Kinetics of the production and loss of ion-molecular complexes $H^+(H_2O)_n$ for $n = 1, 2, \ldots, 6$

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The present paper is devoted to studying the kinetics of the production and loss of ion-molecular complexes $H^+(H_2O)_n$ for $n = 1, 2, \ldots, 6$. Atomic positions in such complexes are calculated *ab initio* by the use of global optimization methods. The frequencies of atomic vibrations are calculated, the heat capacities and thermo-chemical parameters of the production and loss reactions of complexes (heat effects and free energies) are determined.

It was found that the vibration frequencies of ion-molecular complexes $H^+(H_2O)_n$ calculated within the harmonic approximation are in poor agreement with the experimental ones; therefore, it is necessary to take into account the anharmonicity of the vibrations. At the same time, the use of the harmonic approximation to analyze the heat effects of reactions and activation energies gives results that coincide with the experimental ones within the measurement errors. It was found that even for small-sized complexes, the heat capacity weakly depends on the arrangement of atoms, and the dependence of the heat capacity of the $H^+(H_2O)_n$ complex on its size is linear even at $n \geqslant 2$. In the calculations, many different configurations of the $H^+(H_2O)_n$ complexes corresponding to different local minima on the potential energy surface were found. It was found that even for small complexes there is a significant number of vibrational modes with low frequencies, close to the frequencies of the rotational motion of water molecules, which suggests a high probability of the participation of vibrational degrees of freedom in the relaxation of collision energy.