Structure features of hydrogen bonding and their signatures in vibrational dynamics

Yulia V. Novakovskaya

Lomonosov Moscow State University, Chemistry Department, http://www.chem.msu.ru/
Moscow 119991, Russian Federation
E-mail: jvn@phys.chem.msu.ru
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Abstract. Nonempirical simulations of molecular clusters composed of water, ammonia, and hydrogen fluoride carried out at the Moeller-Plesset (MP2) level with 6-31++G(d,p) basis set provided information about electronic-structure peculiarities of hydrogen bonding and frequency ranges of phase and anti-phase H-bond proton oscillations. Combined analysis of H-bond orbitals and bridge-proton migration paths in closed H-bonded sequences confirmed the concept of π-kind conjugation of hydrogen bonds when they are alternating with covalent bonds and revealed the unique characteristic frequency range of bridge proton oscillations in conjugated H-bonded structural rings.

Keywords: hydrogen bonds; conjugation; H-bond network; water; ammonia; hydrogen fluoride; H-bond orbitals; H-bond energy; electrostatic potential; consistent vibrations; bridge protons; characteristic frequency range

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1. INTRODUCTION
On one hand, engineering and technology transfer to micro- and nanoscale is predetermined by the possibilities of modern science in modeling and designing systems of such sizes and, at the same time, it is an indispensable part of the progress in studying mechanisms of various processes that proceed in nature including living organisms. In almost all the natural systems, it is hydrogen bonds that play a key role in the stabilization of states and transformation channels; and seemingly by the present moment there is nearly complete information about this kind of bonds and the ways they are involved in various chemical reactions of primarily redox type and conjugate charge transfer stages. However, despite a century-long story of studies since the first allusion about molecular joining via peculiar intermolecular bonds [1, 2], the data about dynamic peculiarities of hydrogen-bonded systems (which are crucial in view of the reaction mechanisms in such systems) are still incomplete and segmentary.

It was Pauling who suggested a clear concept of hydrogen bonding nearly a quarter of a century after the appearance of a hypothesis about such interactions [3]. In subsequent eighty years, it was supplemented and made more accurate due to the extending possibilities of experimental techniques and, later on, computer simulations aimed at studying the systems stabilized by hydrogen bonds (see [4, 5] and refs. therein). Effects caused by the existence of hydrogen bonds between particles either in solids, liquids, or gas-phase molecular agglomerates manifest
themselves in nearly all the kinds of experiments, whether this be a conventional thermochemical determination of the temperature and heat of a phase transition or a modern investigation of the charge transfer processes based on the data of nuclear magnetic resonance. Spectral manifestations of hydrogen bonds are also well known and included in a list of characteristics that supplements the definition recommended by IUPAC: the formation of an X-H...Y hydrogen bond is accompanied by a decrease in the X-H stretching vibration frequency, an increase in its signal in the infrared absorption spectrum, and the appearance of additional spectral lines [6]. It is realized and widely accepted that hydrogen bonds are directional interactions and, in many situations, they are joined in a spatial network characterized by cooperativity, which is manifested in deviations of a number of properties from those expected for the ensembles with additive pair-wise potentials.

The latter means that, being directional, these interactions are nonlocal. Insofar as the character of physical interactions is predetermined by the forces acting; and the forces in turn depend on the potentials produced by particles, the potentials should be unique in their spatial characteristics. In the case of any particle or functional group that can form hydrogen bonds, they should have a pronounced angular dependence, and, at the same time, be complementary for several particles when these are collected within a relatively small room; and the number of stable contact segments of one particle with its neighbors should be variable, typically in a range of two to four, which corresponds to the formation of one- (1D) to three-dimensional (3D) structures. Furthermore, cooperativity phenomenon implies not only the static correlation between the states of particles, i.e., their charge distributions, but also (and this is very important) the dynamic consistency of their motion, since it is the latter that provides the redistribution of an external perturbative effect of e.g. vibrational excitation (its delocalization), so that a single-particle effect is much (sometimes logarithmically) weaker than the total one. It is this ability that provides a substantial increase in the lifetimes of hydrogen-bonded clusters and agglomerates compared to the lifetimes of individual hydrogen bonds. In the case of water molecules, the increase is as large as an order of magnitude [7-9]. Such a noticeable effect can solely be due to the aforementioned consistent dynamics of an H-bonded ensemble. Insofar as the dynamic features are determined by the existing potential forces and manifested in spectral characteristics, the main attention in this paper is paid to the charge distribution peculiarities of the molecules joined in an H-bonded structure and their vibrational states.

2. NONEMPIRICAL MODELS AND METHODS

A reasonable and founded picture of the dynamic properties of H-bonded molecular agglomerates can be obtained only when data retrieved from experimental spectra are considered in combination with the theoretical predictions. Experimental peaks can by no means be reliably assigned with no reference to model constructs, the correctness of which is checked by comparing to experimental observations.

The main objects in this study are clusters composed of water molecules, which are the most widely spread blocks in natural biological systems, as well as ammonia and hydrogen fluoride. Along with fluoride-containing groups (which are less typical of living species and organisms) it is OH and NH fragments that are most susceptible to the formation of strong hydrogen bonds.

Data discussed in the paper were obtained as a result of nonempirical quantum chemical modeling of the systems with the use of the second order of the Moeller-Plesset perturbation theory (MP2) and an extended
Gaussian-type basis set of double-zeta quality (6-31++G(d,p)). The approximation enables one to reproduce reliably the electron density distribution in the systems of interest, as well as its redistribution that accompanies changes in intermolecular interactions. The basis is sufficiently flexible even in the case of small agglomerates and, at the same time, relatively compact to avoid the linear dependence in large systems. Besides that, the level selected provides a correct dependence of atomic forces on the distortion and mutual arrangement of particles involved in the system, which is crucial in predicting frequencies of vibrational motions. Frequencies themselves were estimated in harmonic approximation and corrected with the use of the following scaling factors (for the stretching vibrations): 0.945 for water; 0.962 for hydrogen fluoride; 0.933 for ammonia.

All quantum chemical simulations were carried out with the use of Firefly 8.2 program package [10] and visualized with Chemcraft graphical software [11].

3. RESULTS AND DISCUSSION

Structure and peculiarities of the electron density distribution of H-bonded ensembles

Thorough analysis of the character of bonding orbitals in the clusters composed of water, ammonia, and hydrogen fluoride molecules enabled us to suggest a more accurate and complete definition of hydrogen bonds [12]: “The hydrogen bond is a hydrogen atom-mediated intermolecular (or interfragment within the same molecule) bond between two electronegative atoms or atomic groups that have valence electron density uninvolved in the formation of intramolecular covalent bonds”. This definition differs from the one recommended by IUPAC, which sounds as follows: “The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation” [6]. The main difference is in the clear indication of the bonding character that is determined by overlapping of those orbitals, which describe spatial distributions of the electrons uninvolved in intramolecular bonds, and the role of hydrogen atom, which (due to its sole electron affected by a localized proton charge) acts as a sort of anchorage of the “electronic bridge” formed between the two electronegative (and typically negatively charged) atoms or atomic groups. Furthermore, insofar as the electrons uninvolved in intramolecular bonds are usually lone pair electrons with a spatial character of p type in the case of the second row elements (oxygen, nitrogen, fluorine), such orbitals can overlap according to either σ- or π-kind. And the principal variant that takes place when individual hydrogen bonds are formed is that of π-kind [12].

In fact, the formation of hydrogen bonds can be treated similarly to the conventional MO LCAO approximation when molecular orbitals are represented by linear combinations of atomic orbitals. The sole difference is that now it is molecular orbitals of individual non-interacting molecules that serve as a basis set, and the approximated functions are orbitals of the cluster composed of such molecules. Taking into account that intermolecular bonds including hydrogen bonds are usually much weaker than intramolecular covalent ones, the approximation is quite founded. π-kind overlapping of the lone pair orbitals of e.g. oxygen atoms of the neighboring water molecules results in the formation of cluster orbitals, the electron density minimum of which is located at the midpoint of OO space interval closely to the position of the bridge proton.

The number of close neighbors is determined by the electrostatic potential of
an individual water molecule shown in Fig. 1. It is this potential with pronounced maxima of positive values at the extension of O-H bond lines and minima of the negative values in a normal direction that predetermines the nearly tetrahedral coordination of the adjacent particles, two of which can act as H-bond proton acceptors being oriented to the maxima of the positive potential values, while the two residual can be H-bond proton donors being oriented to the minima of the negative potential values. As follows from Fig. 1, equipotential domains apparently embrace the water molecule from opposite sides as two half-arcs with different cross-sections and curvatures, which makes it possible to coordinate molecular partners not only accurately along the aforementioned directions but also at a certain deviation from them. That is why hydrogen bonds are relatively labile, and O-H...O or O-H...N angles can differ from the straight one by as much as 30-40º at a concurrent deviation of H...O-H or H...N-H angles from tetrahedral one by as much as 15-20º. Such a distortion undoubtedly causes a decrease in the interaction energy because of the lower electron density fraction spent on the formation of adjacent hydrogen bonds; but the bonds still do exist and restrict individual mobility of the molecules due to the consistency in their motion. For example,

The restricted freedom in the mutual orientation of molecules provides also the joining of ring-like fragments into three-dimensional cages where the close neighbors of a selected molecule are located within the aforementioned spatial segments but not necessarily along their central lines. For example, tetra-, penta-, and hexamolecular rings can serve as building blocks in constructing either a cubic octamer or a cage-like dodecamer, in which angles between the adjacent faces are all about 90º (at $n = 8$) or fall in a relatively broad range from 90º to 126º being on the average close to tetrahedral one (at $n = 12$, Fig. 2).

More detailed information about the character of the electronic binding within the H-bond domains can be retrieved from the analysis of the corresponding orbitals. Fig. 3 shows H-bond orbitals of $(\text{H}_2\text{O})_n$ clusters with $n = 4$ and 8. In the tetramolecular system, there is a pronounced $\pi$-binding. Moreover, orbitals of the neighboring hydrogen bonds overlap in such a way that a conjugate system typical of
π-binding is formed. These are four orbitals, one of which ($\phi_1$) is purely bonding, two are nonbonding (one of them, $\phi_2$, is shown in the figure), and one antibonding ($\phi_3$). In a cubic octamer composed of six fused tetramolecular faces, π-bonding orbitals of the upper and lower faces form a sandwich structure ($\phi_1$), which (conditionally) can be interpreted as representing a π-stacking interaction of the corresponding electron density distributions of the tetramolecular rings. In the vertical direction, that is within the side faces of the cube, the same orbital provides σ-binding at the O-H...O edges. Another cluster orbital of the octamer shown ($\phi_2$) is close to nonbonding and looks like a combination of π-bonding orbitals of the side faces and, at the same time, σ-antibonding within the horizontal O-H...O edges of the cube. These two clusters, tetramer and octamer, were selected for the illustration of electronic binding for the most clear character of their orbitals (predetermined by the spatial symmetry of the clusters) that reflects features inherent in almost any larger water cluster, as well as clusters composed of particles of another chemical nature.

Among all cluster systems stabilized by hydrogen bonds, the most stable ones are those with the aforementioned delocalization or conjugation of H-bond orbitals. A necessary condition for the delocalization is the spatial closeness of two adjacent hydrogen bonds when they are separated with only one covalent bond so that a sequence of alternating covalent and hydrogen bonds of $(R_1)X_1-H...(R_2)X_2-H...(R_3)X_3-H...$ kind, where $X_i$ are electronegative atoms (O, N, F), and $R_i$ are some atoms or atomic groups (such as hydrogen atoms in the case of water molecules or $CH_3CH_2$ radicals in the case of ethanol, etc.) can be distinguished. The most stable configurations of clusters (or, in other words, the strongest networks of hydrogen bonds) are characterized by the largest extent of conjugated H-bonded segments when the corresponding sequences embrace the whole structure.

Besides that, depending on the chemical composition of the molecules involved in hydrogen bonds, the corresponding conjugated chains can form 2D or 3D networks. A hydroxyl group can form two bonds as a proton acceptor and one bond as a donor. By contrast, amino group can be a double proton donor and a single acceptor. The closer the groups to each other, the stronger the correlation in the H-bonds formed. Therefore, water molecules, which can be involved in up to four hydrogen bonds with the neighbors (two as proton donors and two as acceptors), are unique as 3D-network units. For example, in $I_h$ ice, one can distinguish repeatedly intersecting open conjugated bond chains. At the same time, hydrogen fluoride molecules, which can typically form no more than two hydrogen bonds (one as a proton donor and one as an acceptor) because of the peculiarities in the electron density distribution, form closed folded sequences of conjugated H-bonds, which only weakly interact with each other, so that, in a molecular ensemble, one can distinguish nearly parallel two-dimensional
segmented H-bonded layers with a substantial reciprocal translation mobility (Fig. 4).

The length of conjugated H-bonded chains and their branch extension in a 3D space predetermine the correlation of states of the constituting molecules, not only stationary correlation, which can be judged from the bond energies, but also dynamic one, which can be deduced from the shapes and frequencies of vibrations of the corresponding agglomerates.

**Frequencies of vibrations characteristic of the conjugated H-bond sequences**

Insofar as water molecules are unique building blocks of conjugated bond networks, it is (H\textsubscript{2}O\textsuperscript{n}) water clusters that are the most convenient species for the analysis of the consistent vibrational motions in the ensembles of H-bonded particles.

An individual water molecule has three vibrational degrees of freedom, namely, one bending and two stretching (symmetric and antisymmetric) modes. When several molecules approach each other, their nuclear states (as any other quantum eigenstates) begin to interact. The most substantial effect is apparently observed in the case of bridge proton motions (motions of the nuclei of hydrogen atoms involved in hydrogen bonds).

Based on general concepts of quantum mechanics, one could expect to observe the following picture. When \( n \) molecules approach each other in such a way that their close neighborhoods are similar, as in the case of ring-like (H\textsubscript{2}O\textsuperscript{n}) water clusters where any molecule acts as a single proton donor and a single proton acceptor in its two hydrogen bonds with the neighbors, \( n \)-fold degenerate vibration of any kind (e.g., \( Q_{s1} \),... \( Q_{sn} \), where the subscript enumerates variables that represent symmetric stretching vibrations of \( n \) individual water molecules) should transform into \( n \) non-degenerate (when there is no or low spatial symmetry of the whole cluster structure) vibrational states, and the shapes of the resulting vibrations can be approximated by the following linear combinations:

\[
\sum_{i=1}^{n} c_{si} Q_{si} + \sum_{i=2}^{n} c_{s2} Q_{s2} + \cdots \sum_{i=n}^{n} c_{sn} Q_{sn},
\]

where nonzero \( c_{si} \) amplitudes are comparable in absolute values. When the molecules approach each other in such a way that the perturbation of their individual electrostatic potentials (charge distributions) produced by the neighboring particles is different, or when similar perturbations affect the charge distributions of the spatially distant molecules, the interaction of the quantum states of the particles is less pronounced, and the resulting linear combinations of variables that represent shapes of cluster vibrations involve substantially different amplitudes of the motions of different molecules. This should lead to the appearance of noticeably localized vibrational states of a molecular ensemble, and a certain fraction of states may be degenerate. The same frequency should be typical of the vibrations of those molecules which have similar spatial neighborhoods. This is the general solution of the vibrational problem in the absence of a noticeable interaction between the motions of substantially different frequencies.

On the whole, the solution of the vibrational problem for water clusters in a harmonic approximation (when potential energy dependence on any Cartesian or internal coordinate is assumed to be nearly quadratic)
is of this very kind. As an example, Fig. 5 shows shapes and frequencies of some normal (harmonic) vibrations of water tetramer and dodecamer, which are superpositions of the bridge proton oscillations. Note that tetramer is a structure of the former kind where all molecules have similar coordination neighborhoods of $da$ kind (any molecule acts as a single donor, $d$, and a single acceptor, $a$, of H-bond protons). Dodecamer is a relatively small representative of the latter kind systems. It involves two bicoordinate molecules of $da$ kind, five tricoordinate molecules of $daa$ kind and the same number of $dda$ molecules. Here, molecules with the same coordination neighborhood are never close neighbors. According to these structure features, frequencies of the H-bond proton oscillations noticeably differ.

There are tri- and bimolecular sequences of $daa$ and $da$ molecules in dodecamer. In-phase vibrations of bridge protons within such sequences are observed in a frequency range of 3065–3084 (Fig. 5b1) and at 3270 cm$^{-1}$ while their anti-phase vibrations have frequencies around 3185 cm$^{-1}$. Values of 3120 (Fig. 5b2) and 3158 cm$^{-1}$ correspond to proton vibrations in $da$ and $dda$ molecules surrounded with $dda$ molecules exclusively. At still higher frequencies starting from 3370 cm$^{-1}$, bridge protons of $dda$ molecules are already involved in stretching vibrations. Symmetric oscillations of both bridge protons in such molecules have frequencies of 3454–3510 cm$^{-1}$, while those of their antisymmetric vibrations are 3535–3615 cm$^{-1}$. The highest frequencies (3690–3710 cm$^{-1}$) correspond to the vibrations of those protons of seven $da$ and $daa$ molecules, which are not involved in hydrogen bond formation. Thus, in this approximation, consistent vibrational motions are observed only for those molecules which being single proton donors in H-bonds are neighboring in the bond sequences.

In tetramer where all molecules have the same coordination neighborhood, there are four harmonic vibrations, the shapes of which are described by Eq. (1), namely, in-phase oscillations of all four bridge protons (3308 cm$^{-1}$, Fig. 5a1), two degenerate motions when bridge protons of two opposite molecules shift in anti-phase (3386 cm$^{-1}$, Fig. 5a2), and oscillations of all bridge protons when lengths of any two adjacent bonds change in an opposite way (3420 cm$^{-1}$, Fig. 5a3). Around 3713–3714 cm$^{-1}$, one can see nearly degenerate vibrations of the nuclei of those hydrogen atoms which are not involved in hydrogen bonds.

These two examples illustrate important conclusions. First of all, oscillations of bridge protons interact much more strongly compared to the motions of protons uninvolved in hydrogen bonds. If molecules, which have the same number of bridge protons, are successive units of a conjugate sequence, oscillations of their bridge protons are consistent and characterized by the lowest frequencies. The latter peculiarity is typical of conjugation effects in organic molecules, especially aromatic systems; and consistent oscillations of bridge protons in a water hexamer ring (the regularity of changes in hydrogen bond lengths) accurately coincide in shape with the stretching vibrations of $C\cdot C$ bonds of benzene.
As can be seen, the regularities of vibrational dynamics of water clusters discovered in a harmonic approximation are restricted to those fragments of conjugated H-bond sequences that are composed of molecules, which supply the same number of H-atoms to the hydrogen-bond network. Such sequences prevail in defect-free ice specimens, and their extension equals the total linear size of the specimen. Taking into account that in this situation, deviations of the vibrations of all molecules from harmonicity should be the same, it is possible to apply the results of the above general consideration. Then, a reason for strength of ice becomes natural despite its low molecular packing density and the existence of cavities that potentially can be occupied by water molecules, if the latter could slip into them. However, such possibility is seemingly absent. Moreover, the energy of any local perturbation of the system should rapidly be redistributed along all conjugated H-bond sequences that embrace the whole defect-free structure segment.

Then, what are the basic dynamic features of the systems which involve relatively large number of defects and where coordination neighborhoods of the neighboring molecules (as follows from the above analysis of the electrostatic potential of an individual molecule) can vary in broad limits? In such an ensemble of H-bonded molecules, nuclear oscillations scarcely obey a harmonic law, and the deviations (which is essential) are different for different molecules. The actual character of motions can be discovered if one considers a minimum-energy path that corresponds to a forced shift of one H-bond proton. Because of the aforementioned delocalization of H-bond orbitals and the corresponding correlation in the states (positions) of the successively arranged bridge protons, a shift of one of them should promote shifts of its neighbors. When the H-bonded sequence is closed, all bridge protons should change their positions.

Typical energy profile of such path is shown in Fig. 6.

In tetramer where all molecules have the same coordination neighborhood, the expected character of the effective coordinate of the process in question should be a consistent shift of all bridge protons between the oxygen nuclei of the neighboring water molecules according to the shape of a synchronous vibration with a frequency of 3308 cm\(^{-1}\). However, the actual coordinate is a superposition of this motion and a synchronous change in the O...O distances, i.e., compression/extension of the oxygen skeleton of the cluster. Around minimum-energy (stable) configurations, which are the original conformer and its mirror image, it is the size change of the molecular ring that prevails. The ring is compressed when the system moves toward the potential energy barrier. Only at a half-height of the barrier, when the distances between oxygen nuclei are shortened from the initial 2.74 to 2.41 Å, shifts of bridge protons toward the midpoints of O...O edges begin to contribute substantially to the effective coordinate. From the dynamic point of view, this means that there is a strong interaction between the two types of motions, namely oscillations of bridge protons with a frequency above 3300 cm\(^{-1}\) and breathing.
vibrations of the whole molecular structure, whose frequencies are close to 200 cm\(^{-1}\) in a harmonic approximation. Numerical solution of the corresponding 1D stationary quantum problem about the states of an effective system in the constructed potential enabled us [13] to determine the vibrational state spectrum of the system and estimate the anharmonic frequency of bridge proton oscillations as 3212 cm\(^{-1}\), which is noticeably lower (by 100 cm\(^{-1}\)) than the scaled harmonic frequency. Another interpretation may be as follows: a proper scaling factor that should be used in the case of consistent oscillations of bridge protons in closed conjugated H-bonded sequences should be about 0.92. Note that the factor compensates for two errors, namely, an error in solving electronic problem within a certain approximation and an error in solving nuclear problem at an assumption of a nearly quadratic potential energy dependence on the distortions of nuclear configuration. Then, at the same error in the electronic problem solution (which is natural in the systems in question), the smaller scaling factor means that there is strong coupling of certain motions, which is actually illustrated by the character of the effective coordinate of the consistent proton-shift process.

In dodecamer structure, which involves no closed sequences of molecules of the same coordination neighborhood, but involves two hexamolecular rings with conjugated H-bonds (with the same, e.g., clock-wise orientation of all H-bonds), the effective coordinate of the process is similar to that discovered in tetramer: all bridge protons are shifted despite large differences in their vibration frequencies. However, because of the differences in the local neighborhoods of the molecules within the ring and, hence, in their local electrostatic potentials, the shifts of bridge protons are not equal and uniform. In the transition-state structure, they find themselves closer to one of the neighboring oxygen nuclei rather than at a midpoint between them. If we were following dynamic changes in the cluster, we would say that bridge protons are moving at different velocities (because of the differences in the potential energy derivatives which predetermine forces that act on protons). It is \textit{dla} molecules that more tightly bind protons, both their own, which cannot move rapidly far from them, and the neighboring, which, by contrast, move at a higher velocity toward them. Molecules of \textit{dla} kind behave in an opposite way: their own protons detach more rapidly compared to the approaching of the neighboring ones. In the vibrational state spectrum found numerically for this potential, the lowest states (similarly to tetramer) correspond to the prevailing distortion of the oxygen skeleton. The state which represents an already noticeable shift of bridge protons has energy of 3127 cm\(^{-1}\). This value, which can be referred to as the anharmonic frequency of consistent bridge proton oscillations is, on one hand, lower than a similar value in the individual tetramolecular ring by almost 100 cm\(^{-1}\) and, at the same time, intermediate between the lowest values of 3065-3084 cm\(^{-1}\) and the highest value of 3270 cm\(^{-1}\) obtained as a result of normal-coordinate analysis for the in-phase bridge proton vibrations within the conjugated bi- and trimolecular sequences of the dodecamer. The value is actually very close to an arithmetic mean of the frequencies of all in-phase motions in the ring considered.

The latter means that the harmonic analysis supplemented with proper scaling of the frequencies can reliably be used for predicting spectral signatures of conjugated H-bond sequences in the case of large molecular ensembles, for which accurate anharmonic frequencies can scarcely be obtained. In water clusters where most of molecules are tri- and tetra-coordinate, these are frequencies in a range of 3130-3230 cm\(^{-1}\).

Similar ranges can be found for the clusters composed of molecules of another chemical nature as well. For example, in the aforementioned hydrogen fluoride clusters...
where all molecules are of *da* kind, and any closed sequence of bonded molecules involves only similarly oriented units (H-bonds), the following trend can be discovered. All clusters have a normal vibration that is a synchronous oscillation of all bridge protons. In the rings that comprise no less than eight molecules, one can also distinguish vibrations when only a part of bridge protons oscillate around equilibrium positions; and typically there are two or more such segments of the whole ring which are separated with the molecules which do not practically move, while consistent oscillations of protons within neighboring segments proceed either in phase or anti-phase with respect to each other. For example, in a dodecamer ring, one can see such motions (i) within two pentamolecular segments separated with two immobile molecules; (ii) within alternating tri-molecular and monomolecular segments separated with four immobile molecules; (iii) within four bimolecular segments separated with four immobile molecules; and finally (iv) within six monomolecular segments separated with six almost immobile molecules. All the motions of the latter kinds, which are consistent within short-molecular chains at a dynamic correlation between the chains, have definitely higher frequencies compared to the consistent motion of all the bridge protons in the whole H-bonded ring. In the dodecamer, the frequencies are 3089 cm\(^{-1}\) for the latter kind motion and (i) 3147, (ii) 3238, (iii) 3293, and (iv) 3354 cm\(^{-1}\) for the above listed motions at the in-phase oscillations within the neighboring segments. These motions strongly correlate with the character of \(\pi\)-binding orbitals of this cluster, among which there are completely bonding one and those partially bonding with four or six zero surfaces, which accurately separate the aforementioned segments where consistent bridge proton oscillations take place.

It is worth noting also that the frequencies of consistent vibrations of bridge protons in \((\text{HF})_n\) rings decrease with an increase in \(n\), and already at about \(n = 10\) reach an asymptotic value about 3085 cm\(^{-1}\) (see Fig. 7). The value is close to the discovered range of consistent motions of H-bond protons in water clusters. If we additionally take into account that the highest mean H-bond energy is typical of a hexamolecular ring (about 9.2 kcal/mol versus only 8.3 kcal/mol in a nonamolecular ring), and the frequency in \((\text{HF})_6\) equals 3146 cm\(^{-1}\), we can state that characteristic frequencies of the consistent bridge proton motions in conjugated molecular rings of hydrogen fluoride should fall in a range of 3085-3150 cm\(^{-1}\). This range is not only close, but already overlaps with that of water clusters despite numerous differences between the H-bonded systems, including different coordination neighborhoods of HF and \(\text{H}_2\text{O}\) molecules involved in the conjugated rings and substantially different vibrational frequencies of the individual molecules. The latter experimental values are 3657 and 3756 cm\(^{-1}\) in \(\text{H}_2\text{O}\) and 3961 cm\(^{-1}\) in HF. Note that it is HF molecule where the monomolecular frequency is higher, and \((\text{HF})_n\) clusters where the frequency is lower. This means that when one speaks about the bridge proton vibrations, it is \(\pi\)-binding that determines not only the character (shapes) of motions, but also their frequencies; and the chemical nature of the adjacent functional group and even the nature of the electronegative atom play only a secondary role.

An additional example in support of the statement is provided by small rings composed of ammonia molecules. In the tri-, tetra-, penta-,
and hexamolecular rings, the consistent bridge proton oscillations proceed at frequencies of 3240, 3204, 3200, and 3182 cm$^{-1}$ respectively. Note that in individual ammonia molecule, stretching vibrations are characterized by frequencies of 3337 (symmetric) and 3444 cm$^{-1}$ (degenerate); the molecules form hydrogen bonds that are weaker compared to those of water and hydrogen fluoride; and π-binding delocalization is less substantial because of the lower electron density spent on the bond formation. In ammonia clusters, pentamolecular ring seems the largest possible: already hexameric ring is so noticeably folded that looks like a bath with side walls nearly normal to the bottom and parallel to each other, with weak additional H-contacts between molecules at distances larger than 2.5 Å. Moreover, ammonia molecules cannot act as fully valid joints in a 3D network. Therefore, it is reasonable to speak about characteristic frequency range of the consistent bridge proton oscillations within conjugated H-bonded rings based on the data of small ammonia clusters. Then, the range can be estimated as 3180-3200 cm$^{-1}$, which is a middle subrange of that typical of water clusters above the one found for hydrogen fluoride.

4. CONCLUSIONS
Analysis of hydrogen-bonded clusters of diverse molecules (water, hydrogen fluoride, and ammonia) enabled us to distinguish structural and dynamic features of a particular kind of hydrogen bonding referred to as conjugated H-bond network. In accurate agreement with the classical concept of conjugation elaborated in organic chemistry, conjugation of H-bonds appears when they are alternating with covalent bonds within extended structure segments. It is due to the π-kind bonds within the X-H...Y fragments between electronegative X and Y atoms or atomic groups that can spend their p-kind lone pair electrons on the binding. The alternation of covalent and hydrogen bonds provides the spatial closeness of successive π-bound fragments, so that a delocalization takes place. This peculiarity predetermines the correlation in states and positions of bridge protons within such conjugated polymolecular segments. The most interesting picture is observed when the conjugated sequences are closed rings. In any such ring, there is a consistent vibration of all bridge protons (whose amplitudes may differ because of the differences in the local electrostatic potentials determined by the coordination neighborhoods of the molecules), and the vibrations always fall in a range of 3080-3230 cm$^{-1}$, the lower part of the interval being characteristic of strongly coupled hydrogen bonds in water and hydrogen fluoride, while the upper part being typical of relatively weak bonds in ammonia and small water rings.

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