

Article

Geometry-Based Description for Hydrogen Bond Organization in Small Water Clusters Derived from Spectroscopic and Quantum Chemical Data

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Abstract

Hydrogen-bond organization plays a central role in determining the structure and properties of water from molecular to macroscopic scales. In this study, we propose a geometry-based descriptor for small hydrogen-bonded water clusters, $(\text{H}_2\text{O})_n$, with $n = 2\text{--}6$. The central element of the proposed geometric framework is the dimensionless geometric index, $S_n = d/l$, where d is the center-to-molecule distance in a cluster configuration and l is the nearest-neighbor $\text{O}\cdots\text{O}$ distance associated with hydrogen-bonded water molecules. The geometric descriptor is not intended to replace quantum-chemical calculations or to provide a direct measurement of hydrogen-bond energy, lifetime, or number. Instead, it provides a compact geometric framework for describing the structural organization of small hydrogen-bonded water clusters. The obtained geometric trend is compared with selected Nuclear Magnetic Resonance (NMR), Møller–Plesset perturbation theory (MP2), and radial distribution function data as complementary qualitative and semi-quantitative references. The proposed geometric index $S_n = d/l$ was further compared with MP2 quantum-chemical $\text{O}\cdots\text{O}$ distances for $(\text{H}_2\text{O})_n$ clusters, $n = 2\text{--}6$, using the oxygen atoms as structural nodes of the hydrogen-bonded motifs. This comparison showed that the exponential increase in S_n is consistent with the characteristic $\text{O}\cdots\text{O}$ donor–acceptor length scale of approximately 2.8 Å, linking the geometric framework with calculated molecular geometries. Over the limited interval $n = 2\text{--}6$, the geometric index S_n increases monotonically and nonlinearly with cluster size. The quantum-chemical reference data previously reported in our study, comprising GIAO-DFT-calculated ^1H chemical shifts obtained for MP2-optimized water-cluster geometries, show a rapid nonlinear increase from the dimer to the pentamer, followed by the onset of saturation in the pentamer–hexamer range. The semi-empirical stabilization parameter evaluated in the present study indicates increasing relative stabilization, with a reduced incremental change around $n \approx 4\text{--}5$. The qualitative consistency of these size-dependent trends supports the use of S_n as a compact geometric descriptor of hydrogen-bond organization in small water clusters, without interpreting it as a direct quantitative measure or mechanistic framework of hydrogen-bond cooperativity. Importantly, liquid water is not treated as a system of closed cyclic clusters; cyclic motifs are used only as frameworked geometric reference configurations for small hydrogen-bonded aggregates. The geometric trend is qualitatively compared with selected quantum-chemical, spectroscopic, and radial distribution function data and should be regarded as an empirical geometric approximation



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over the limited interval $n = 2\text{--}6$. These findings indicate that geometric, spectroscopic, and quantum-chemical descriptors reflect related, but not identical, aspects of hydrogen-bond organization. The proposed approach links cluster geometry, $\text{O}\cdots\text{O}$ intermolecular distances, and hydrogen-bond connectivity in a simplified geometric description.

Keywords: water clusters; quantum chemistry; NMR spectroscopy; nonlinear description

1. Introduction

Contemporary studies of water clusters demonstrate that they are not merely theoretical constructs but molecular assemblies that can be resolved under specific experimental conditions, particularly as surface-supported clusters at low temperature, using low-temperature scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) [1]. In particular, it has been shown that individual small clusters, such as trimers, tetramers, pentamers, hexamers, and heptamers, can be resolved on Au(111) surfaces, indicating that water molecules form specific, structurally distinguishable geometries stabilized by hydrogen bonding [1]. More recent studies reveal a common water-cluster motif observed on both hydrophilic Pt(111) and hydrophobic Cu(111) surfaces, suggesting that the early stages of ice nucleation may involve universal structural arrangements of water molecules [2].

In the solid phase, water occurs predominantly as hexagonal ice I_h , whose structure arises from tetrahedral hydrogen-bond coordination and the arrangement of molecules into puckered six-membered rings. This organization provides a natural transition from small surface-supported water clusters to the ordered structure of solid ice. In this context, the study by Priante et al. is particularly important, as AFM imaging resolves mono- and bilayer ice nanoclusters on metal surfaces and relates their atomistic motifs to the early stages of ice-structure formation [3]. In addition, recent STM/nc-AFM and AFM studies show that water on surfaces forms well-defined hydrogen-bonded clusters and networks, and that the solid water phase evolves toward more ordered ice configurations [4,5].

Spectroscopic and quantum-chemical studies of small water clusters provide molecular-level insight into hydrogen-bond dynamics and structural diversity. Isomer-selective detection of hydrogen-bond vibrations in the protonated water hexamer demonstrates that vibrational signatures are highly sensitive to cluster geometry and proton localization [6]. These findings support the interpretation that hydrogen-bond cooperativity in small clusters may evolve toward more extended ordered networks. In this context, the formation of Ice I_h clusters in solid-phase water represents a structurally consistent transition toward hexagonal hydrogen-bond organization [7].

The onset of ion-pair formation in $\text{HCl}(\text{H}_2\text{O})_n$ clusters at $n \approx 5$ provides an illustrative example of size-dependent solvation and hydrogen-bond stabilization in acid-water clusters and the emergence of liquid-water-like behavior [8]. Experimental results show that HCl remains largely covalent for $n < 5$. In contrast, the addition of a fifth water molecule enables dissociation into a contact ion pair $\text{H}_3\text{O}^+ \cdots \text{Cl}^-$, reflecting a marked increase in ionic character and stabilization by the hydrogen-bond network. This behavior can be understood in the broader framework of hydrogen-bond cooperativity, where earlier spectroscopic studies of small water clusters have demonstrated that cooperative interactions increase with cluster size and enhance the stability of hydrogen-bonded structures [9].

In addition, structural evolution from planar to three-dimensional configurations, together with nuclear quantum effects, further supports the existence of a characteristic cluster size at which extended hydrogen-bond connectivity becomes established [10]. These

quantum effects contribute to proton delocalization and facilitate charge separation within the cluster network. Within this framework, the nonlinear hydrogen-bond network model captures the same size-dependent behavior as an emergent property of cluster growth, linking spectroscopic observations, structural transitions, and thermodynamic stabilization in small water clusters [11].

The exponential increase in hydrogen-bond cooperativity in small water clusters provides a framework for interpreting the dissociation behavior in $\text{HCl}(\text{H}_2\text{O})_n$ systems [9,11]. As cluster size increases, the hydrogen-bond network becomes sufficiently developed around $n \approx 5$ to stabilize charge separation, consistent with the formation of the $\text{H}_3\text{O}^+ \dots \text{Cl}^-$ ion pair [8]. Thus, the exponential trend and ion-pair formation reflect size-dependent hydrogen-bond cooperativity [9].

Recent studies demonstrate that the evolution of hydrogen bonding in small water clusters follows a pronounced nonlinear, specifically exponential trend with increasing cluster size. In particular, GIAO-DFT-calculated ^1H chemical shifts obtained for MP2-optimized cluster geometries show a nonlinear increase in chemical shift as the number of water molecules grows from dimers to pentamers, reflecting a rapid enhancement of hydrogen-bond cooperativity within the cluster [11]. This exponential behavior is accompanied by a sharp decrease in free and internal energy per molecule up to $n \approx 5$, after which the system approaches a saturation regime, indicating the emergence of a stable hydrogen-bond network [11]. Importantly, this transition highlights the $(\text{H}_2\text{O})_5$ cluster as a representative size at which enhanced connectivity of the hydrogen-bond network becomes evident, providing a useful reference point for discussing the emergence of extended cooperative effects [11].

Complementary multiscale analyses of sessile water droplets further support the existence of nonlinear, cooperative hydrogen-bond behavior across scales, showing that macroscopic observables, such as contact angle, can be interpreted in terms of collective hydrogen-bond interactions consistent with trends observed at the level of small clusters [12]. These findings suggest that the exponential growth of hydrogen-bond cooperativity in clusters up to five water molecules represents a fundamental transition point, providing a conceptual connection between discrete molecular aggregates and the continuous hydrogen-bond network characteristic of liquid water. The observed dependence follows an approximately exponential trend, with the effect becoming pronounced around the tenth water molecule [13].

The exponential trend in small water clusters with $n = 2\text{--}6$ arises from cooperative hydrogen bonding, in which each additional molecule enhances the stability and polarization of the entire network [5,6]. Xie et al. (2024) demonstrate that hydrogen-bond cooperativity in small water clusters leads to nonlinear stabilization and drives a structural transition from planar to three-dimensional configurations, enhanced by nuclear quantum effects [8].

For small water clusters with $n = 2\text{--}6$, the structural parameter exhibits a systematic dependence on cluster size, reflecting the progressive development of hydrogen-bond cooperativity [14]. Over this interval, the observed variation is well described by an empirical exponential function, consistent with nonlinear stabilization and structural evolution reported in recent studies [11,12]. This behavior is associated with the collective enhancement of hydrogen-bond interactions and the transition toward a three-dimensional network as cluster size increases [15–17].

The infrared spectroscopic behavior of water provides spectroscopic evidence for hydrogen-bond cooperativity in small clusters. The observed red shift in the O–H stretching vibrations to lower frequencies, together with the increase in band intensity, reflects the strengthening of hydrogen bonds due to cooperative interactions within the network [18,19]. As hydrogen bonding becomes stronger, changes in the transition dipole moment lead to enhanced infrared absorption, while band broadening indicates a distribution of hydrogen-

bond strengths, as demonstrated in recent high-resolution spectroscopic studies of water clusters [20].

These spectroscopic features are consistent with recent theoretical and experimental studies showing that hydrogen-bond cooperativity leads to nonlinear stabilization and structural evolution in small water clusters [10,21]. In particular, the shift toward lower vibrational frequencies corresponds to the collective strengthening of hydrogen bonds as cluster size increases, supporting the transition from weakly interacting molecules to a cooperative hydrogen-bonded network [22]. Furthermore, modern simulations and spectroscopic analyses demonstrate that this evolution is accompanied by the emergence of three-dimensional hydrogen-bond connectivity and many-body interactions, thereby reinforcing the interpretation of cooperative growth as a nonlinear, scale-dependent process [23].

Despite extensive experimental and theoretical studies, a unified quantitative description of the nonlinear evolution of hydrogen-bond cooperativity in small water clusters ($n = 2-6$), including its dependence on cluster size and structural origin, remains unresolved. In particular, the transition from discrete molecular interactions to collective hydrogen-bond network formation lacks a consistent description linking structure and cooperativity.

Recent studies have demonstrated that structural and connectivity descriptors derived from cluster geometry can be used to characterize water-cluster aggregation and compare structural patterns across different cluster sizes [24]. In this context, $S_n = \frac{d}{7}$ is introduced here as a simplified geometric descriptor for small water-cluster configurations. In this work, a geometric descriptor for $(\text{H}_2\text{O})_n$ configurations ($n = 2-6$) is introduced and compared qualitatively with previously calculated ^1H chemical shifts and MP2-optimized geometries for $n = 2-5$ [11]. Broadband rotational spectroscopy, combined with high-level ab initio calculations, has demonstrated that geometric frameworks based on the oxygen-atom arrangement can be used to distinguish water-cluster isomers and determine their $\text{O}\cdots\text{O}$ structural parameters [25]. The study extends a previously developed approach, in which a nonlinear relationship between structural organization and hydrogen-bond network formation was established, showing that cooperative effects emerge from collective molecular behavior across spatial scales [11].

2. Materials and Methods

2.1. Multiscale Approach: NMR and MP Analysis

The structural evolution and hydrogen-bond cooperativity in small water clusters $(\text{H}_2\text{O})_n$ ($n = 2-6$) were investigated using NMR spectroscopy and quantum-chemical calculations (MP2).

Cluster geometries were optimized, followed by MP2 calculations for accurate energetic evaluation. The values used in the present analysis are GIAO-DFT-calculated ^1H chemical shifts obtained for MP2-optimized cluster geometries and reported in our previous study with Gaussian 16 [11]. The analysis focuses on structural, spectroscopic, and energetic trends as a function of cluster size, enabling a qualitative comparison of cluster-size-dependent structural and spectroscopic trends.

2.2. Calculated ^1NMR Chemical Shifts

GIAO-DFT-calculated ^1H chemical shifts were used as spectroscopic descriptors of the local electronic environment associated with hydrogen bonding. In the present work, the cluster-dependent chemical-shift values are treated as quantum-chemical reference data for selected water-cluster configurations rather than as direct experimental measurements of isolated clusters in liquid water. The values were calculated using the Gauge-Including Atomic Orbital (GIAO) approach at the DFT level for MP2-optimized cluster geometries, as reported previously in Ref. [11]. Increasing hydrogen-bond interaction and polarization

can reduce the magnetic shielding of donor protons, producing a downfield ^1H chemical shift. Accordingly, the calculated chemical shifts are used here as qualitative electronic descriptors of hydrogen-bond-related changes and not as direct quantitative measures of hydrogen-bond cooperativity.

Quantum-chemical calculations at the MP2 level were used to characterize the geometries of small water clusters and to obtain structural parameters, including $\text{O}\cdots\text{O}$ distances and hydrogen-bond geometries. These MP2-optimized structures provide the geometrical basis for comparison with the present geometric descriptor $S_n = \frac{d}{l}$.

For $n = 3\text{--}5$, the lowest-energy configurations are predominantly cyclic, whereas for $n = 6$ three-dimensional structures become energetically more favorable than the cyclic hexamer. Therefore, the cyclic configurations considered in the present work are used only as descriptive geometric reference configurations and are not intended to represent the global minimum-energy structure for every cluster size.

2.3. Geometric Descriptor

Based on the optimized structures, a dimensionless geometric index $S_n = \frac{d}{l}$ was introduced, where d is the distance from the cluster center to a molecule (center-to-vertex distance), and l is the nearest-neighbor $\text{O}\cdots\text{O}$ distance obtained from diffraction data ($l \approx 2.8 \text{ \AA}$) [26].

The proposed descriptor is explicitly geometric. It is based on the ratio between two structural distances: the center-to-molecule distance d and the nearest-neighbor $\text{O}\cdots\text{O}$ distance l . The $\text{O}\cdots\text{O}$ distance is used because it is directly related to the geometry of hydrogen-bonded water molecules. Thus, the dimensionless index $S_n = \frac{d}{l}$ is introduced as a compact descriptor of cluster organization. It should be emphasized that S_n is not a direct measure of hydrogen-bond energy, hydrogen-bond lifetime, or the absolute number of hydrogen bonds. Rather, it is an indirect geometric descriptor that reflects how the spatial arrangement of hydrogen-bonded water molecules changes with increasing cluster size.

In this geometric description, cyclic configurations for $n = 3\text{--}6$ are used as geometric reference structures, not as a claim that liquid water consists of closed cyclic clusters. Liquid water is better described as a dynamic, tetrahedrally coordinated hydrogen-bond network. Therefore, the role of the present cluster frameworks limited to representing local geometric motifs and hydrogen-bond-related $\text{O}\cdots\text{O}$ distances in small molecular aggregates. This interpretation is consistent with the description of liquid water as a locally reorganizing hydrogen-bond network, as discussed by Perez et al. (2013) [25], with the network-based analysis of H-bonded molecular aggregation in liquid water reported by Lin et al. (2021) [26], and with the dependence of hydrogen-bond strength on intermolecular distance, molecular orientation, and local environment reported by Ojha (2018) [27].

2.4. Radial Distribution Function as a Structural Reference

This geometric descriptor provides a simplified representation of structural evolution in water clusters and enables direct comparison with experimentally derived radial distribution functions (RDF). The geometric descriptor is consistent with the multiscale interpretation of hydrogen-bond cooperativity proposed in [12], where local structural ordering is linked to macroscopic physical behavior.

2.5. Integration with Experimental Structural Data

To ensure consistency with experimental observations, the geometric description was correlated with structural parameters derived from diffraction techniques. Radial distribution function data are used in the present work only as structural reference information for characteristic intermolecular $\text{O}\cdots\text{O}$ distances in water. The first RDF maximum near $2.8 \text{ \AA}$ [24] corresponds to the nearest-neighbor $\text{O}\cdots\text{O}$ separation in the hydrogen-bonded

network of water and provides an empirical basis for selecting the parameter l in the geometric index $S_n = \frac{d}{l}$.

3. Results

3.1. Geometric Index and Nonlinear Scaling in Water Clusters

The regions of electron density around the oxygen atom in the water molecule are arranged in approximately tetrahedral symmetry. The ideal tetrahedral angle is 109.47° , whereas the actual H–O–H bond angle is approximately 104.5° .

We denote by l the distance between two neighboring molecules connected by a hydrogen bond, and by d the distance from a selected structural point of a molecule (e.g., the oxygen atom) to the geometric center of the configuration under consideration (Figure 1).

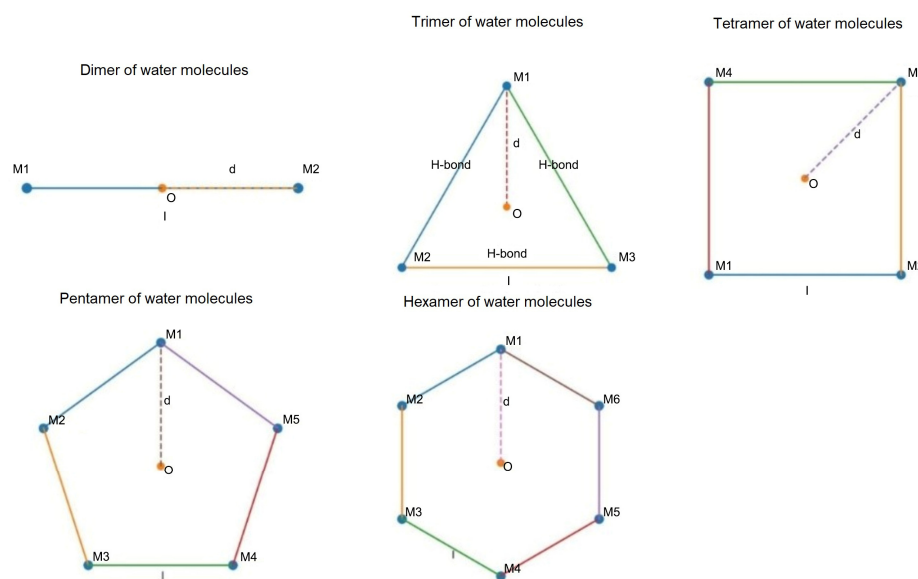


Figure 1. Schematic representation of geometric parameters (d and l) in a water cluster configuration.

In the present work, the geometric ratio d/l is introduced as a structural index, $S_n = \frac{d}{l}$, that describes the change in the descriptive geometric arrangement of cluster configurations with increasing n . For regular polygonal arrangements with $n \geq 3$, the geometric index is given by

$$S_n = \frac{d}{l} = \frac{1}{2} \sin\left(\frac{\pi}{n}\right) \quad (1)$$

where d is the center-to-vertex distance, and l is the nearest-neighbor O...O distance. For the dimer, $S_2 = 0.500$ is treated separately as a linear reference configuration.

In this sense, S_n may be used only as an indirect geometric descriptor of structural change and may be qualitatively compared with reported trends in hydrogen-bond cooperativity, without implying a direct physical measure of cooperativity.

For small water clusters of the form $(\text{H}_2\text{O})_n$, $n = 2\text{--}6$, the variation in the geometric index can be described by the following local relation

$$k_n = \ln\left(\frac{S_n}{S_{n-1}}\right). \quad (2)$$

The quantity k_n is defined as the logarithmic increment of the geometric index when passing from $(\text{H}_2\text{O})_{n-1}$ to $(\text{H}_2\text{O})_n$. For $S_n = \frac{d}{l}$, the obtained values are $k_3 = 0.143$, $k_4 = 0.204$, $k_5 = 0.185$, and $k_6 = 0.161$. These values are consistent with an approximately exponential trend over the dimer-to-hexamer interval, with the largest increment observed at the trimer-

to-tetramer transition. For $n > 6$, the dependence should be considered separately, since the simple planar geometric model is no longer sufficient to describe the actual lowest-energy structures. The values 0.077, 0.130, 0.144, and 0.150 correspond to the difference $S_n - S_{n-1}$ between consecutive geometric-index values for $n = 3-6$.

Table 1 presents the d/l ratio for clusters containing 2–6 molecules in descriptive geometric configurations. For $n \geq 3$, the values correspond to descriptive planar cyclic arrangements in which each molecule is connected to two neighboring molecules; these configurations are used here as simplified geometric models rather than as exact representations of all lowest-energy cluster structures. For $n = 2$, the configuration is a dimer and does not constitute a cyclic ring.

Table 1. Geometric index $S_n = \frac{d}{l}$ for water clusters containing 2–6 water molecules.

Number of Water Molecules	2	3	4	5	6
$S_n = \frac{d}{l}$	0.500	0.577	0.707	0.851	1.0

The exponential relation

$$S_n = S_2 e^{k(n-2)} \quad (3)$$

provides an empirical geometric approximation for the limited interval $n = 2-6$. It should be used only as a local fitting function for descriptive configurations and not as a general quantum chemical model of hydrogen-bond cooperativity.

The normalized exponential calculations provide a good empirical fit for the limited interval ($n = 2-6$), with an RSS of 0.00039. When the same approximation is formally extended to $n = 7-12$, the agreement deteriorates substantially (RSS = 1.374). This indicates that the exponential approximation should be regarded only as a local empirical fit for the limited $n = 2-6$ interval and not as a structural model for larger water clusters.

In Figure 2a, the dimer, trimer, tetramer, pentamer, and hexamer are represented within the framework of the normalized exponential relation (3), which describes the increase in the geometric index with the number of molecules in the cluster. Figure 2b demonstrates that the ratio $\frac{S_n}{S_2}$ increases nonlinearly with n and is well fitted by an exponential function over a limited interval $n = 2-6$. For Figure 2, k is an effective parameter averaged over the interval $n = 2-6$.

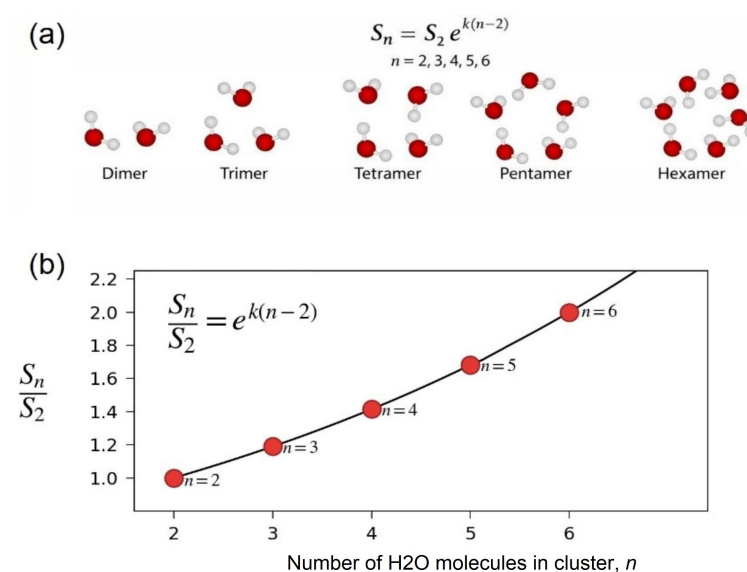


Figure 2. Schematic representation of water clusters from dimer to hexamer (a) and the exponential trend $S_n = S_2 e^{k(n-2)}$ for $n = 2-6$; normalized geometric index S_n/S_2 as a function of cluster size (b).

3.2. Quantum-Chemical and Spectroscopic Comparison

The geometric analyses show qualitative consistency with trends reported in quantum-chemical calculations, while the present geometric framework provides a simplified structural representation that complements, rather than substitutes, detailed electronic-structure descriptions. Published results obtained using Møller–Plesset perturbation theory (MP2) are used here for qualitative comparison with the present geometric description.

Figure 3 presents a qualitative comparison between the geometric index $S_n = \frac{d}{l}$ and reference ^1H chemical-shift values for selected small water-cluster models $(\text{H}_2\text{O})_n$, ($n = 2–6$). The geometric index describes the framework topological expansion of the cluster configuration, whereas the chemical-shift values are used only as spectroscopic descriptors of the proton electronic environment and hydrogen-bond-related deshielding. The calculated ^1H chemical shift increases from the dimer to the pentamer within the published $n = 2–6$ dataset. This trend is qualitatively consistent with enhanced proton deshielding in hydrogen-bonded cluster models, but it should not be interpreted as direct structural proof from NMR data alone. Hydrogen-bond formation polarizes the donor O–H bond and redistributes electron density toward the acceptor molecule, thereby reducing the magnetic shielding of the donor proton and producing a downfield ^1H chemical shift. The guide curves are included only to visualize the nonlinear tendencies of the two descriptors.

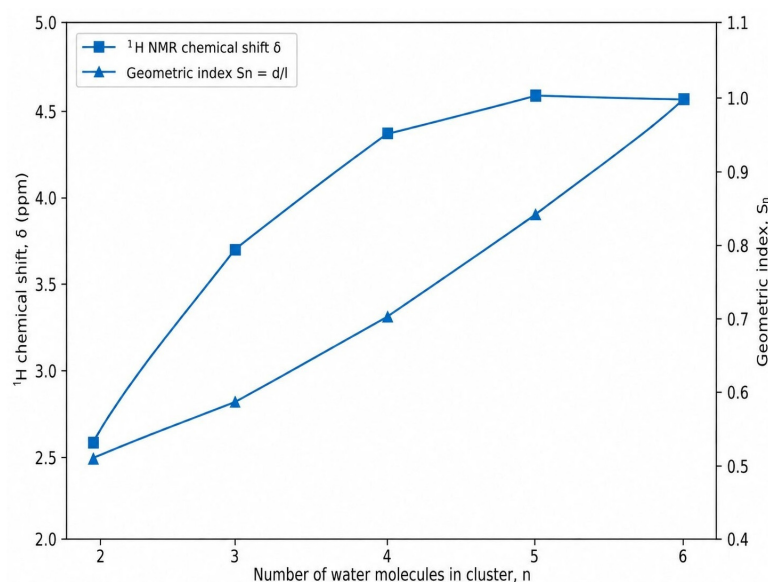


Figure 3. Qualitative comparison between the geometric index $S_n = \frac{d}{l}$ for framework configurations ($n = 2–6$) and previously calculated ^1H chemical-shift values for selected $(\text{H}_2\text{O})_n$ water cluster frameworks ($n = 2–6$) [11]. The chemical-shift values are used as spectroscopic descriptors, while the guide curves only visualize the observed trends.

For small water clusters $(\text{H}_2\text{O})_n$ with $n = 2–6$, the reported chemical shift values increase from the monomer/dimer region to the pentamer and then approach saturation. In the cited data set, the values rise from 2.56 ppm for the dimer and about 4.6 ppm for the pentamer, and the hexamer isomer is considered here, suggesting a tendency toward saturation. The two size-dependent trends are compared qualitatively; no direct functional correlation between S_n and the calculated ^1H chemical shifts is inferred.

Quantum-chemical and spectroscopic studies of isolated small water clusters, mainly in the gas phase and in quantum-chemical cluster models, demonstrate that for $(\text{H}_2\text{O})_n$ with $n = 3–5$, cyclic structures are generally among the lowest-energy configurations, whereas for $n = 6$ the global minimum corresponds to three-dimensional arrangements. These results provide a molecular-level reference for cluster stability and hydrogen-bond organization.

The geometric descriptor proposed in the present study is a representation that uses selected cluster geometries as structural references for describing the nonlinear development of hydrogen-bond organization. In the context of liquid water, these cluster models are used as simplified structural analogues for discussing local hydrogen-bond ordering. In the present geometric descriptor, the hexamer is retained only as an idealized reference isomer for geometric comparison. The trimer (H_2O)₃, tetramer (H_2O)₄, and pentamer (H_2O)₅ form nearly planar ring-like structures in which each water molecule acts simultaneously as both a hydrogen-bond donor and acceptor. In these configurations, the number of hydrogen bonds is equal to the number of molecules (3, 4, and 5, respectively), and the average oxygen–oxygen distances are approximately 2.75–2.90 Å [19].

Let us consider Table 2. Quantum-chemical and spectroscopic studies demonstrate that small water clusters (H_2O)_n with $n = 3$ –6 are the most stable (minimum-energy) structures. For $n = 6$, structures are included as representative configurations within the present geometric description, alongside known three-dimensional arrangements. In Table 2, however, the cyclic hexamer isomer is listed because it is the isomer considered within the present geometric description [20–22].

Table 2. Reference GIAO-DFT-calculated ^1H chemical shifts reported in Ref. [11] for selected water-cluster calculations ($n = 2$ –6).

Cluster	Number of Hydrogen Bonds	δ , ppm	Comment
H_2O	0	1.83	
(H_2O) ₂	1	2.56	
(H_2O) ₃	3	3.69	Cyclic
(H_2O) ₄	4	4.38	Cyclic
(H_2O) ₅	5	4.60	Cyclic
(H_2O) ₆	6	4.58	Cyclic

The quantum-chemical NMR chemical shifts δ (ppm) show a nonlinear, saturation-like increase with cluster size and with the number of hydrogen bonds. The strongest increase is observed from the monomer to the tetramer, while the pentamer and hexamer values remain close to 4.6 ppm, indicating the onset of saturation in the electronic response of the hydrogen-bonded network. The cluster geometries used for the quantum-chemical interpretation are consistent with the benchmark MP2 study of Shields et al. [11,12,22], which provides a robust reference set of optimized water-cluster structures and formation energies for (H_2O)_n, $n = 2$ –10.

It should be noted that for cyclic clusters with $n = 3$ –6, the number of hydrogen bonds is structurally determined to be approximately equal to the number of water molecules. Therefore, the trend is largely topology-driven rather than an independent empirical dependence. The RSS analysis shows only that the saturating exponential function reproduces this limited data set better (RSS = 0.2359) than the linear (RSS = 0.4190) and logarithmic (RSS = 1.2288) framework.

The quantum-chemical NMR chemical shifts show a clear nonlinear, exponential saturation-like increase with both cluster size and the number of hydrogen bonds, indicating that the electronic response of water molecules becomes progressively stronger with hydrogen-bond cooperativity and reaches a plateau for the pentamer–hexamer range.

3.3. Comparison Between the Geometric Index and Møller–Plesset Distances Between Oxygen Atoms of Water Molecules

The quantum-chemical O...O distances used for comparison were taken from Ref. [11] and were used here to evaluate the correspondence between the calculated local hydrogen-bond geometry and the proposed geometric index $S_n = \frac{d}{l}$.

The value $l \approx 2.8 \text{ \AA}$ was used as the characteristic O...O donor–acceptor distance between hydrogen-bonded water molecules. This value is supported by experimental X-ray pair-distribution data for ambient liquid water, where the first O...O coordination-shell maximum occurs at approximately $2.80 \text{ \AA}$ [28,29], and by ab initio simulations showing that hydrogen-bond rearrangement and nearest-neighbor O...O distances in liquid water are centered close to this length scale [29,30].

The O...O distances were included because the geometrical motifs shown in Figure 1 are defined by the spatial arrangement of oxygen atoms, which represent the structural nodes of the hydrogen-bonded water-cluster network (Table 3).

Table 3. Comparison between the geometric index $S_n = \frac{d}{l}$ and O...O distances recalculated from the available MP-2 optimized Cartesian coordinates for selected water-cluster models.

Number of Water Molecules	Descriptive Structural Motif	Geometric Index $S_n = \frac{d}{l}$	Mean O...O Distance MP2/aug-cc-pVTZ, $\text{\AA}$	Mean O...O Distance MP2/6-31*G, $\text{\AA}$
2	Dimer reference	0.500	2.971	2.915
3	Trimer motif	0.577	2.950	2.791
4	Tetramer motif	0.707	2.732	2.756
5	Pentamer motif	0.850	2.716	2.743
6	Hexamer reference motif	1.000	2.800	2.803

The comparison between the geometric index $S_n = \frac{d}{l}$ and the quantum-chemical O...O distance provides a direct link between the proposed geometrical description and calculated molecular geometries. The exponential fit of S_n gives $RSS = 0.00039$ and $R^2 = 0.998$, confirming a local nonlinear increase in geometric organization over the interval $n = 2$ –6. At the same time, the quantum-chemical O...O distances remain close to the characteristic value $l \approx 2.8 \text{ \AA}$ in the geometric description and show that the increase in S_n reflects progressive spatial ordering in hydrogen-bonded water molecules.

3.4. Radial Distribution Function (RDF) as a Structural Reference

The study of water structure originates from the pioneering work of Bernal and Fowler (1933), who introduced the concept of local ordering in liquids [23]. This framework was later extended through diffraction studies, in which radial distribution functions (RDFs) revealed characteristic intermolecular distances in liquid water [31,32].

Further insight into the microscopic structure of water was provided by spectroscopic and theoretical studies of small clusters $(\text{H}_2\text{O})_n$, which demonstrated the existence of stable cyclic and three-dimensional configurations [9,33]. These results were complemented by quantum-chemical investigations of larger clusters [34].

The role of hydrogen bonding as a directional and cooperative interaction has been extensively studied [18,35], showing that intermolecular distances and structural organization are strongly influenced by collective effects.

In this context, a comprehensive synthesis of experimental and theoretical results was provided, including diffraction-based distances ($\sim 2.8 \text{ \AA}$) and coordination shells ($\sim 4.5 \text{ \AA}$ and $\sim 6.7 \text{ \AA}$), which serve as an empirical basis for structural modeling [36].

RDF analysis reveals well-defined peaks at approximately $2.8 \text{ \AA}$, $4.5 \text{ \AA}$, and $6.7 \text{ \AA}$, corresponding to successive coordination shells in the hydrogen-bonded network of wa-

ter [24,29]. The first peak defines the characteristic nearest-neighbor O···O distance, l , while the higher-order peaks reflect the intrinsic three-dimensional tetrahedral organization of the network, rather than simple integer multiples of l [23]. These results establish an experimental structural framework that supports the interpretation of the geometric index $S_n = d/l$ as a dimensionless descriptor of cluster organization, linking diffraction-derived spatial correlations with the geometric evolution of water clusters [33].

Importantly, the present geometric description provides a direct link between these experimentally observed distances and the topology of small water clusters. While the higher-order RDF peaks are typically interpreted as signatures of tetrahedral ordering, here they are additionally viewed as emergent consequences of underlying structural motifs.

In this framework, clusters (trimer, tetramer, pentamer) represent minimal geometric units that reproduce the local ordering reflected in the RDF. The geometric index $S_n = \frac{d}{l}$ introduces a dimensionless parameter that connects intermolecular spacing (from diffraction data) with cluster topology (from geometric framework).

This establishes a conceptual bridge between real-space structural correlations and descriptive cluster geometry, suggesting that the evolution of S_n is consistent with the transition from discrete molecular aggregates to a cooperative hydrogen-bond network.

3.5. EIS Analysis of Hydrogen-Bond Network Dynamics near Freezing

To evaluate the behavior of the hydrogen-bond network in the vicinity of the phase transition and to test the validity of the proposed geometric description under boundary conditions, electrochemical impedance spectroscopy (EIS) was applied at temperatures around the freezing point [7].

The EIS results reveal clear differences between the freezing states within a narrow temperature interval around 0 °C. The formation of Ice I_h -type clusters during freezing can be considered a limiting case of the proposed hydrogen-bond description. In this state, the hydrogen-bond network attains a highly developed three-dimensional tetrahedral organization, indicative of a high degree of cooperativity.

Quantitative analysis of the EIS data shows that at -0.1 °C, higher values of the real part of the impedance Z' , as well as the impedance modulus $|Z|$, are observed compared to the state after thawing at $+0.1$ °C [7]. This corresponds to reduced charge-carrier mobility and limited transport, characteristic of a more ordered, structurally stable hydrogen-bond network. In addition, the relaxation time $\tau = 1/2\pi f_{\max}$ [37] is larger at -0.1 °C, indicating slower structural dynamics.

At $+0.1$ °C during thawing, a decrease in Z' and $|Z|$ is observed, along with a shift in the relaxation maximum toward higher frequencies (corresponding to smaller τ), indicating increased molecular mobility and partial disruption of the Ice I_h -like structure. However, differences in impedance characteristics between -0.1 °C and $+0.1$ °C at nearly identical temperatures demonstrate that the system does not transition to a fully disordered state upon melting.

The observed difference in impedance response under these conditions represents quantitative evidence of hysteresis and is consistent with the presence of reproducible structural characteristics in liquid water under the studied conditions.

Within the framework of the exponential trend, this behavior can be interpreted as a continuation of the cooperative growth observed in small water clusters ($n = 2-6$), where the transition around $n \approx 5$ marks the onset of network formation. The Ice I_h phase can be viewed as a limiting case of this process within the proposed framework.

3.6. Semi-Empirical Gibbs Free Energy Analysis

To compare the relative stabilization of small water clusters $(\text{H}_2\text{O})_n$ for $n = 2-6$, a semi-empirical stabilization parameter of the Gibbs free energy denoted as ΔG_n [11,38–40] was estimated using additive hydrogen-bond contribution and an effective entropic penalty:

A semi-empirical stabilization parameter denoted here as ΔG_n , was estimated using additive hydrogen-bond contribution and the effective entropic penalty. The quantity should be interpreted as a comparative stabilization index rather than as absolute Gibbs free energy obtained from statistical thermodynamics.

$$\Delta G_n \approx -m_n \varepsilon_{\text{HB}} + (n - 1)T\Delta S \quad (4)$$

where m_n is the number of hydrogen bonds in the cluster, ε_{HB} is the effective hydrogen-bond energy, and $T\Delta S$ represents the entropic cost of molecular ordering.

Using $\varepsilon_{\text{HB}} \approx 5$ kcal/mol and $T\Delta S \approx 2.5$ kcal/mol, the calculated values of ΔG_n show a pronounced decrease with increasing cluster size n .

The results show that $\Delta G_n < 0$ for all $n = 2-6$, indicating increasing relative stabilization within the semi-empirical geometric framework. The strongest decrease occurs between $n = 2$ and $n = 3$, corresponding to the onset of cooperative hydrogen bonding.

To further analyze the stabilization per molecule, the normalized quantity G_n/n was evaluated. This reveals a rapid decrease followed by a plateau around $n \approx 4-5$, indicating a transition from discrete cluster formation to a network-like hydrogen-bond structure. The resulting semi-empirical stabilization parameters for $n = 2-6$ are summarized in Table 4 and Figure 4.

Table 4. Variation of the semi-empirical stabilization parameter, ΔG_n with increasing cluster molecularity (n).

Cluster Size n	2	3	4	5	6
ΔG_n	−2.5	−10.0	−12.5	−15.0	−17.5

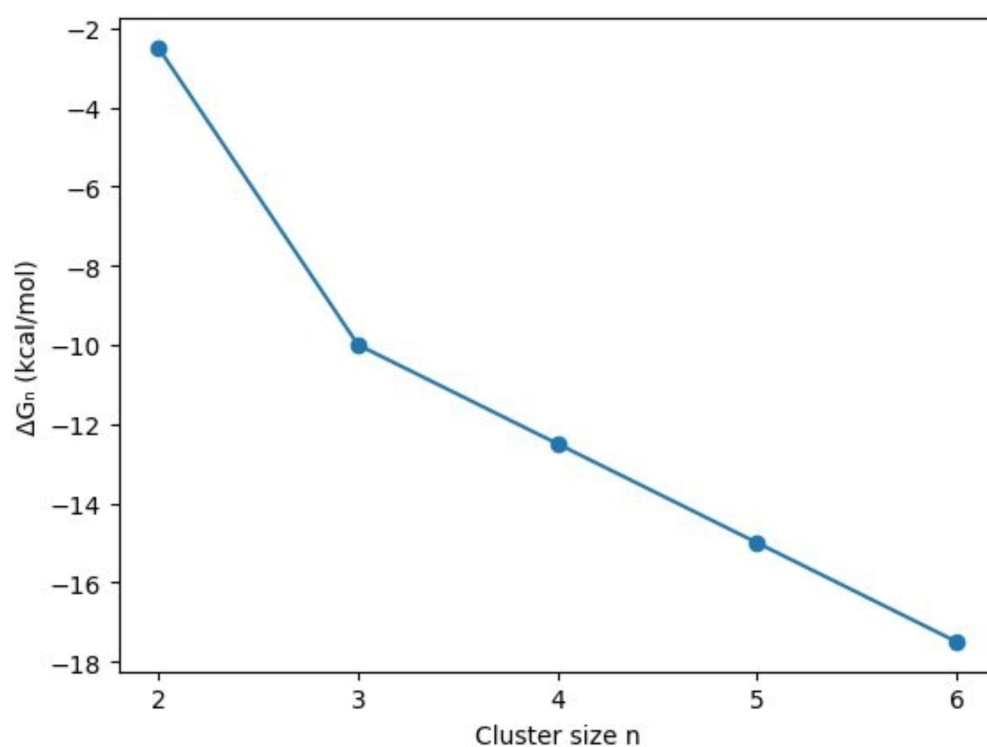


Figure 4. Semi-empirical stabilization parameter (ΔG_n) as a function of water cluster size (n).

The RDF analysis should not be interpreted as evidence that liquid water is organized as closed cyclic clusters. Liquid water is a fluctuating hydrogen-bond network with local tetrahedral coordination. Therefore, the RDF comparison is used only to connect the geometric framework with experimentally observed intermolecular distance scales, not to infer permanent cyclic cluster structures in the liquid phase.

3.7. Unified Cooperative Scaling Across Structural, Spectroscopic, and Thermodynamic Observables

The results obtained in the present study enable a direct comparison between geometric, spectroscopic, and thermodynamic descriptors of hydrogen-bond evolution in small water clusters (H₂O)_n.

A key observation is that all considered quantities—namely the geometric index S_n , the NMR chemical shift δ , and the semi-empirical Gibbs free energy ΔG_n —exhibit a consistent nonlinear dependence on cluster size within the interval $n = 2$ –6.

This behavior can be interpreted as a manifestation of a unified cooperative scaling, where different physical observables respond in a correlated manner to the progressive development of the hydrogen-bond network.

From a geometric perspective, the increase in the index $S_n = \frac{d}{l}$ reflects the expansion and reorganization of molecular configurations. In parallel, the NMR chemical shift increases due to enhanced proton deshielding, indicating stronger and more cooperative hydrogen bonding. At the same time, the decrease in ΔG_n demonstrates increasing thermodynamic stabilization of the cluster.

The simultaneous evolution of these quantities suggests that they can be viewed as different projections of a common underlying process—namely, the growth of a cooperative hydrogen-bond network.

This interpretation is further supported by comparison with quantum-chemical (MP2) data, where similar trends in structural stabilization and energy lowering are observed. The numerical similarity between the geometric scaling parameter and selected MP2-derived trends suggests a qualitative correspondence between the simplified geometric index and the structural evolution of small clusters. However, S_n should not be interpreted as a direct quantitative measure of many-body hydrogen-bond interactions.

4. Discussion

The interval $n = 2$ –6. The central descriptor of the framework is the dimensionless geometric index $S_n = \frac{d}{l}$, where d represents the center-to-molecule distance and l represents the nearest-neighbor O···O distance associated with hydrogen-bonded water molecules. In this formulation, S_n provides a compact structural descriptor linking cluster size, molecular topology, O···O intermolecular distance, and hydrogen-bond connectivity.

The main contribution of the present framework is its geometric interpretation. The increase in S_n from 0.500 for the dimer to 1.000 for the hexamer reflects progressive spatial organization of hydrogen-bonded molecular aggregates. The local exponential approximation of S_n over $n = 2$ –6 gives $RSS = 0.00039$ and $R^2 = 0.998$, supporting a local nonlinear geometric trend in the organization of small water-cluster motifs. This trend complements the nonlinear hydrogen-bond network described in Ref. [11], where NMR, DFT, and EIS descriptors revealed size-dependent hydrogen-bond behavior. Thus, Ref. [11] provides the spectroscopic and quantum-chemical basis, while the present study provides the corresponding geometric representation.

The correspondence between the geometric index and quantum-chemical O···O distances further supports the model. The calculated O···O distances remain close to the characteristic value $l \approx 2.8 \text{ \AA}$, whereas S_n increases systematically with cluster size. This

shows that the O...O distance defines the local hydrogen-bond length scale, while S_n describes how this local scale is arranged within the larger cluster geometry. Therefore, the increase in S_n reflects progressive spatial and topological organization of hydrogen-bonded water molecules.

The use of cyclic configurations for $n = 3-6$ provides framework reference structures for analyzing local hydrogen-bond geometry. These configurations allow a clear comparison between the number of water molecules, the corresponding geometric arrangement, and the development of hydrogen-bond-related O...O contacts. In this context, the trimer, tetramer, pentamer, and hexamer serve as simple reference motifs for discussing the emergence of ordered hydrogen-bond organization in small molecular aggregates.

Recent experimental and theoretical studies provide additional support for this geometric interpretation. Chen et al. identified a common ice-nucleus motif on hydrophilic and hydrophobic metal surfaces [2], while Priante et al. resolved ice nanocluster structures using atomic force microscopy [3]. Li et al. showed that nuclear quantum effects contribute to the structural evolution of neutral water clusters from planar to three-dimensional configurations [14]. Wang et al. reported structural motifs of the water undecamer cluster, $(\text{H}_2\text{O})_{11}$ [15], and Xie et al. demonstrated size-dependent stabilization and ion-pair formation in $\text{HCl}(\text{H}_2\text{O})_n$ clusters [8]. Together, these studies support the importance of cluster size, hydrogen-bond connectivity, and recurring structural motifs in water-cluster organization.

The interpretation is also consistent with modern descriptions of liquid water as a dynamic hydrogen-bonded network. Gao et al. applied hierarchical clustering methods to hydrogen-bond networks in liquid water [16] and later described water clusters and density fluctuations using extended hierarchical clustering methods [17]. Lin et al. investigated molecular aggregation in liquid water through Laplace spectra and spectral clustering of the hydrogen-bonded network [26]. These studies support the use of cluster-like descriptions as structural and topological tools for analyzing local organization in liquid water.

Spectroscopic and local-environment studies further strengthen this interpretation. Pérez et al. related O-H stretching-frequency fluctuations to hydrogen-bond strength, charge transfer, and local solvent reorganization in liquid water [25]. Huš and Urbič showed that hydrogen-bond strength depends on intermolecular O...O distance, molecular orientation, and local environment [27]. Oka et al. demonstrated that long-lived water clusters can be characterized by standard ^1H NMR techniques in hydrophobic solvents under ambient conditions [41,42]. These works support the relevance of O...O distance, local molecular environment, and NMR-sensitive descriptors for analyzing water-cluster organization.

Taken together, these results show that the proposed geometric description provides a coherent structural framework for identifying regularities in hydrogen-bond organization. NMR chemical shifts, FT-IR vibrational behavior, RDF-derived O...O distances, DFT/MP2 structural data, semi-empirical stabilization trends, and clustering studies describe complementary aspects of the same broader process: the progressive organization of hydrogen-bonded water molecules. The geometric framework therefore offers a useful structural bridge between descriptive small-cluster geometries and hydrogen-bonded network organization in water.

5. Conclusions

The present study introduces a geometry-based framework for describing hydrogen-bond organization in small water clusters, $(\text{H}_2\text{O})_n$, over the interval $n = 2-6$. The central element of the geometric description is the dimensionless geometric index $S_n = \frac{d}{l}$, where d represents the center-to-molecule distance and l represents the nearest-neighbor O...O distance associated with hydrogen-bonded water molecules.

The obtained values of S_n show a clear local nonlinear geometric trend with increasing cluster size. The monotonic increase from the dimer to the hexamer, together with the

non-uniform increments between consecutive cluster sizes, indicates progressive structural organization of hydrogen-bonded molecular aggregates. This behavior supports the interpretation that small water clusters exhibit regular size-dependent geometric development associated with increasing hydrogen-bond connectivity.

The present model extends the nonlinear hydrogen-bond network described in Ref. [11]. In that study, NMR, DFT, and EIS descriptors revealed nonlinear behavior in the organization of hydrogen-bonded water systems. The present work adds a geometric representation of this behavior through the index $S_n = d/l$. In this way, Ref. [11] provides the spectroscopic and quantum-chemical basis, while the present study provides the corresponding geometric interpretation.

The comparison with NMR chemical shifts, FT-IR vibrational behavior, RDF-derived O...O distances, DFT/MP2 structural data, and semi-empirical stabilization trends shows that these descriptors reflect complementary aspects of hydrogen-bond organization. Their qualitative agreement with the S_n trend supports the view that the geometric evolution of small water clusters follows a regular pattern linked to the progressive development of hydrogen-bonded arrangements.

The discussion of recent studies on hierarchical clustering, spectral clustering, molecular aggregation, water clusters in liquid water, and NMR-resolved long-lived water clusters in hydrophobic conditions further strengthens the structural interpretation of the framework. These studies show that hydrogen-bonded water systems can be described through local molecular motifs, transient cluster-like domains, and organized network regions in liquid-phase environments.

The comparison with MP2 O...O distances confirms that the geometric description is physically connected to the local donor–acceptor geometry of hydrogen-bonded water molecules. While the O...O distances remain confined around $l \approx 2.8$ Å, the exponential trend is expressed primarily by the geometric index S_n , indicating progressive spatial organization of the water-cluster motifs.

Overall, the proposed geometric description provides a compact geometric framework for identifying regularities in the organization of hydrogen bonds and small water clusters. The approach links cluster geometry, O...O intermolecular distance, and hydrogen-bond connectivity, and offers a useful structural bridge between descriptive small-cluster models and broader hydrogen-bonded networks.

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