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PROPERTIES OF ICE AND FROZEN GROUND

INVESTIGATING THE STRUCTURE AND PROPERTIES OF ICE-LIKE SYSTEMS: A NOVEL APPROACH

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A novel combinatorial topological approach is suggested to investigate the structure and properties of ice and other ice-like systems. The approach is based on discrete models of molecular interaction, as well as on combinatorial optimization algorithms, and provides a general idea of the energetics and other properties of numerous proton configurations with different arrangements of hydrogen atoms (protons) in hydrogen bonds. The new approach was applied to develop a special crystallographic database of proton configurations for unit cells of widespread gas hydrate frameworks. A new type of hidden molecular asymmetry of ice-like systems was discovered which is caused by non-invariance of hydrogen-bound frameworks with respect to direction changes in all H-bonds. The optimal proton configurations of polyhedral water clusters has been calculated using a specially developed max-plus-algebraic method for combinatorial optimization of quasi-one-dimensional systems.

The ordinary ice is remarkable for having disordered positions of hydrogen atoms (protons). The proton positions in hydrogen bonds (H-bonds) make up a great number of configurations, and this number grows exponentially with the size of the system [*Eizenberg and Kautsman, 1975*]. Yet, the energy and other characteristics depend on the specific arrangement of protons in H-bonds. Energy difference within the set of all possible proton configurations may exceed the ice melting heat. It is extremely difficult to investigate in detail ice properties with regard to the proton positions in H-bonds. Note that the complexity of an object is defined by the minimum of information required for its detailed description [*Kolmogorov, 1965*].

A novel combinatorial topological approach suggested by *Kirov* [*2010*] to investigate the structure and properties of ice and other ice-like systems with a tetrahedral coordination of H-bonds is based on discrete models of molecular interaction. These approximate models are designed to provide a generalized idea of properties that characterize the set of all proton configurations. The discrete models of molecular interaction have a clear physical background, and this makes the new combinatorial topological approach advantageous over the more frequently used statistical approach which aims at finding formal correlation relationships between the energy (or other parameters) and the set of structural invariants.

The discrete models of molecular interaction estimate the energy of a system from the number of preferred structure fragments. The high predictive capacity and utility of the models have been validated through our collaboration with experts in quantum-chemical modeling (S.S. Xantheas, Pacific Northwest National Laboratory, USA). Figure 1 shows for polyhedral water clusters in the form of gas hydrate cavities and distributions of discrete optimized proton configurations [*Kirov et al., 2008*]. The energy detachment of these proton configurations (black fields in Fig. 1) is especially prominent in the plane "energy U – total dipole moment D". Additional geometrical optimization of proton configurations calculated from the discrete models of molecular interaction was performed using rigid intermolecular potentials. For cavity D, we used also one of the most advanced potentials (TTM2-F) that takes into account the inner degrees of freedom of molecules (Fig. 1, panel *b*). Gray points in the left in this case correspond to the configurations that lost their original polyhedral geometry on optimization.

The properties of large macroscopic samples of ice and other ice-like systems commonly do not manifest explicitly their dependence on the structure of the proton subsystem because of averaging over all possible configurations. However, in simulation with a small model cell, the result obviously depends on the position of protons in H-bonds, i.e., on the original orientation of molecules. It should be emphasized that this dependence records the real nanostructural heterogeneity of ice-like systems. A good solution for this difficulty, feasible with advanced computing facilities, may come from special proton configuration databases which include all possible positions of hydrogen atoms

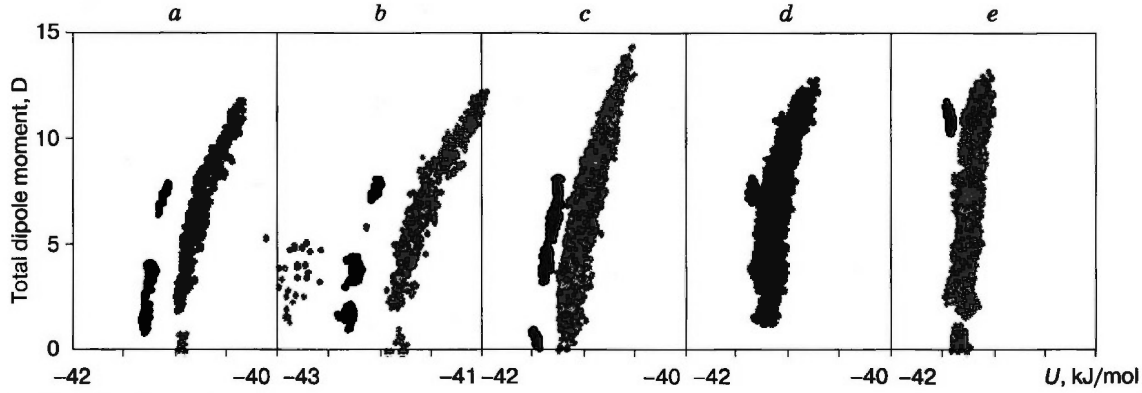

Fig. 1. Distribution of proton configurations at ground (black) and following (gray) energy levels, for polyhedral water clusters in the form of gas hydrate cavities.

Gas hydrate cavities and number of pentagonal and hexagonal faces in polyhedra: *a* – D(5^{12}), *b* – D, TTM2-F, *c* – T($5^{12}6^2$), *d* – H($5^{12}6^4$), *e* – E($5^{12}6^8$).

(protons), along with the position of oxygens in the unit cell. At present, exhaustive databases have been developed for most widespread gas hydrate frameworks: TS-IV, HS-III, CS-I, which allows upgrading the methods of studying gas hydrates due to regard for the structure of the proton subsystem.

The simplified combinatorial topological approach allowed discovering a new type of hidden molecular symmetry in ice-like systems, or more precisely an *antisymmetry*. Changing the directions of all H-bonds may be tried as an additional antisymmetry operation. The discovered symmetry was found out to be approximate (not exact) because the hydrogen-bonded ice-like systems were not invariant with respect to the removal of all H-bonds. The antisymmetry of proton configurations, as well as its relation with stability, were investigated for a great number of ice-like systems (cyclic and polyhedral water clusters and various gas hydrate frameworks). The study has led to a hypothesis that the supramolecular asymmetry of ice-like systems associated with the approximate antisymmetry can define a particular type of ordering in these systems and be the primary cause of the origin and stability of mirror asymmetry in living systems at the molecular level (homochirality of biopolymers).

The combinatorial topological approach was applied in developing a special max-plus algebraic method for global combinatorial optimization of quasi-one-dimensional discrete systems. Max-plus algebra is a field in modern mathematics which uses the simpler operations of maximization and summation instead of the common arithmetic summation and multiplication. With the new optimization method, the classes of energy-lowest proton configurations were exactly calculated for polyhedral water clusters from a cube to a fullerene, including those in the form of cavities of commonest gas hydrates. The new max-plus-algebraic method of combinatorial structural optimization is easily programmable and can be extended to systems of any chemical nature.

The high efficiency of the approximate combinatorial topological approach to modeling ice-like systems is due to their complex multilevel molecular organization. Different modeling levels correspond to specific organization levels. For instance, the model of H-bonded networks takes into account the topology and geometry of the bond framework. The discrete models of molecular interaction take an approximate account of the energy preferability of the proton positions in H-bonds. The approximate antisymmetry of hydrogen bonding reflects a new virtually unexplored organization level in complex ice-water systems. Complex multilevel systems of this kind are increasingly becoming the focus of modern natural sciences.

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