of (CO₂)_n clusters for n = 6–13 at MP2 level employing Dunning's correlation consistent basis sets. The initial structures were generated systematically by employing the molecular cluster building algorithm.²⁵⁷ The calculated asymmetric C–O stretching frequency exhibits a blue shift with increasing cluster size, in agreement with the recent experimental findings of Oliaee et al.^{63,64} Within this range of clusters, the computed blue shift was found to be 10.9 cm⁻¹, against the experimental

value of 14.2 cm^{-1} . The optimized stable geometries for $n = 6$ –10, were found to match the structures reported by Takeuchi.⁴⁵¹ For larger clusters, beyond $n = 10$, new geometries, lower in energy than the earlier reported ones were found.⁴⁵¹ However, the energy rank ordering of the isomers can be altered during the FCs as the MTA-based energies are always in error due to the approximate nature of MTA and may change after applying the newly proposed grafting procedure,^{258,260} a fact confirmed very recently.⁴⁵³ Upon energy correction through the grafting procedure, the most-stable structures for $n = 10$ –13, are found to be in good qualitative agreement with those reported by Takeuchi.⁴⁵¹ From the analysis of spatial distribution of monomers, the number of T- and slanted T-type interactions among monomers was seen to increase with cluster size.

Recently, Lemke and Seward⁴⁵⁴ investigated the structures and energetics of $(\text{CO}_2)_n$ clusters up to $n = 16$, employing the dispersion corrected density functionals, viz. M06-2X, B2PLYPD, and B3PW91. For dimers and trimers, CCSD(T) calculations were effected. The binding energies from the M06-2X functional were found to resemble their CCSD(T) counterparts, in comparison to the B2PLYPD functional. The latter, however, was found to yield geometries which are in better agreement with CCSD(T) ones. Furthermore, the calculations at M06-2X are readily feasible for large-sized clusters, due to the low scaling factor $O(N^3)$. Large CO_2 clusters, for $n = 9$ –16, the M06-2X/aug-cc-pVQZ optimized geometries were found to contain a 3–6–3 combination of ring motifs. For $n = 13$, a staggered equatorial ring of six monomers is capped by two rings of three CO_2 monomers with one centrally placed CO_2 monomer, in agreement with the recent MD-based studies by Takeuchi.⁴⁵¹ With further increase in the size from $n = 14$ –16, the structures are built by aufbau addition of CO_2 monomers onto the surface of the $(\text{CO}_2)_{13}$. For instance, out of several geometries of $(\text{CO}_2)_{14}$ scanned at MP2/aug-cc-pVQZ level of theory, the most stable isomer is indeed found to have the $(\text{CO}_2)_{13}$ core intact with a monomer situated at the periphery.⁴⁵³

Several MD-simulation studies on CO_2 clusters of various sizes have been reported in the literature.^{451,455–460} The potentials for dimers mainly developed by Muentner⁴⁵⁷ and Domanski et al.,⁴⁵⁸ were used for these studies. Parallel-tempering Monte Carlo simulation technique was applied for the structure determination of large $(\text{CO}_2)_n$ clusters, with $n = 6$, 8, 13, and 19 by Liu and Jordan.⁴⁶⁰ Six low-lying minima were found for $(\text{CO}_2)_6$ cluster, within a narrow gap of 0.57 kcal/mol. Among these, the most stable isomer, having two interacting trimers, was seen to lie lower than the second most stable isomer only by 0.04 kcal/mol. Similarly, for octamers,^{431,432} several minima were identified within a 1 kcal/mol energy window. The previously reported icosahedral structure⁴⁴⁸ was found to be the most stable one for $(\text{CO}_2)_{13}$. Similarly for the $(\text{CO}_2)_{19}$ cluster, six minima were observed within a range of 0.5 kcal/mol. All the isomers were found to possess an icosahedral $(\text{CO}_2)_{13}$ core to which six monomers were attached on the surface. Recently,⁴⁵¹ Takeuchi has reported the geometry optimization of CO_2 clusters in the range of 4–40 through MD-based geometry optimization. During this optimization process, for some of the clusters, the global minimum geometries were found to match the earlier reported global minimum geometries of respective size. However, for $(\text{CO}_2)_n$ cluster with $n = 23$, 25, and 35, new global minima were identified.⁴⁵¹ It would be worthwhile to benchmark these

calculations using correlated methods, a task that appears to be an uphill one at the time of writing this review. Innovations such as fragmentation-based methods need to be explored for investing larger-sized aggregates.

4.2. Benzene

Benzene clusters incorporating $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ interactions play a vital role in many fields of biology and chemistry.⁴⁶¹ They are important in molecular recognition processes,^{462–464} crystal packing of organic molecules with aromatic rings,⁴⁶⁵ three-dimensional structures of proteins,^{461,466} base–base interaction in DNA,^{467,468} and many more phenomena. Due to this, theoretical as well as experimental investigations on benzene clusters are of perennial interest.

The benzene dimer has been studied in great detail^{93–95,469–480} since 1960. In the early ab initio investigations,^{469,470,472} the T-shaped dimer was reported to lower in energy than the sandwiched one. Later, the calculations by Hobza and co-workers⁴⁷³ at the MP2 level showed the parallel-displaced structure to be more stable than T-shaped one, with the orientation of the two benzene rings in agreement with the earlier experimental findings.⁴⁷¹ In further investigations employing MP2, MP4, and CCSD(T) methods, the energy barrier between the displaced parallel and T-shaped isomers was 0.2 kcal/mol, indicating the isoenergetic nature of the isomers.^{93–95} The MP2 and MP4 level calculations were found to overestimate the binding energy, whereas MP2(SDQ) and CCSD methods underestimated it with reference to the CCSD(T) level calculation. This indicated the importance of the triple excitations which are of attractive in nature, for the evaluation of attractive dispersion interactions present in benzene clusters.

Investigations at highly correlated level incorporating basis set superposition correction led to a debate on the order of stability of these isomers.^{475–480} Both T-shaped and planar sandwich isomers were observed to be saddle points for the low-energy and high-energy interconversion of the two parallel displaced isomers, respectively. The geometries of these three isomers of the benzene dimer are displayed in Figure 10.

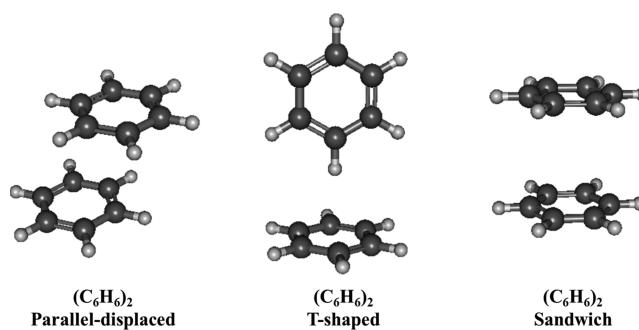


Figure 10. Three low-lying geometries for benzene dimer at the MP2/aug-cc-pVQZ* level of theory. Data derived from ref 477.

Tsuzuki and co-workers⁴⁷⁶ stated that the major source of attraction is not only the short-range interactions such as charge-transfer but also the long-range electrostatic and dispersion interactions. The dispersion interactions were found to be dominant over the electrostatic ones at larger distances, whereas at equilibrium geometry, the latter had a substantial contribution toward the binding energy.^{476–478} On the other hand, the CCSD(T) level induction (polarization) energies for the parallel-displaced, T-shaped and the sandwich

dimers were only -0.21 , -0.17 , and -0.25 kcal/mol against the total binding energies -2.48 , -2.46 , and -1.48 kcal/mol respectively, indicating that induction is not important for attraction in the benzene dimer.⁴⁷⁶

Calculations on benzene clusters require treatment at a high-level of theory, say CCSD(T)/CBS, due to the presence of strong dispersion interactions in the π -electron cloud and the overestimation of binding energies at the MP2/CBS level. Engkvist et al.⁴⁸¹ used simple potentials derived from CCSD(T) energies of benzene dimer, to obtain the minimum structures of benzene trimers and tetramers. Since the stability of the isomers was mainly accounted for by two-body interaction energies, the cyclic benzene trimer containing three deformed T-shaped dimeric patterns was found to be the most stable isomer. The double T- and H-shaped structure having two dimeric interactions were the next two stable isomers (cf. Figure 11), in agreement with the earlier

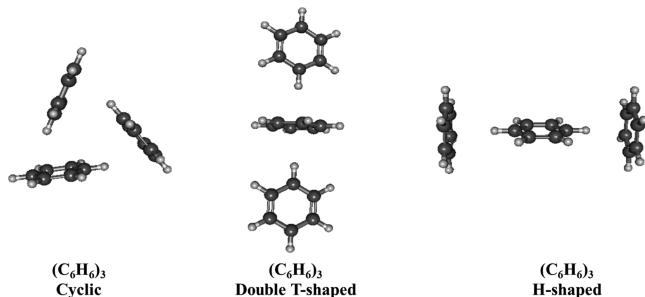


Figure 11. Cyclic, double T-shaped, and H-shaped benzene trimers at MP2/cc-pVDZ+ level of theory. Data from ref 488

observations.^{482,483} These observations were further confirmed at MP2 level⁴⁸⁴ and with the Hartree–Fock dispersion (HFD) model,⁴⁸⁵ in which the dispersion interaction is perturbatively added at the end of the SCF calculation. For MP2/6-31G optimized geometries of dimers through tetramers, the relative

trend in binding energies estimated from the single-point energy calculations at MP2/6-31G and HFD/6-31G levels of theory was in agreement with each other. More importantly, the HFD as well as MP2 level calculations predicted identical global minimum isomers for each of the benzene dimer through tetramer. Despite this success, the HFD method underestimates the relative stability of some of the conformers of trimers and tetramers. For example, relative stability of the H-shaped and stacked trimeric clusters and edge-sandwiched and edge-triangular tetramers were altered on switching from the MP2 level to the HFD level.⁴⁸⁵ Probably, due to all these limitations, there has not been much follow-up of the HFD model in the past decade.

The number of ab initio investigations beyond benzene trimers is indeed very small. Engkvist et al.⁴⁸¹ investigated five structures of benzene tetramer. Out of these, four different isomers were formed by an additional monomer to the cyclic trimer cluster either in a T-shaped or parallel-shifted manner. The cyclic structure with a 4-fold dimeric interaction was observed to be the global minimum for the tetramer. Since the relative energies of these isomers were within 1 kcal/mol from each other, the correct rank ordering and stability of these were much more complicated and may change through the inclusion of many-body corrections to the dispersion interactions. Further, from the MP2 level calculations⁴⁸⁴ four different isomers, viz., face-triangular, tetrahedral, edge-sandwich, and edge-triangular were found. The lowest energy structure was formed from the cyclic trimer with a benzene molecule placed either above or below of the trimeric ring, in good agreement with the earlier observations.^{481,486} The edge-sandwich structure was identical to the earlier reported structure.⁴⁸¹ Similarly, the structure of benzene pentamers was generated by the removal of an axial monomer from a square-bipyramidal cluster or by the removal of a ring molecule from the square bipyramidal cluster or through the removal of two neighboring monomers from the pentagonal heptamer.⁴⁸² Later, Gonzalez

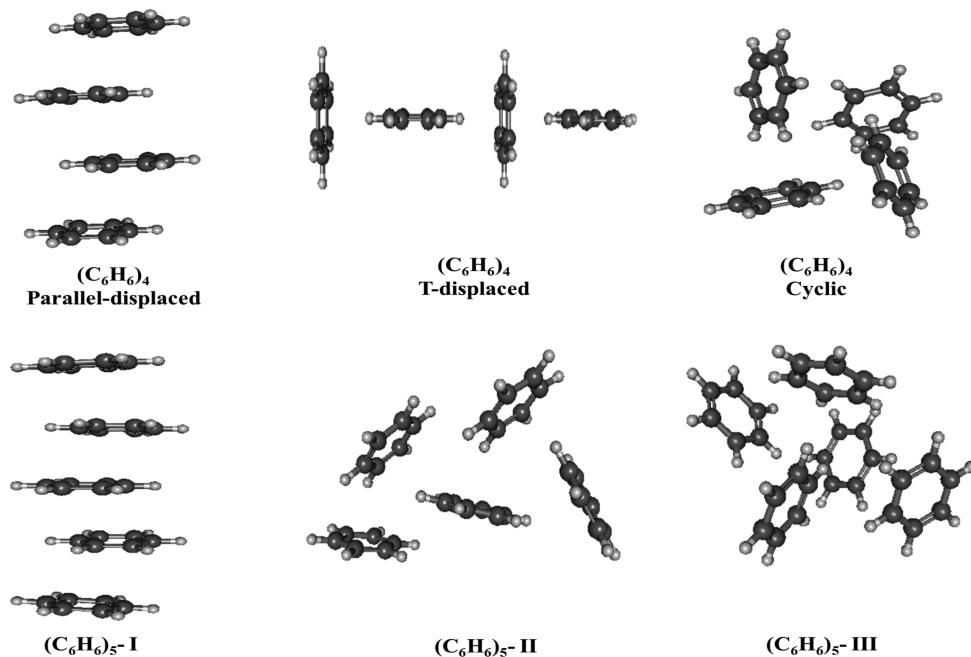


Figure 12. Three low-lying geometries of benzene tetramers and pentamers either at MP2/6-31G* or MP2/cc-pVDZ+ levels of theory. Data derived from refs 161 and 488.

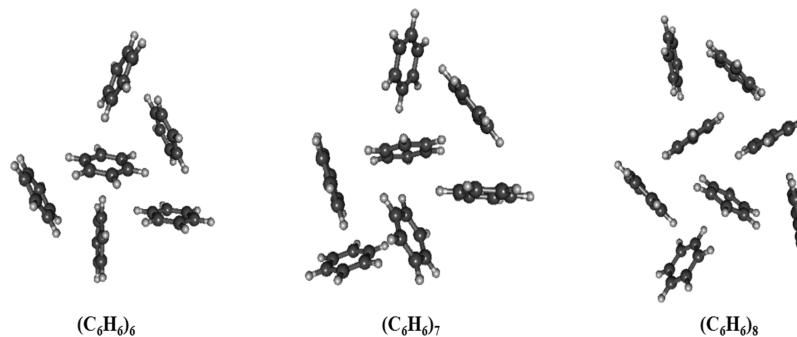


Figure 13. Low-lying geometries of hexameric, heptameric, and octameric benzene clusters at MP2/6-31G* level of theory. Data derived from ref 161.

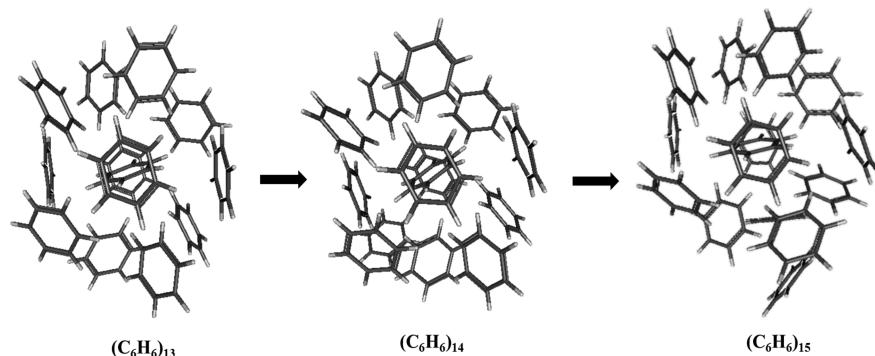


Figure 14. Heuristic method based optimized structures of $(C_6H_6)_n$ clusters, $n = 13-15$. Data derived from ref 498.

and Lim⁴⁸⁴ extended the investigations on benzene pentamers at the MP2 level of theory using 6-31G and 6-31G* basis sets. One isomer with a fused double tetrahedron sharing a face and the other with a trigonal bipyramidal geometry were reported at this level. The former isomer was the most stable over the later isomer, in agreement with the earlier force field⁴⁸² and MD-studies.⁴⁸⁷ Similarly, the trigonal bipyramidal geometry formed by the removal of two neighboring monomers from the heptamer resembled the previously proposed structure.⁴⁸²

Based on the approximations of the dimeric interactions for the stability of benzene clusters due to Engkvist et al.,⁴⁸¹ the investigations were extended to trimers and tetramers through the $\pi \cdots \pi$ pair interactions by Tauer and Sherrill.⁴⁸⁸ Two-body interactions were found to be dominant and mainly responsible for the aggregation in benzene clusters. Particularly, in trimers and tetramers, the presence of the third monomer is seen to influence the stability of the dimeric interactions.⁴⁸⁸ To the contrary, the three- and four-body terms were insignificant toward the binding energy of the benzene clusters. However, the three-body interaction energies arising from three closely placed monomers (cyclic isomer as shown in Figure 11) have substantial contribution toward the binding of the clusters. Since the three- and four-body terms and non-nearest dimer pairs were insignificant for the overall binding of the clusters, it was considered worthwhile to treat the two-body pairs at a high-level and others at a low-level of computations as recently examined for cyanogen and diacetylene trimers.⁴⁸⁹ Thus, it may be noted that, despite the large dispersion interactions of the π -electron cloud, only the interaction between neighboring dimers or trimers seems to contribute significantly to the total binding energy of large benzene clusters.

This observation warranted more ingenious approaches for treating larger benzene clusters at high-level of theory. In 2010,

Gadre and co-workers¹⁶¹ reported such a systematic study of $(C_6H_6)_n$ clusters for $n = 2-8$, at the MP2 level of theory, employing MTA. Some of the possible geometries for the benzene tetramers and pentamers are displayed in Figure 12 and the low-lying geometries each of the hexamer, heptamer, and octamer are displayed in Figure 13. The investigations on hexamers, heptamers, and octamers were carried out by extensive search over several potentially favorable structures generated from EPIC model.⁴⁴⁴⁻⁴⁴⁶ As discussed above, low-lying geometries of each clusters are found to be dominated by the distorted T-shaped benzene dimeric interactions.⁴⁸¹ Yeole and Gadre²⁵⁷ have recently employed their cluster building code for generating large benzene clusters, wherein the earlier reported octamers by Mahadevi et al.¹⁶¹ are used as starting structures for the building of nonameric benzene clusters. Further, decameric benzene clusters were built from the most stable nonameric structure. The cluster geometries thus generated were optimized at MP2/6-31+G* level of theory within MTA-framework.

For understanding the evolution of the structures of clusters with increasing size and the stability of benzene clusters with varying temperature, a MC-based study was reported by Dulles and Bartell.^{490,491} Further investigations employing genetic algorithm were performed for $(C_6H_6)_n$ clusters for n in the range of 2–15 by Pullan⁴⁹² and Sheng et al.⁴⁹³ The smaller clusters up to heptamer resembled the ones reported earlier in the literature.⁴⁹² The edge-to-face orientation of the monomer units can be heuristically explained in terms of the electrostatic interaction between the positively charged hydrogen and negative carbon atoms.⁴⁹² For small-sized benzene clusters, the average binding energy per molecule was generally found to increase with the size of the cluster. Among these, the average binding energy per molecule for the icosahedral $(C_6H_6)_{13}$

cluster was found to be larger than the corresponding ones in $(C_6H_6)_{12}$ and $(C_6H_6)_{14}$ clusters.^{490,491} Besides this, the 13-membered cluster, being considered as a magic cluster^{11,12} was found to have some extra stability at the transition temperature than other clusters, consistent with its closed-shell icosahedral structure. This icosahedral moiety of $(C_6H_6)_{13}$ remains intact upon the removal of one benzene molecule from the $(C_6H_6)_{13}$ cluster or upon the addition of further benzene molecules up to 19 molecules (cf. Figure 14). The C_3 structure of $(C_6H_6)_{13}$ was also in agreement with the earlier reported icosahedral one.^{482,483,486} This structure was further investigated by Easter⁴⁹⁴ through a combination of free jet expansion experiment and MC study. However, the newly⁴⁹⁴ found structure with C_3 symmetry was seen to differ from the previously reported structure.⁴⁹² Two closely spaced isomers respectively with C_3 and C_i symmetry were further refined through MC-based low-temperature simulations.⁴⁹⁵ In a recent study,⁴⁹⁶ based on high-level DFT(SAPT) calculations, another low-lying conformer with S_6 symmetry was observed for the $(C_6H_6)_{13}$ cluster, including a C_3 global minimum as reported earlier. The organization of the low-lying isomers (C_3 , C_i , and S_6) on the PES suggests that the S_6 structure acts as a kinetic trap and hinders the efficient relaxation to the global minimum structure, supporting the hypothesis of the existence of two isoenergetic isomers.⁴⁹⁶

In 2007, Takeuchi⁴⁹⁷ developed a heuristic method for the geometry optimization of large benzene clusters in the range of 16–30 monomers by using three geometric operators viz. interior, surface, and orientation operators. These operators were used for the geometrical adjustment of the monomers in the benzene clusters. In this extensive study,⁴⁹⁷ new global minima for clusters containing 11, 14, and 15 monomers were reported and for the first time in the literature, global minima for larger benzene clusters viz. $(C_6H_6)_{16}$ through $(C_6H_6)_{30}$ were identified. Recently, this study was further extended⁴⁹⁸ with all-atom OPLS potential where the geometry optimization was performed through the above heuristic method. The magic numbers of the clusters were found to be 13, 19, 23, 26, and 29, in agreement with the results of the LJ atomic clusters. Since the current review only deals with the quantum chemical investigations of molecular aggregates, only few of the MD studies have been discussed here. Many more investigations appear in the literature.^{499–506}

Several theoretical investigations were reported for the structures and lattice energy determination of benzene crystal.^{507–511} About 60 years' ago, Cox and Smith⁵⁰⁷ determined the crystal structure of benzene at $-220\text{ }^\circ\text{C}$ and found that it comprises an orthorhombic unit cell (space group $Pbca$) containing four centro-symmetrical molecules per unit cell. On the basis of this information, Gibson and Scheraga⁵⁰⁹ performed energy minimization of 60 possible geometries of crystals of benzene with $Pbca$ symmetry using pairwise interatomic interactions. Out of these, ten (four orthorhombic, five monoclinic, and one tetragonal) possible low-lying lattice structures were investigated. Among these, four were found to be similar to those reported earlier.⁵¹⁰ The lattice energy (11.8 kcal/mol) of crystalline benzene was calculated using an additive system based on the interaction energies of benzene dimers at the CCSD(T)/CBS level of theory.⁵¹¹ The dimers in the first coordination sphere were indeed found to contribute 90% to the lattice energy, whereas the contributions from those in the outside of first coordination sphere were small. Generally, the contribution from the cyclic trimers in the first

coordination sphere for the benzene crystal was less than 0.1 kcal/mol and was seen to decrease rapidly with increasing intermonomeric separation.⁵¹¹ A very recent study⁵¹² also reports that the three-body dispersion effects have a small contribution to the lattice energy of the benzene crystals. For instance, the nonadditive three-body interaction contributes 0.89 kcal/mol (7.2%) of the revised lattice energy of -12.3 kcal/mol. Hence, the total lattice energy of the benzene crystal was calculated by multiplying the dimer interaction energies with the appropriate number of interactions. The estimated energy was found to be approximately 11.8 kcal/mol against the experimental value lying in the range of 10.3–11.2 kcal/mol.⁵¹¹ This study presented a very important result that only the two-body interaction energies suffice for the determination of lattice energy of benzene crystal within the chemist's accuracy, viz. 1 kcal/mol to the corresponding experimental values.

Acetylene clusters possessing both of the $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ interactions are regarded as the nonaromatic analogue of benzene clusters and are detailed out in the following subsection.

4.3. Acetylene

The early HF calculations on acetylene dimers by Aoyama et al.⁵¹³ found the T-shaped geometry to be more stable as compared to the slipped parallel one, in agreement with the earlier experimental finding due to West and Kraihanzel⁵¹⁴ and Handy and co-workers.⁵¹⁵ The slipped parallel isomer was found to be a transition state with an imaginary frequency at HF as well as MP2 level,⁵¹⁵ whereas the T-shaped isomer was found to be a minimum, in agreement with the earlier experimental findings.^{516,517} Further, the internal rotation barrier and vibrational spectrum of $(\text{C}_2\text{H}_2)_2$ at MP2 level of theory revealed that the T-shaped isomer tunneled between four geometrically equivalent slipped-parallel configurations.^{435,518} Yet another confirmation of T-shaped dimer being a minimum and slipped parallel shaped isomer being a first-order saddle was given by Karpfen⁵¹⁹ at MP2 level of theory employing correlation consistent basis sets. Besides these two stationary points, a second order saddle having a nonplanar structure (D_{2d} symmetry) was also observed on the PES of $(\text{C}_2\text{H}_2)_2$.

Handy and co-workers⁵¹⁵ reported the structures of acetylene trimers and concluded that the geometries at HF level of theory were comparable to those from the MP2 level theory. However, due to the lack of electron correlation, the HF level treatment yielded smaller binding energies and larger $\text{CH}\cdots\pi$ bond lengths compared to those at MP2 level. The earlier reported⁵²⁰ planar C_{3h} structure was found to be the minimum at this level of theory. An extensive study was further performed for small acetylene clusters of size 2–5 at HF, MP2, and MP3 levels of theory.⁵²¹ The T-shaped dimer (see Figure 15) was found to be more stable than the slipped parallel dimer as observed in earlier investigations. For trimers also, the results were in agreement with earlier findings, viz. the planar C_{3h} structure with three $\text{CH}\cdots\pi$ interactions was the most stable trimer.⁵²¹ Similarly, for tetramers, two isoenergetic conformers with S_4 and C_{4h} symmetries were observed at both HF and MP2 levels of theory.⁵²¹ More importantly, the former isomer resembled the structure derived from the earlier experimental investigation.⁵²² In the case of pentamers, a nonplanar isomer was found to be more stable than the planar isomer at the HF level of theory. The structural investigations for trimers and

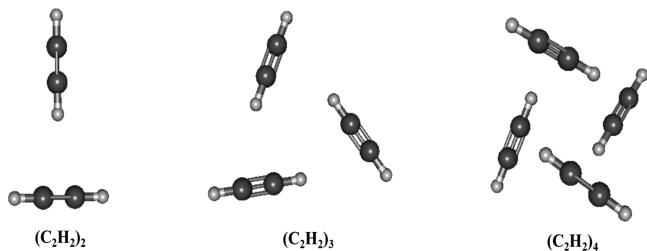


Figure 15. Low-lying isomers for $(\text{C}_2\text{H}_2)_2$, $(\text{C}_2\text{H}_2)_3$, and $(\text{C}_2\text{H}_2)_4$ clusters at the MP2/aug-cc-pVTZ level of theory. Data derived from ref 526.

tetramers, from this extensive study,⁵²¹ were later confirmed at the HF level with the 4-31G basis set.^{523,524}

Another extensive study on tetramers and pentamers was reported at both HF and MP2 levels of theory employing the DZP basis set.⁵²⁵ However, the geometrical parameters (rotational constants) of C_{4h} isomer after the MP2 optimization were in a poor agreement with the experimental findings. This isomer was a transition state, lying at the top of an energy barrier separating two minimum-energy equilibrium configurations of S_4 symmetry. The overall stability of the acetylene aggregates⁵²⁵ was attributed to the number of quadrupole interactions originating from the $\text{CH}\cdots\pi$ contacts. Therefore, the cyclic conformers (cf. Figure 15) for both of the trimer and tetramer turned out to be stable with respect to their acyclic analogues. On the other hand, a noncyclic pentamer geometry with C_{2h} symmetry (five quadrupole interactions) was found to be the global minimum structure instead of the cyclic analogue which was a local minimum structure on the PES.⁵²⁵ Hence, it may be conjectured that the single-ring cyclic structures become less favorable for larger clusters and the stability of these aggregates is affected by the energy and number of the quadrupole interactions.

Kim and co-workers⁵²⁶ reported high-level calculations for $(\text{C}_2\text{H}_2)_n$ clusters for $n = 2\text{--}5$, employing dispersion corrected DFT (M06-2X) and MP2 as well as CCSD(T) methods with Dunning's correlation consistent basis sets. The CCSD(T)/CBS values were calculated assuming that the difference in binding energies between MP2/aug-cc-pVDZ and MP2/CBS calculations was comparable to that of CCSD(T)/aug-cc-pVDZ and CCSD(T)/CBS calculations. These CCSD(T)/CBS findings were found to be similar to those of the experimental counterparts. The structures of the dimers and trimer were found to be identical to those in the earlier investigations. However, the tetrameric isomers with C_{2h} and S_4 symmetry were observed to be the two most stable isomers instead of C_{4h} and S_4 ones.⁵²⁶ Similarly, for pentamers, two low-lying isomers with C_1 and C_s symmetry were seen to be more stable than the previously reported C_{5h} and C_{2h} structures. The most stable C_1 pentamer was found to have eight $\text{CH}\cdots\pi$ interactions and one $\pi\cdots\pi$ interaction. Considering the predominance of dispersion interactions in acetylene clusters, usage of dispersion-corrected functional was recommended.⁵²⁶

Considering both the accuracy and feasibility of calculations, Gadre and co-workers⁵²⁷ recently reported a CC study of acetylene pentamers and hexamers employing the fragment-based MTA. Six pentameric and six hexameric clusters lying within a 3 mH range were treated at MP2 and CCSD(T) levels of theory. Two of the planar pentameric isomers were found to be identical to the earlier reported structures.⁵²⁶ Similarly, the hexameric isomer exhibiting both inter- and intraplanar

interactions was found to be the most stable isomer. In all the cases, the MP2 level was found to overestimate the binding energy even with a large basis set, warranting the use of a better method such as CCSD(T). Looking at the accuracy as well as the feasibility of high-level calculations, the methodology was then extended up to a decameric cluster.⁵²⁸ Molecular cluster building algorithm⁵²⁷ was used for the generation of the initial trial geometries of $(\text{C}_2\text{H}_2)_n$ clusters in the range of $n = 8$ and 10 from the smaller ones. CBS interaction energies at MP2 level were estimated for the low-lying isomers of each cluster. Five structurally diverse isomers each of $(\text{C}_2\text{H}_2)_8$ and $(\text{C}_2\text{H}_2)_{10}$ lying within a narrow range of 1 and 3 kcal/mol were found.⁵²⁸ However, the vibrational patterns of these clusters were found to be very different from each other, suggesting that these could be of practical use for interpretation and assignment of experimental spectra.

Several MD- and classical potential model-based studies have been reported for acetylene aggregates.^{529–533} In one of such earlier studies,⁵²⁹ PES of acetylene clusters ranging from dimers to tetramers was examined through molecular mechanics of clusters method. For acetylene trimers and tetramers, cyclic conformers with zero dipole moments were investigated. Furthermore, the interconversion between the planar and T-shaped dimer pair was found to be in agreement with earlier investigations.^{516,517} A combined study at HF and MP2 levels with cc-pVTZ basis sets and MC-based model potential for acetylene dimers was reported by Shuler and Dykstra.⁵³¹ Three different structures with C_{2v} , C_{2h} , and D_{2d} symmetry were characterized, with the C_{2v} (T-shaped) being the global minimum, in agreement with the earlier investigations.

This interaction potential⁵³¹ was applied to large clusters in the range of 3 to 391 molecules for estimating the lattice energy and structures of acetylene crystals.⁵³² In acetylene clusters, generally T-shaped pairing ($\text{CH}\cdots\pi$) was seen to strengthen the structures through quadrupole–quadrupole interactions. At cluster size of 13, the minimum structure resembled the fragments of a cubic crystal which showed predominant T-shaped pairings as compared to those in the orthorhombic one. However, the energy per pairing (1.36 kcal/mol) in the orthorhombic crystal pattern was more than that in the cubic pattern (1.03 kcal/mol). This small difference suggested that these two polymorphs could exist for acetylene crystal. The potential developed in this study⁵³² was able to yield accurate values of structural parameters of crystal forms (cubic and orthorhombic) which is crucial for getting the lattice energies. Recently, Takeuchi⁵³³ reported geometry optimization of $(\text{C}_2\text{H}_2)_n$ clusters, in the range of $n \leq 55$ using the intermolecular potential of Garrison and Sandler,⁵³⁴ comprising a Morse potential, damped dispersion terms, and damped Coulomb terms. In this extensive study, for the first time, acetylene clusters of size beyond 20 were reported.⁵³³ Similar to CO_2 clusters, 13 happened to be the first magic number and all acetylene clusters beyond 13 were also found to possess a $(\text{C}_2\text{H}_2)_{13}$ core. Further, the clusters in the range of 10–30 were found to show patterns akin to those in cubic crystal.

A few theoretical and experimental investigations have also been reported on benzene–acetylene complexes.^{535–541} However, due to the advancement of the experimental set up and computational hardware, these investigations are expected to grow in the near future. Especially, understanding the formation of cocrystals of benzene–acetylene complexes and their characterization by

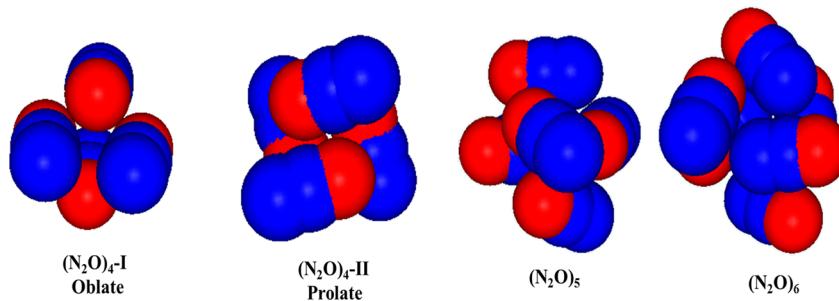


Figure 16. Low-lying isomers for N_2O tetramer, pentamer, and hexamer at the B2PLYPD/aug-cc-pvTZ level of theory. Data derived from ref 109.

spectroscopic tools and assignment of structures by quantum chemical methods will be more indeed useful.^{542,543}

In summary, long-range dispersion interaction is the main contributing factor for the aggregation of monomers in CO_2 , C_6H_6 , C_2H_2 , and similar clusters. Hence, the accurate estimation of the energetics of such clusters requires high-level correlated methods. It is found that the dimeric interactions dominate the overall stability of the molecular assemblies.⁵¹¹ The T- and slanted T-types of dimeric orientations are the most significant patterns found in higher-sized clusters. It is a surprising fact that 13-mer clusters of CO_2 , C_6H_6 , and C_2H_2 are the magic ones that exhibit extra stability at the transition temperature as compared to their 12- and 14-meric counterparts. As noted, the geometries of acetylene clusters containing 10–30 monomers resemble the pattern shown by the cubic crystal structure. It would indeed be valuable to assemble polymorphs from the energetically favorable patterns found in the clusters. The determination of the lattice energy of the polymorphs using an additive system based on the individual interaction energies of dimers is also a significant advance in this area. As noted above, such an investigation by Ringer and Sherrill⁵¹¹ has enabled quite accurate determination of the lattice energy of benzene (to within 1.5 kcal/mol of the experimental value). In another earlier attempt, the structures of CO_2 molecular crystals were also predicted based on the intermolecular interaction energies obtained by CO_2 dimeric interactions. In the years to come, fragmentation-based methods will certainly play a significant role in bridging the gap between the cluster geometries and crystal structure and also provide quantitative data on lattice energy.

4.4. Hydrogen, Nitrous Oxide, Ethylene, etc

Unlike the clusters discussed so far, there are some clusters (e.g., H_2 , N_2O , and C_2H_4 among others) that are not studied extensively, but the investigations on them growing steadily. The theoretical investigations on such clusters are summarized below.

The investigations on $(\text{H}_2)_n$, another weakly bonded molecular cluster have also been a subject of immense interest as it is an ideal carrier for storage, transport and conversion of energy.^{544,545} Several papers have been published for understanding the interaction potential, tunneling phenomena, electron transfer as well as the spectrum of such smallest cluster viz. H_2 dimer, employing both ab initio level and simulation studies.^{546–556} The T-shaped isomer, being interconnected through a saddle point with rhomboid structure, was found to be the most stable isomer of the H_2 dimer.⁵⁵⁴ Later, from a combined model potential and ab initio study, this

T-shaped isomer was also observed to be the minimum for the H_2 dimer.^{555,556}

In an extensive work in 2004, hydrogen clusters up to $(\text{H}_2)_{13}$ were reported using MP2 as well as a model potential.⁵⁵⁷ The T-shaped dimer was the equilibrium structure which passes through a parallel C_{2h} structure during its interconversion, in agreement with the earlier investigations.^{554,555} Similarly, the trimer exhibited a trigonal (C_{3h}) geometry whereas the tetramer was endowed with a square planar geometry with D_{4h} symmetry. The T-shaped pairwise arrangements of adjacent molecules were preserved in higher clusters beyond octamers. Small para-hydrogen clusters were found almost hollow whereas the larger ones were more densely arranged so as to yield maximum density for 14 molecules.⁵⁵⁸ The density was found to decrease in the range of 15–20 molecules indicating a structural transition beyond 14 molecules. Further, from a combined theoretical investigation at LDA-DFT and experimental study,⁵⁵⁹ most of the clusters containing less than 27 hydrogen molecules were found to behave similar to liquid phase. The magic numbers for hydrogen clusters are observed to be 13, 32, and 55, for which enhanced Raman intensity of the signals has been noted.⁵⁶⁰ Large clusters are seen to assemble in layered form retaining the T-shaped dimeric interactions. Recently, MC-study⁵⁶¹ of para-hydrogen clusters in the range of 4–40, reported that clusters in the range of 18–31 contain 3 shells whereas those beyond 32 molecules contain 4 shells of molecules. However, these extra shells disappeared on lowering the temperature below 1.5 K.

Being isoelectronic to CO_2 , nitrous oxide (N_2O) clusters exhibit properties which are similar to those of CO_2 clusters, although the N_2O molecule possesses a dipole moment of value 0.166 D whereas CO_2 molecule has no dipole moment. The N_2O moiety acts a precursor for the production of various nitrogen oxides, which are vital in the formation of stratospheric ozone.^{562–564} N_2O is one of the greenhouse gases in the terrestrial region of the troposphere and plays a key role in global warming.

The N_2O dimer has been extensively studied by experimental as well as theoretical techniques.^{77,565–577} In 1990, Sadlej and Siciński⁵⁶⁵ reported the slipped parallel geometry with two N...O antiparallel interactions as the most stable isomer, later confirmed in a combined study by means of matrix isolation IR spectroscopy along with molecular beam technique and DFT-based calculations.⁵⁶⁷ The nonpolar N...O antiparallel isomer was found to be the most stable isomer in agreement with experimental findings^{77,568–573} as well as with the theoretical investigations at MP2 and CCSD(T) levels of theory.^{574–576} The investigations beyond trimers of N_2O are indeed very rare in the literature. The cyclic isomer with three N...O interactions was found to be the most stable, with the linear isomer being

the least stable at the DFT level,⁵⁶⁷ in good agreement with experiments.⁵⁷⁸ Further experimental findings^{579,580} were also in agreement with these observations wherein the trimer formed from a nonpolar dimer with a N₂O sitting on the top was observed to be the most stable isomer.

In case of tetramer, a nonpolar structure having the monomers parallelly aligned was revealed in combined IR spectroscopy and theoretical study wherein the geometrical parameters indicated that the isomer was nearly a spherical top.⁵⁸¹ However, in a recent experimental study,^{63,582} two symmetric and closely spaced isomers were observed for tetramers in contrast to the report by Miller and Pedersen.⁵⁸¹ Similarly, for pentamers, two distinct isomers were observed with same basic structure, showing a difference in one or two of the constituent monomer orientations. In a very recent study,¹⁰⁹ the present authors investigated (N₂O)_n clusters with $n = 4\text{--}6$ at MP2 and CCSD(T) levels with Dunning's correlated consistent basis sets (cf. Figure 16). A comparative study was also carried out using Grimme's dispersion corrected B2PLYPD functional. The rank ordering of structures and the values of rotational constants obtained at MP2 level showed poor agreement with the experimental observations.^{63,582} However, the B2PLYPD results were found to match quite well the experimental ones. This work¹⁰⁹ demonstrated the suitability of the dispersion-corrected functionals for studying large clusters, in combination with a powerful fragmentation-based method.

Due to the small size and simple structure of ethylene, the nonbonding interactions of ethylene dimers have for long been a subject of interest for the ab initio investigations. In 1988, Alberts et al.⁵¹⁵ reported two possible dimer geometries viz. T- and staggered-shaped (parallel-displaced), at MP2 level of theory wherein the earlier one was found to be the minimum on the PES. However, the crossed dimer with D_{2d} symmetry derived from the pairwise additive potential was found to be more stable by 0.72 kcal/mol than the T-shaped one,⁵⁸³ in conformity with the MP2 level calculation due to Tsuzuki and Tanabe^{584,585} and the experimental spectroscopic studies.^{586,587} Due to the presence of dispersion interactions in the ethylene aggregates, the MP2 level calculations were further extended to higher levels of theory.^{588\text{--}590} The MP4(SDTQ) electron correlation energy for the dimers was found very close to that of the CCSD(T) ones. In a recent study,⁵⁹¹ the binding energy of the ethylene dimers was reported at the CCSD(T)/CBS level of theory. The internal geometries of the individual ethylene molecules were found to change upon the dimerization due to the cooperatively and long-range interactions. Similar to the acetylene clusters, the CH \cdots π quadrupole moments were seen to stabilize the binding of the ethylene molecules. Therefore, the trimers and tetramers are ring-shaped ones containing deformed T-shaped CH \cdots π contacts.⁵⁸³ In an extensive work, Takeuchi⁵⁹² reported the geometry optimization and putative minima search for (C₂H₄)_n clusters ($n \leq 25$), employing a dimer-based intermolecular potential. Unlike acetylene aggregates, the 13-membered ethylene cluster does not possess an icosahedral motif, and the structure of this cluster is complicated as compared to that of acetylene clusters.

Aggregates of carbonyl sulfide (OCS) provide another example of experimentally explored clusters,⁵⁹³ on which there are very few theoretical investigations, those too being limited up to pentamers.^{577,594\text{--}599} Assemblies of CS₂ offer another example of weakly bonded molecular clusters. Like

OCS clusters, the number of studies on CS₂ clusters is also scanty^{577,600\text{--}602} and hence are not discussed here. Similarly, a few investigations on naphthalene aggregates are available in the literature.^{603\text{--}607}

5. EXPLICIT HYDRATION: HETEROCLUSTERS OF WATER

Heteroclusters of water with other substrates represent the phenomenon of hydration at the molecular level. Microhydration studies may offer valuable insights on properties of the solute molecules such as solubility, hydrophobicity, etc.⁶⁰⁸ Enhanced computational power has rendered possible quantum chemical studies for the hydration of a range of substrates at ab initio level. Some representative works on the heteroclusters of water are reviewed below.

Hydrophobic interactions, e.g., those between the nonpolar hydrocarbon moieties of alcohols or those of acetylene and benzene with water, are a topic of active interest due to their importance in biology.^{609\text{--}612} Mainly, an aqueous solution of methanol has been a subject of active investigations due to its industrial as well as biological applications. Both methanol and water molecules can act as a HB donor as well as a HB acceptor resulting in two different HBs with different structural patterns and binding energies. In particular, due to its amphiphilic character (presence of both hydrophilic and hydrophobic end), the methanol molecule is a good candidate for study at the molecular level. Understanding the solvation of methanol in water is a prerequisite for the study of chemistry of alcohols in aqueous solution. Several theoretical^{392,398,613\text{--}629} as well as experimental^{630\text{--}634} studies have been reported in the literature for understanding the energetics and structural properties of the water-methanol systems.

In an earlier study,⁶¹⁵ MP2 and B3LYP level calculations were carried out for studying the nature of the PES of water-methanol dimer and methanol(water)₂ trimer. The methanol-water heterodimer containing a water as an HB donor was found to be the most stable isomer, in agreement with the experimental evidence.⁶³³ Similarly, the global minimum for the trimers corresponded to a structure with the methyl group on one side of the O-O-O plane and the two free OH groups of the water molecules on the other side. Further, from the DFT calculations⁶¹⁷ and Raman spectroscopy study,⁶³⁴ it was observed that a dimer where the methanol molecule acts as an HB acceptor was the favorable one. However, in a further study at the MP2 level,⁶¹⁶ it was noticed that the dimer associated with a water molecule as HB acceptor was observed to be more favorable than the isomer with water as HB donor. Due to the extensive HBs, blue shifts were observed for the C=O stretch, whereas red shifts were noticed for the O-H stretch.⁶²⁰

In a recent work, the investigations have been further extended to tetrameric clusters of methanol and water.⁶²² Clusters possessing the largest number of primary HBs in a cyclic pattern are energetically more favorable than other isomers, wherein CH \cdots O interactions are much weaker than those from the OH \cdots O HBs. Recently, Subramanian and co-workers⁶²⁴ performed extensive ab initio calculations for understanding the molecular features of both homo- and heterosystems of water-methanol clusters containing 4 molecules. The methanol-methanol and water-methanol clusters were found to be energetically more stable than the corresponding water ones. This was attributed to the electron-donating property of the methyl groups making the HBs in the

methanol–water frameworks more stable than the water–water HBs. This cooperative polarization and charge transfer in the methanol and mixed clusters is seen to increase with increasing size of the clusters.

Due to the tendency to form both inter- and intramolecular HBs, the structure and stability of the alkanediols and alkanediols–water systems have been studied during the last few decades.^{635–638} At the MP2 level of theory,⁶³⁹ both 1,*n*-diols and 2,4-pentanediols possess more negative MESP minima (3,+3) than those for vicinal diols. Besides this, with an increase in the separation between the two –OH, the minima become deeper, indicating that the 1,*n*-diols and 2,4-pentanediols are more basic than vicinal diols. However, the water···water interactions are found to be more favorable in vicinal diols than those in 1,*n*-diol complexes, due to the extensive HB networks in water clusters with two consecutive –OH groups.⁶³⁹ Thus, vicinal diols, being more effective at strengthening water···water network, are expected to act as water structuring agents, whereas the nonvicinal diols are expected to be water destructure agents. The presence of the ethylene group favors the glycol molecules to act as HB acceptors rather than donors.⁶⁴⁰ The stepwise addition of water molecules to the glycol moiety is responsible for the disruption of the HB interaction between ethylene glycol molecules. For instance, the addition of two water molecule breaks a HB between two glycol molecules, indicating the dominance of the ethylene glycol–water interactions over the ethylene glycol–ethylene glycol and water–water ones.⁶⁴⁰

Benzene–(H₂O)_{*n*} clusters have also been extensively studied employing spectroscopic techniques^{641–649} and theoretical calculations.^{195,650–661} A water molecule is bound to benzene wherein the hydrogen atom of water interacts with the π-electron cloud of the latter.⁶⁵² The presence of the benzene molecule was found to weaken the HBs in water clusters, in comparison with those in free water clusters. In the case of the 1:1 complex, the water is positioned over the aromatic ring with the oxygen atom pointing away from the center of mass of benzene with one of the hydrogen atoms oriented toward the ring,⁶⁵³ in agreement with the experimental findings.⁶⁴² This work was extended up to six water molecules using a similar level of theory.⁶⁵⁵ In all of the cluster systems, the water framework was found to be on one side of the benzene plane. The HB networks in water clusters remained unaltered upon the aggregation although there was a lengthening of the C–C bond lengths of the benzene ring.⁶⁵⁵

In a recent work, the geometries, vibrational frequencies, and dissociation energies of both (H₂O)_{*n*} and C₆H₆(H₂O)_{*n*} (*n* = 1–7) clusters were reported at DFT and MP2 levels of theory.⁶⁵⁷ As noticed earlier, the presence of the benzene ring does not affect the HB networks of the water clusters, although the latter becomes weak in the presence of benzene. For all the clusters within this range, one water molecule is found to be situated over the benzene ring as discussed above. On the other hand, the other portion of the water frameworks is oriented around the edges of the benzene rings with extended HBs due to the water oxygen and benzene hydrogen.⁶⁵⁷ Clusters of benzene with two- and six-water molecules are found to have extra stability over others. Further, the structures and binding energies of water–benzene complexes (1–8 water molecules and 1–2 benzene molecules) have been studied employing the effective fragment potential method.⁶⁵⁸ The structures with different numbers of water–water, benzene–water, and benzene–benzene bonds are found to have very similar binding

energies. For clusters containing more than one benzene moiety, the benzene clusters separate from each other and interact mainly with water molecules residing in between the benzene molecules. This indicates the OH···π interaction is more favorable than π···π ones in water–benzene clusters.⁶⁵⁸

In another work,⁶⁵⁹ investigations on benzene–(water)_{*n*} clusters were extended up to *n* = 10, employing the M05-2X density functional. In the case of the benzene–(H₂O)₆ cluster, the isomer containing cage-like HB network of the water clusters is found to be the global minimum rather than the isomer having prism-shaped water hexamer. The O–H group participating in the HB formation with the benzene molecule shows a red shift in the range of 13 to 95 cm^{−1}. In a very recent study, the crystal structure of the benzene–water complex revealing stacked benzene molecules with water molecules sandwiched between them, the system was modeled by CCSD(T) level calculation.⁶⁶¹ Either the water molecule or one of the O–H bonds is found to align parallel to the aromatic ring plane although these parallel interactions are somewhat weaker than OH···π bonds. In crystals, both O and H atoms of the water molecule can form classical HBs simultaneously with the benzene monomers, in a manner very similar to the slipped parallel benzene dimer.⁶⁶²

Very similar to benzene–water complexes, the CH···O and OH···π interactions between water and acetylene aggregates have been widely investigated employing experimental^{663–665} as well as theoretical^{666–673} tools. In an earlier investigation,⁶⁶⁹ putative minima for the water–acetylene dimer complex were searched employing MP2, MP4, and CCSD(T) levels of theory. The HB network in these complexes may be formed by two different ways. In the first one, the water molecule acts as the proton acceptor whereas in the other case, the water molecules act as the proton donor and binds with the π-electron cloud of the acetylene molecule. The isomer formed due to the former configuration was found to be the global minimum structure for the water–acetylene dimer complex. This study was further extended to the water–acetylene complex containing up to four water molecules.⁶⁷⁰ It was found that the acetylene molecule somewhat affects the HB networks in aggregates containing three water molecules. However, the tetrameric water pattern remains intact in the presence of acetylene molecule. In a very recent work,⁶⁷³ the structures, energetics, and nature of hydrocarbon/water interactions were examined employing MP2 and CCSD(T) levels of theory as well as B3LYP, B97-D, ωB97X-D, and M06-2X functionals. Among these functionals, B97-D, ωB97X-D, and M06-2X were found to produce binding energies to within 0.10 kcal/mol from their CCSD(T)/CBS counterparts. On the other hand, although B3LYP provides better optimized geometries compared to the MP2 level, it was unable to produce reliable binding energies.

Besides these, several microhydration studies on a variety of biomolecules such as amino acids, nitrogen bases in DNA and RNA as well as different ionic species have been reported in the literature. Such investigations shed light on understanding the assembly of the tertiary and quaternary structures of proteins, stability of the DNA as well as in charge transfer phenomena due to the microhydrated anions within the living bodies. In view of this, the investigations on the microhydration of amino acids, carbohydrates, nitrogen bases of nucleic acids as well as some anions e.g. HCO₃[−], NO₃[−], (SO₄)^{2−}, (CO₃)^{2−}, and halide anions are briefly summarized below.

Many studies explaining the effect of solvation on the relative stability of the neutral amino acids and their zwitterions have

been reported in the literature.^{674–696} In earlier studies, Jensen and Gordon⁶⁷⁵ and Xu et al.⁶⁷⁶ found that the 1:1 zwitterion:water complex possesses higher energy with respect to the neutral glycine–water complex.^{677,678} This is due to the role of water molecule as both HB donor and acceptor, preventing the transfer of proton from the carboxylic group to the amino group.⁶⁷⁷ The stability of the zwitterion structure was found to increase with the number of water molecules due to the stronger HBs with the charged moieties.⁶⁷⁹ Thus, the tendency for the intermolecular proton transfer is enhanced in the presence of water molecules, thereby confirming the enhancement in the acidic character of the OH group of the carboxylic moiety in aqueous media.⁶⁸⁰ Therefore, the water molecule binds more strongly to the carboxylic acid group of glycine than to the amine group in gas phase whereas it is the reverse in solution phase.⁶⁸¹ The interconversion of the neutral and zwitterionic glycine occurs in the 1:3 glycine–water complex.⁶⁸² It was observed that, up to six solvent water molecules, neutral glycine is more favorable than the zwitterion^{685,686} and on further addition of water, the zwitterion complex becomes progressively more stable.⁶⁸⁶

Similar observations were also made for the microsolvation of neutral and zwitterionic form of alanine.^{690,691} In 2008, Chuchev and BelBruno⁶⁹¹ performed B3LYP and MP2 level calculations for investigating the structures and energetics of neutral alanine–(H₂O)_n and zwitterionic alanine–(H₂O)_n ($n = 2–10$) clusters. The process of intramolecular proton transfer from neutral alanine to a zwitterionic one was feasible by increasing the number of water molecules, making the hydrated zwitterionic complex as the thermodynamically stable conformer. With six or seven water molecules, both of the hydrated complexes became isoenergetic.⁶⁹¹ Beyond eight water molecules, i.e., after the completion of the first solvation shell, the zwitterionic complex was found to be more stable than its neutral counterpart, indicating the dominance of the former in bulk solution.⁶⁹¹ Further, the proton transfer pathway in phenylalanine was investigated through a CPMD study by Rodziewicz and Doltsinis.⁶⁹³ In the gaseous phase, the neutral form was found to dominate over the zwitterion, whereas with an increase in the degree of solvation, the stability of the zwitterionic form was seen to increase, and the proton transfer barriers were found to decrease. The zwitterion was found to be more stable than the neutral structure with three water molecules.⁶⁹³ Similarly, for phenylisoserine, one neutral and one zwitterionic conformer were found to be in equilibrium in water.⁶⁹⁴ One and two water molecules were necessary to stabilize the cationized arginine and protonated tryptophan, respectively.^{695,696} Thus, in general, the addition of the extra water molecules favors the stability of the zwitterion.

Carbohydrates, the prominent energy sources in living bodies, are found to be sensitive to the neighboring ions or molecules and particularly to the aqueous environment around them.^{697,698} During the past decade, numerous investigations have appeared in the literature for understanding the HB cooperativity^{699,700} and the effect of water addition on the conformational changes in sugar molecules.^{701–714} A combined study by means of resonant two photon ionization (R2PI) dissociation spectra and DFT had shown that α -phenylxylose favors the insertion of water molecule between OH4 and OH3 groups or between OH3 and OH2 groups whereas β -phenylxylose favors for the OH2 and OH3 position.⁷⁰¹ The detailed pattern of the numbering of the atoms in both α - and β -xylose (pyranose form) sugar moiety is shown in Figure 17.

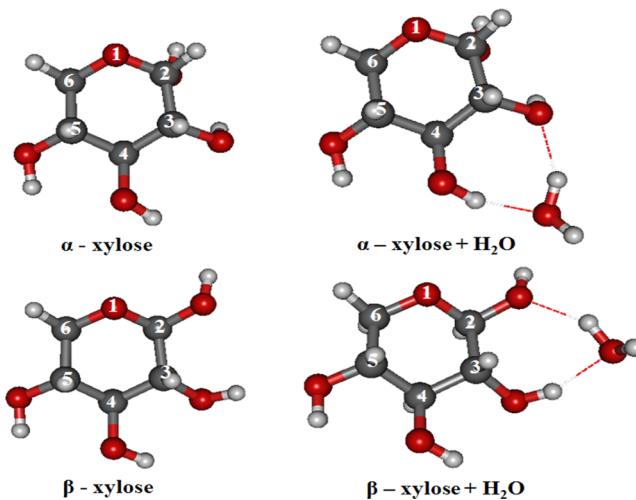


Figure 17. Illustration of the nomenclature and numbering of atoms in the pyranose structure of α - and β -xylose and in their monohydrates. Data derived from ref 701.

However, for the formation of phenyl substituted xylose derivatives, only the hydrogen of the OH2 group (OH attached to second atom of the ring; cf. Figure 17) is replaced by the phenyl group without changing the positions of other atoms. For all sugars and for both α - and β -anomers, the water molecule preferably inserts into the weakest link of the HB network. Particularly, the hydroxyl groups around the pyranose ring are seen to form extended HB networks with the water molecules.⁷⁰¹ The conformational preference of the singly hydrated complexes of gas phase glucose and galactose was found to be sustained in aqueous solution. This indicates that explicit hydration is able to reveal the influence on the selectivity of the conformational preferences in solution.⁷⁰²

Similar type of selectivity was noticed for glucose, mannose, and galactose, wherein the water molecule adds to the carbohydrate through two stronger HBs at the cost of a weak HB in the isolated sugar molecules.⁷⁰⁰ The regioselectivity and conformational changes in singly- and multiply hydrated sugar molecules are driven by the cooperativity effect of the HB networks in the hydrated sugars.⁷⁰⁷ As expected, the first water molecule prefers the (4,6) site and the second one occupies the (5,6) position (cf. Figure 17 for atom numbering). In general, for dihydrated monosaccharide complexes, the extended sequence of the water interactions to the sugar moiety is OH2 → OH3 → OH4 → W1 → OH6 → W2 → O5 whereas for trihydrated complex, it is OH2 → OH3 → OH4 → W1 → OH6 → W2 → W3 → OH2.^{707,708}

In a recent study based on infrared-ultraviolet double resonance ion-dip (IRID) spectroscopy and DFT calculation, Simons and co-workers⁷⁰⁹ investigated glucose, galactose, fucose, and xylose hydrated by one or two water molecules. For doubly hydrated complexes, α -glucose adds a dimeric water at (4,6) position whereas α -mannose adds two separate water molecules in between (4,6) and (3,6) positions in an axial manner. To the contrary, β -anomers add two separate molecules within (4,6) and (6,3) or (6,1) positions. It may be noted that though in isolated sugar molecules α -anomer is more stable than the β -one, this order may be reversed in solution phase. For example, in the solution phase, the population of α : β changes to ~1:2 from ~2:1 in bare sugar

environments whereas in the case of mannose, it remains $\sim 2:1$ in both the environments.⁷¹⁵ This observation is in agreement with the earlier investigation at B3LYP/6-311++G** level of theory.⁷¹⁶ The α/β anomeric ratio was found to increase monotonically with the number of water molecules. For monohydrated analogues, after applying the zero point energy correction, this ratio was observed to be 32/68%, in good agreement with the experimental value of 36/64% value, suggesting the extra stability of the β -isomer in aqueous media. In summary, for both α - and β -anomers, the water molecule preferably inserts into the weakest link of the H-bonded chain in order to create a stronger HB network.

Besides the HB and stacking interactions, the hydration phenomenon is found to play a vital role in the secondary and tertiary structure of nucleic acids.^{467,717–719} This calls for understanding the effects of hydration on the energetics and stability of the nitrogen bases and hence the nucleic acid.^{720–723} The presence of solvent is found to destabilize the cytosine–cytosine base stacking interactions, indicating the hydrophilic nature of the stacked dimer pair toward water.⁷²⁴ In an earlier study at HF and MP2 levels,⁷²⁵ the stacked cytosine base pair was found to hydrate better than that of the H-bonded base pair. The interaction energies and the relative stability were found to increase with number of water molecules. Since, the electrostatic interaction rather than correlation contribution is the main contributing factor for the overall stability of the base pairs, the ordering of the relative stability of the isomers is retained at HF and MP2 levels of theory.⁷²⁵

The work of Sivanesan et al.⁷²⁵ was further extended to microhydration of guanine–cytosine and 9-methylguanine-1-methylcytosine base pairs.^{726–728} For monohydrated guanine–cytosine base pairs (GC-1W), no stacked configuration was detected whereas 20 planar H-bonded structures were observed. Similarly, for the dihydrated complexes, the planar H-bonded isomers were found to be lower in energy than the stacked ones. Water seems to affect the tautomeric equilibrium of nucleic acid bases^{726,727} and the replacement of hydrogen atoms by the methyl groups at N9 of guanine and N1 of cytosine does not result in any dramatic changes in system stability and arrangement of the bases. For monohydrated 9-methylguanine–1-methylcytosine base pair also the planar H-bonded base pair happens to be the most stable isomer. In the case of dihydrated 9-methylguanine–1-methylcytosine base pair, the population of planar H-bonded structures was reduced to 36.5% from 68.3% for GC-1W whereas the populations for nonplanar H-bonded and T-structures increased from 10.7% to 17.7% and from 17.8% to 30.7%, respectively.⁷²⁶ However, the planar structure was still found to be the most populated one over the other isomers. Since the populations are in general proportional to the free-energy change, the planar H-bonded isomer was considered as the global minimum on both PES and free energy surface (FES). Such planar configurations are indeed present in the DNA and RNA frameworks. During further hydration, eight water molecules formed the first hydration shell around the planar guanine–cytosine base pair.⁷²⁹

Similar observations were made from the IR-UV double resonance spectroscopy experiment and MP2 and CCSD(T) level theoretical calculations.⁷³⁰ Though the stacked structure was stabilized by the addition of water, the planar structures of both methylated guanine–guanine and guanine–cytosine base pairs were found to be unaffected by the hydration process. For dihydrated complexes, the stacked isomer was found to be more stable by 0.5 kcal/mol than the H-bonded planar

structure. Thus, it can be concluded that the hydration does not lead to any noticeable change on the conformations of the conjugate base pairs in DNA or RNA, which is responsible for the stability of the secondary structures of these nucleic acids.

Studying the systematic growth of the water HB networks during microhydration is an arduous task. In an earlier study, Gadre and co-workers⁷³¹ reported a MESP-guided topographical study of the addition of water molecules around uracil moiety followed by geometry optimization at HF/6-31G** level employing EPIC model.^{444–446} The HB networks around the uracil molecule were found to exhibit square and cubic patterns of water molecules with maximum number of eight water molecules in the first hydration shell.⁷³¹ Bachrach and Dzierlenga,⁷³² recently extended this study at DFT (B3LYP and PBE1PBE) level for exploring the role of hydration on the acidity of the conjugate bases of uracil. In gas phase, the deprotonation energy difference between the two conjugate bases N1 and N3 (as shown in Figure 18) was found to be 13

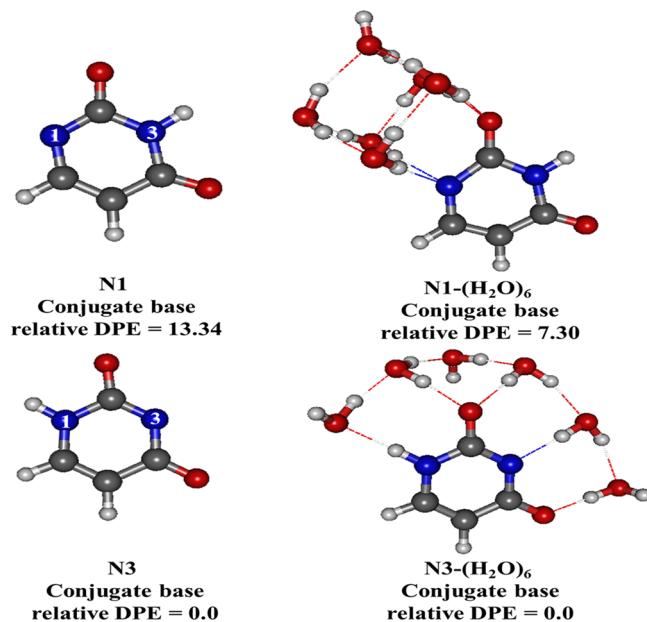


Figure 18. Relative deprotonation energies (DPE) in kcal/mol of N1 and N3 conjugate bases of uracil in gas phase as well as in six water molecules. Data derived from ref 732.

kcal/mol.⁷³³ This value was found to decrease with the addition of water molecules, resulting in the relative deprotonation energy difference of about 7 kcal/mol for six water molecules and further reduced to zero in solution. This indicates that the added water molecule stabilizes both N1 and N3 conjugate bases, and further, the bases attain equal stability in bulk.⁷³⁴ Thus, it can be concluded that extensive H-bonding in water clusters enhances the stability of the zwitterions as well as the conjugate bases of the amino acids in solution than that in the isolated gaseous phases.

Understanding the reactivity of the ions as well as the influence of HB networks of the water clusters on the ions in aqueous phase is a topic of great interest.^{735–738} The nitrate, bicarbonate, sulfate, and suberate anions are four prototypical conjugate base anions that are ubiquitous species in aqueous phase chemistry. For example, nitrate (NO_3^-) is one of the most abundant ionic species in the troposphere, formed from the dissolution of nitric acid in aerosol particles.⁷³⁵ Bicarbonate

(HCO_3^-) ion plays a vital role in acid–base equilibrium and CO_2 transportation processes,⁷³⁶ sulfate (SO_4^{2-}) anion is one of the vital species for the control of many metabolic and cellular processes as well as the homogeneous nucleation of ice particles on the upper troposphere⁷³⁷ and suberate dianion (${}^-\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2^-$) acts as the building block for metal organic framework materials.⁷³⁸ On account of these extensive applications, the hydration of the above anions is important in chemical and biological problems.^{739–747}

For microhydration of the nitrate (NO_3^-) anion, the oxo groups are found to be the binding sites for the bridging of water clusters. For the monohydrated complex, the water molecule forming two HBs with C_s symmetry was found to be the global minimum at the B3LYP/6-31+G* level computation as well as from infrared photodissociation spectra,⁷³⁹ whereas the other two isomers with C_{2v} and C_s symmetry had a similar stability at the B3LYP/6-31++G** level of theory.⁷⁴¹ For the dihydrated complex, the C_{2v} structure was the most stable one. For three water molecules, the anion was found to be symmetrically hydrated and showing no splitting in the N–O stretching frequency region.^{739,740} For $n = 4$ or more, extensive water–water H-bonding was observed around the anionic moiety. Up to $n = 6$, the water molecules were found to be in direct contact with the anion indicating the formation of a first hydration shell.

A similar trend was observed for the microhydration of the bicarbonate (HCO_3^-) ion at the MP2/6-311+G** level of theory as well as from IR multiple photon dissociation spectra^{740,745} where the negatively charged CO_2 moiety was more favorable for water binding than the other two sites. For most of the large stable complexes containing more than four water monomers, the tetramer unit was retained and stabilized through extensive intermolecular HBs. The migration of the water molecules to the second solvation shell was observed for $n = 6$, and hence, 5 was regarded as the solvation number for the bicarbonate anion. At similar level of theoretical calculations and using the same experimental set up, the solvation numbers for sulfate^{740,746,748} and suberate dianion (${}^-\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2^-$) turned out to be 12 and 14 respectively.⁷⁴⁰ In a recent study,⁷⁴⁷ water rings beyond $n \geq 3$, were also observed as a stable solvation shell motif for HSO_4^- anion. Thus, though the H_2O molecules form HBs with the charged moieties, still the intermolecular HBs within the water networks are found to contribute largely toward the overall stability of the systems. This indicates that the extra stability of the complexes is driven by the extensive HB networks between the water clusters rather than the water–anion interactions.

Besides these, microhydration of halide anions and halide dimer anion radicals has been an important subject of interest in both solution chemistry and biochemistry⁷⁴⁹ and has been extensively investigated during last few decades.^{750–764} Among the halide anions, Cl^- , Br^- , and I^- –water complexes exhibit somewhat similar structural behavior but, different from the F^- –water systems.^{750–754} For example, Cl^- , Br^- , and I^- –water systems show surface structures against the semisurface or semi-internal structures of F^- –water. The strength of the anion–water interaction goes on decreasing from F^- to I^- anion. The water–water interaction is found to be stronger than the iodide–water interaction whereas the F^- –water interaction is much stronger than that of water–water HBs. The bromide–water interaction is comparable to the water–water interaction.^{750–754} However, with an increasing number of water molecules, the water–water interactions are found to

be more important than the halide–water interactions, resulting in the surface structures for Cl^- , Br^- , and I^- and semisurface structure for F^- . For the halide dimer anion radicals, a maximum of four H_2O monomers reside in the interwater HB network.^{758–764} It is observed that a maximum of six H_2O units are independently linked to the anion having four double HBs and two single HBs suggesting the hydration number for these anionic radicals is six.^{758–764}

Similar to anion hydration works, many investigations exist in the literature on hydration of cations. In a very recent work, Miliordos and Xantheas⁷⁶⁵ investigated the stabilization shift of the $\text{M}^{+k}(\text{H}_2\text{O})_n$ gas phase metal complexes for $\text{M} = \text{Mg}, \text{Ca}$, and Al . A systematic theoretical analysis of the various electronic states arising from the sequential hydration of the Ca^{2+} , Mg^{2+} and Al^{3+} cations with up to $n = 6$ molecules is presented. In another experimental and theoretical investigation by Carl and Armentrout,⁷⁶⁶ $\text{Mg}^{2+}(\text{H}_2\text{O})_n$, $n = 2–10$ were studied. In this work,⁷⁶⁶ they studied the threshold collision induced dissociation of the metal cations–water complexes. The results obtained were found to be in agreement with their experimental counterparts. They have extended this work to study the dissociation in Ca and Fe metals also.^{767,768} The theoretical investigations on the detachment of water molecule from the aqueous clusters of the alkaline earth dications $[\text{M}(\text{H}_2\text{O})_n]^{2+}$, $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$, and Ba , for $n \leq 6$, was reported by Miliordos and Xantheas.⁷⁶⁹ They further investigated the water and hydronium loss channels from the monohydroxide water clusters with up to four water molecules.⁷⁶⁹ Minimum energy paths corresponding to the various channels were constructed at the MP2 level. Small clusters dissociate to fragments involving the hydronium cation and formation of the Zundel cation for the heavier metals with three water molecules. In another work, Babiaczyk and co-workers⁷⁷⁰ investigated the hydration structure of the quaternary ammonium cations by MD simulations, exploring the characterization of the relative hydrophobicity of ammonium cation via the geometrical analysis of the orientation of neighboring solvent water molecules. The relative hydrophobicity scale for the ammonium cations was determined based on two conditional indicators viz. water dipole's vector and the HB vector orientations.⁷⁷⁰

Most of the hydration studies on cations are mainly comprised of metal cations, and molecular cationic hydration studies are consistently lacking in the literature. Also it is worthwhile to mention here that almost all (except few) of the cation hydrations are carried out on the clusters containing up to six water molecules. A larger number of water molecules are expected to reveal the structure of the second and higher hydration shells. Authors would like to point out here that there are many more investigations on the microhydration of both cationic and anionic species in the literature. However, looking at the broadness of the topic and limitation of space, the above discussion concerns only some of the recent investigations.

Yet another case study of explicit hydration is that of clathrate hydrates. These are the crystalline compounds in which guest molecules, such as methane, carbon dioxide, ethane, and hydrogen, are trapped inside the H-bonded three-dimensional networks consisting of polyhedral cages of water molecules.^{771,772} Especially, the methane hydrate has gained importance due to its abundance as well as the potential to serve as a future energy source.^{773–775} Methane hydrates are formed due to the migration of methane from a depth followed by crystallization due to the contact of the gas with cold water.

The possibility of a large scale hydrate destabilization and the release of methane to the atmosphere can cause an increase in the temperature of the earth. It has been stipulated that the release of only 10% of the methane hydrates can cause an impact equivalent to 10 times the actual amount of CO₂ in the earth's atmosphere.^{776,777} Thus, in addition to being the potential energy resources, methane hydrates are stipulated to play a vital role in climate change.⁷⁷⁸ Hence, the gas hydrates, especially, methane hydrates, have been a subject of intense experimental and theoretical investigations.^{779–792} We present below a brief summary of recent quantum chemical investigations of the gas hydrates.

Khan⁷⁷⁹ investigated the stability of (H₂O)₂₈ cluster enclosing the guest molecules such as Ne, N₂, CH₄, and C₂H₆ at HF level. For N₂ and CH₄ molecules, the cluster with single occupancy of the guest molecule was found to be more stable than that with the double occupancy,⁷⁷⁹ with the stability of the complex being maximum for CH₄ (singly occupancy). The stability of the complex was reduced with increasing size of the guest molecule, e.g., (C₂H₆), and was enhanced for Ne as compared to CH₄. Another interesting observation was the substantial off-center location of the guest molecule inside the cage, which holds good even with higher level calculations. In another work, Lebsir et al.⁷⁸⁰ studied the structures and properties of various molecules such as methane, ethane, carbon dioxide, and nitrogen in the cavity of the dodecahedral water cluster. It was found that the embedding guest molecules inside the cage provides better stabilization of the irregular (H₂O)₂₀ dodecahedron cages, wherein the host–guest interaction was found to be weaker for nonpolar guest molecules than of the polar molecules. MP2 level calculations on methane hydrates showed that the introduction of methane in cage does not alter main properties of the cage significantly.⁷⁸¹ The electron density of the HBs formed due to the methane–water interactions is found to be about ten times lower than those formed in water–water interactions, indicating that the guest molecules have very small influence on the water HB networks. Similar observations are made from the MP2/CBS level calculations,⁷⁸³ on (H₂O)₂₀ clusters in the presence of monatomic (He, Ne, Ar, Kr, and Xe), diatomic (CO, H₂, N₂, O₂, and NO), triatomic (CO₂, NO₂, and O₃), and polyatomic (CH₄ and NH₃) guest molecules.

In 2012, Tang et al.⁷⁸⁴ reported the stability of methane hydrates with (H₂O)_n cages, for *n* in the range of 16–24, in both gas and aqueous phase employing dispersion corrected density functional. Among these hollow cages, the CH₄(H₂O)₂₀ cage was found to have the highest stability. In vacuum, the hollow cages of (H₂O)_n for *n* = 16–24 were found to be less stable than the corresponding pure (H₂O)_n clusters. However, the former was stabilized in the presence of the methane guest molecule, in agreement with the earlier observation.⁷⁸⁰ To the contrary, both of the hollow (H₂O)_n cages as well as the endohedral CH₄(H₂O)_n clusters, except at *n* = 24 were favorable in aqueous media. With increasing cavity size, C–H symmetric stretching frequencies of the encapsulated methane molecule showed a red-shift and the ¹³C NMR chemical shifts moved toward negative values.⁷⁸⁴ This comprehensive spectroscopic study is expected to help in understanding and identification of the methane gas hydrates.

Recently, Ramya and Venkatnathan⁷⁸⁵ have reported the interaction energies and reactivity indices for the methane encapsulated in (H₂O)₂₀ and (H₂O)₂₄ water cages. The calculations employing M05-2X and B97D density functionals

show the encapsulation of methane in (H₂O)₂₀ dodecahedral cage to be more favorable than in the (H₂O)₂₄ cage. The characterization of vibrational Raman modes in the cages of pure and THF doped hydrogen clathrate hydrates are discussed. The calculated symmetric stretch of the H₂ molecule in THF doped hydrate showed a blue shift as compared to pure hydrogen clathrate.⁷⁸⁶ All the vibrational modes of water molecules show red shift, suggesting the reduction of interaction between the H₂ molecule and water molecules in THF doped clathrate. These studies^{785,786} have provided the theoretical spectroscopic data and thermodynamic parameters for the spontaneous formation of methane and hydrogen hydrates, which could be very useful for further experimental studies.

Investigations on methane hydrates within DFT framework are reported by Bravo-Peréz and Saint-Martin,⁷⁸⁷ for exploring the structures and energetics of CH₄(H₂O)_n complexes, for *n* up to 20 employing ω B97X-D functional. The calculations show that for the dodecahedral cavity confinement of methane resulted in a significant stabilization relative to a (H₂O)₂₀ cluster interacting with an external methane molecule. The inclusion of dispersion interactions led to a free rotor behavior (levitation effect) of methane in the cage, in agreement with the experiments.^{793,794} Very recently, Song and Wang⁷⁸⁸ have predicted the energetic rank ordering for the CH₄(H₂O)₂₀ clusters using the DFT supplemental potential approach. For small-sized cluster containing up to five molecules, this approach is validated by calculating binding energies of the clusters at various other density functionals such as BLYP, X3LYP, M06-L, BLYP-D3, and BLYP-SP and also by QCISD level calculations. It is found that the structure containing methane on edge-sharing pentagonal prisms is the lowest energy configuration, with the methane centered hydrate structure being less stable by 6.2 kcal/mol. Since the supplemental approach provides a post-Hartree–Fock quality potential energy surface at the cost of DFT and predicts somewhat better energetics than DFT-D methods, this method can be used for the reliable description of noncovalent interactions and for benchmarking the binding energies obtained from high-level quantum chemical methods. Chen and co-workers⁷⁸⁹ have tested out many density functionals for studying small methane hydrates and compared the results to MP2 and CCSD(T) calculations. They have recommended that the B97D, ω B97X-D, and M06-2X functionals as a best compromise between accuracy and efficiency for methane hydrates, based upon their results.

The structure and stability of crystal structure of CH₄- and CO₂-hydrates has been explored by Sainz-Díaz and co-workers⁷⁹⁰ at the HF and DFT levels. A comparison of the binding energy indicates that the methane molecule in small cages is more stable than in large ones. However, it is worthwhile to mention herewith that the entropic and kinetic effects may change the adsorption and the relative occupancy in the crystal lattice. The vibrational behavior of the methane molecule in small cages is found to be similar to that of methane gas. This is attributed to the combination and balance of opposite forces between the methane and water molecules within the cages of the hydrate crystal.⁷⁹⁰ MD studies shows that under normal conditions of stability the crystalline structures of the methane hydrates remains unaltered. On the other hand, with the rise in temperature it decomposes, resulting into a disorder in water HB networks and the aggregation of methane molecules. Therefore, the diffusion of

methane molecules from a small cage to a larger one is not favorable.

After a rather lengthy account of the theoretical investigations on a variety of weakly bonded molecular clusters, conclusions and future perspectives follow.

6. SUMMARY AND CONCLUDING REMARKS

Molecular clusters form an area of science that is receiving increasing attention from cross-disciplinary researchers. Clusters exhibit size-dependent properties and find wide applications in industry as well as in day-to-day life. Understanding the growth patterns as well as the structure and stability of clusters is a topic of immense interest in contemporary science. In view of the growing interest in this area, it was felt that it is the opportune time to summarize the developments in quantum chemical investigations on molecular clusters, especially those bound by weak intermolecular forces.

With the advents in spectroscopic techniques and computational resources, molecular clusters provide a meeting point for experimentalists and theoreticians. Among the experimental techniques, microwave, photoelectron, and, especially, infrared spectroscopy are the most popular and powerful tools for probing molecular clusters. These experimental techniques do not reveal the complete molecular structure, but provide some data from which structural information needs to be unearthed. Most of the investigations on molecular clusters employing the above-mentioned spectroscopic techniques are carried out in the gas-phase. Hence, the structural parameters extracted from the experiments can be directly connected to those derived from the *ab initio* level calculations. Furthermore, the number of closely spaced minimum energy structures on the potential energy surface of molecular clusters increases rapidly with the size of the systems. The proper separation and characterization of such individual structures is indeed difficult even with powerful experimental techniques. Therefore, a judicious combination of these experimental techniques with the quantum chemical methods is of immense utility for probing molecular clusters.

It may be noticed from the present review that the *ab initio* studies are predominantly carried out on water, benzene, and methanol clusters: the studies on clusters of atmospheric gases such as carbon dioxide, nitrous oxide, etc. being relatively fewer in number. On the other hand, the experimental investigations on large water clusters are very few, as compared to those on benzene, methanol, carbon dioxide, nitrous oxide, etc. As pointed out earlier, a recent combined experimental and theoretical study on large water clusters is noteworthy.³²⁸ On the theoretical front, lack of electron correlation effects in the HF level prevents accurate estimation of the stability and energetics of many of the molecular clusters. Therefore, high-level methods are needed for the reliable theoretical investigations of weakly bound molecular clusters. In the literature, most of the recent high-level studies on geometry optimization of molecular clusters are carried out at MP2 level of theory, which scales as $O(N^5)$ and are affordable for treating medium-sized molecular clusters. Very few single point energy calculations on large molecular clusters employing the CCSD(T) (which scales as $O(N^7)$) method have been reported in the literature. Thus, the nonlinear scaling of quantum chemical methods and the requirement of high-level correlated theory, coupled with the presence of several local energy minima are the main bottlenecks that severely restrict the applicability of the *ab initio* methods to large molecular clusters.

In order to circumvent this problem of nonlinear scaling, fragmentation-based methods such as FMO, DC, MTA, GEBF, etc. (cf. section 2) are of immense use for investigating large-sized clusters at high-levels of theory with limited computational power offered by off-the-shelf hardware. The MP2 level geometry optimization and property calculations on molecular clusters containing typically 200 atoms are currently feasible with fragment-based methods, in particular with MTA. However, being approximate in nature, the energies obtained by using these methods carry some errors vis-à-vis the corresponding full calculation values. The introduction of many-body energy corrections^{160–164} in the fragmentation frameworks or the newly proposed grafting procedure^{258,260} may lead to the minimization of the errors and bring them to within chemical accuracy.

The use of DFT, employing less expensive density functionals, offers an attractive alternative for investigating structures, energetics, and vibrational frequencies of a variety of large molecular clusters. However, DFT has not been applied so extensively to all clusters due to the nonuniform performance of various functionals. In recent years, the dispersion corrected functionals such as M05-2X, M06-2X, B97D, B2PLYPD, etc. are shown to provide a better alternative, especially in molecular clusters dominated by long-range dispersion interactions. For instance, M06-2X functional employing extended basis sets offers a satisfactory description of the noncovalent interactions among the CO₂ molecules. Similarly, M05-2X, X3LYP, and BLYP functionals are found to yield accurate estimates of binding energies, geometrical parameters and structural properties of water clusters, akin to those derived from MP2 method. The DFT functionals mentioned above are prone to BSSE and hence use of large basis set is recommended for studying weakly bound clusters and complexes. It is thus anticipated that the search for a gold standard density functional suited for dispersion would continue until such a functional is indeed found and thoroughly tested.

It is evident from the present review that most of the studies on clusters focus on the structures and energetics of clusters and very few deal with the properties of these clusters. Many of the studies have predicted the stability of clusters based on the hydrogen bond topology, different dimeric motif patterns in a molecular clusters, etc. There are indeed very few studies addressing the growth patterns in molecular clusters. Recently, an electrostatics-based aufbau algorithm has been proposed for building molecular clusters.²⁵⁷ However, such a systematic method has a limitation that it cannot be used for systems that exhibit extra stability due to a sudden change in the structure with increasing size. Therefore, the aufbau-based systematic growth as well as the introduction of stochastics in the generation of molecular clusters are still the most crucial steps in the quantum chemical treatment of molecular clusters. Several simulation techniques based on molecular dynamics studies such as basin-hopping,^{795–798} genetic algorithm,^{795,799–802} simulated annealing, etc.^{795,803–805} have been employed for introducing the stochastics in geometry optimization. Yet these methods are generally implemented within simulation techniques and the calculations based on these start from random geometries, which may be responsible for overlooking an energetically favored conformer. Hence, there is a need to make a combination of such techniques with quantum chemical methods (cf. ref 258) for gaining better

understanding and insights about structures, properties and structural transitions in molecular clusters.

Another important aspect in studying molecular clusters is the following: How does a large molecular aggregate develop bulk-like behavior? From the present review, it can be seen that there are indeed very few investigations on this front. For example, beyond six methanol molecules, the clusters are found to behave similar to liquid methanol.^{378,379} Such an understanding at molecular level will ultimately lead to insights on not only the reactivity of liquids but also on the crystal structure and the phenomenon of nucleation of the crystalline phases of molecules. Furthermore, accurate estimation of the lattice energies would be useful for energetically ranking competing crystal structures, as shown by the works of Gibson and Scheraga,⁵⁰⁹ Ringer and Sherrill,⁵¹¹ and very recently by Kennedy et al.⁵¹² at MP2 and CCSD(T) level through three-body dispersion effects in benzene crystals. It is felt that the introduction of fragmentation-based hybrid many-body interaction models for the implementation of numerical gradients and subsequent geometry optimization of molecular crystals may be crucial for predicting the lattice parameters.^{806,807} Furthermore, the predicted lattice energies from these methods can be systematically improved to fall within a couple of kJ/mol of the corresponding experimental values.

How far will these investigations on molecular clusters go in the coming years? Whether the highly accurate studies will continue on the moderate-sized clusters (say for water, it is currently in the range of $(\text{H}_2\text{O})_{30}$) followed by the extrapolation of the results for investigating the stability and energetics of large aggregates? Will they shed light on structures of molecular crystals and enable estimation of lattice energies of polymorphs? Considering the recent advancement in the spectroscopic tools and computational resources, it appears that the investigations on stability and energetics of large-sized clusters would become amenable, ultimately providing a link with crystal structure. In the coming decade, prediction of the structures and energetics of clusters at CCSD(T) or similar high-level correlated methods will become feasible and replace HF, MP2, etc. Furthermore, the estimation of the binding energies at CCSD(T)/CBS, i.e. the present gold standard of quantum chemistry, will indeed be routinely possible in the era of advanced computing.

It may be hoped that the present comprehensive survey of the area of weakly bound molecular clusters is of use to experimentalists as well as computational chemists and acts as a catalyst to future investigations in this important area of research.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +91-512-259 6706. E-mail: gadre@iitk.ac.in.

Notes

The authors declare no competing financial interest.

Biographies



Shridhar R. Gadre was born in May 1950 in Akola (Maharashtra), India. He received his Ph.D. under the supervision of Professor Palliakaranai T. Narasimhan from the Indian Institute of Technology (IIT), Kanpur, India in 1978 and joined for postdoctoral research notably with Professor Robert G. Parr and Robert L. Matcha for two years, before joining University of Pune in 1980. After spending 30 years, he retired from University of Pune in 2010 and joined to IIT Kanpur, in 2010. His research area includes molecular scalar fields, software development and parallel computing, information entropy, electron density in momentum space, and ab initio treatment for large molecules employing molecular tailoring approach.



Sachin Dilip Yeole was born in November 1984 in Bhusawal (Maharashtra), India. He completed his B.Sc. (2006) and M.Sc. (2008) degrees from University of Pune, India and joined as a Ph.D. student to Professor Shridhar R. Gadre in 2008 and has recently completed his Ph.D. His research interests are molecular clusters, topography of scalar fields, and algorithm development in Fortran. He is currently working as Dr. D. S. Kothari Postdoctoral Fellow at Department of Chemistry, University of Pune.



Nityananda Sahu was born in July 1987 in Dhenkanal (Odisha), India. He obtained his B.Sc. (2008) and M.Sc. (2010) degrees from Utkal university, Bhubaneswar, India. He joined as a Ph.D. student under the supervision of Professor Shridhar R. Gadre in January, 2011 at the Indian Institute of Technology, Kanpur, India. His area of research includes ab initio investigations of large water clusters and explicit hydration of molecules.

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ABBREVIATIONS AND ACRONYMS

ALMO	absolutely localized molecular orbital	H-bonded	hydrogen-bonded
AMOEBA	atomic multipole optimized energetics for biomolecular applications	HF	Hartree–Fock
B2PLYPD	Becke 2-parameter Lee–Yang–Parr dispersion	HFD	Hartree–Fock dispersion
B3LYP	Becke 3-parameter Lee–Yang–Parr functional	HOMO	highest occupied molecular orbital
BLYP	Becke Lee–Yang–Parr functional	HP	hydrogen peroxide
BP86	Becke Perdew 86	HSAB	hard soft acid base
BSSE	basis set superposition error	IR	infrared
CBS	complete basis set	IRID	infrared ion-dip
CC	coupled cluster	LCAO	linear combination of atomic orbitals
CCSD(T)	coupled clusters single and doubles with perturbative triples	LDA	local density approximation
CI	configurational interaction	LPMO	locally projected molecular orbital
CP	counterpoise correction	LUMO	lowest unoccupied molecular orbital
CPMD	Car–Parrinello molecular dynamics	MBIA	many-body interaction analysis
DC	divide-and-conquer	MBPT	many-body perturbation theory
DFT	density functional theory	MC	Monte Carlo
DPE	deprotonation energy	MD	molecular dynamics
DZP	double zeta valence	MESP	molecular electrostatic potential
EDA	energy decomposition analysis	GGA	generalized gradient approximation
EPIC	electrostatics potential for intermolecular complexation	MMC	molecular mechanics of clusters
FC	full calculation	MM	molecular mechanics
FMO	fragment molecular orbital	MP2	Møller–Plesset second order perturbation
FMO–CC	fragment molecular orbital-coupled cluster	MP4	Møller–Plesset fourth order perturbation
FT	Fourier transform	MP4(SDTQ)	Møller–Plesset fourth order perturbation for single, double, triples, and quadruple substitutions
FTIR	Fourier transform infrared	MTA	molecular tailoring approach
FTMS	Fourier transform microwave spectroscopy	MW	microwave
GEBF	generalized energy-based fragmentation	M05-2X	Minnesota 05 global hybrid functional with 52% HF exchange
HB	hydrogen bond	M06-2X	Minnesota 06 global hybrid functional with 54% HF exchange
		ONIOM	our own N-layered integrated molecular orbital and molecular mechanics
		OPLS	optimized parameters for liquid simulation
		PBE	Perdew–Burke–Ernzerhof
		PES	potential energy surface
		PW91	Perdew and Wang's 1991 functional
		QCISD(T)	quadratic configurational interaction singles, double with purterbative triples
		QM	quantum mechanics
		R2PI	resonant two photon ionization
		RHF	restricted Hartree–Fock
		RIMP2	resolution-of-the-identity Møller–Plesset second order perturbation
		SAMBA	stratified approximation many-body approach
		SAPT	symmetry adapted perturbation theory
		SCF	self-consistent field
		SMF	systematic molecular fragmentation
		SPC	single-point charge
		THF	tetra-hydro furan
		TIP3P	transferable intermolecular potential-3 point
		TIP4P	transferable intermolecular potential-4 point
		TIPS2	transferable intermolecular potential functions-2
		UHF	unrestricted Hartree–Fock
		UD	up–down
		UU	up–up
		VRT	vibration–rotation–tunneling
		vdw-DF	van der Waal-density functional
		X3LYP	Xu, 3-parameter, Lee–Yang–Parr functional
		ZPE	zero-point energy

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