



Quantum chemical studies of trace gas adsorption on ice nanoparticles

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We have investigated the interaction of atmospheric trace gases with crystalline water ice particles of nanoscale size by modern quantum chemical methods. Small ice particles which can be formed in different altitudes play an important role in chemistry and physics of the Earth atmosphere. Knowledge about the uptake and incorporation of atmospheric trace gases in ice particles as well as their interactions with water molecules is very important for the understanding of processes at the air/ice interface. The interaction of the atmospheric trace gases with atmospheric ice nanoparticles is also an important issue for the development of modern physicochemical models. Usually, the interactions between trace gases and small particles considered theoretically apply small-size model complexes or the surface models representing only fragments of the ideal surface.

Ice particles consisting of 48, 72, 216 and 270 water molecules with a distorted structure of hexagonal water ice Ih were studied using the new SCC-DFTBA method combining well the advantages of the DFT theory and semiempirical methods of quantum chemistry. The largest clusters correspond to the minimal nanoparticle size which are considered to be crystalline as determined experimentally. The clusters up to (H₂O)₇₂ were studied at the B3LYP/6-31++G(d,p) and B3LYP/6-311++G(2d,2p) levels. The larger clusters were studied using DFTBA and DFTB+ methods. Several adsorption complexes for the (H₂O)₂₇₀ water ice cluster were optimized at the RI-BLYP/6-31+G(d) theory level to verify the DFTB+ results. Trace gas molecules were coordinated on different sites of the nanoparticles corresponding to different ice Ih crystal planes: (0001), (10-10), (11-20). As atmospheric trace gases we have chosen CO, CO₂, HCO*, HCOH*, HCHO, HCOOH and (HCO)₂, which are the possible products and intermediates of the UV photolysis of organic molecules such as HCHCHO adsorbed on the ice surface.

The structures of the corresponding coordination complexes, their vibrational frequencies, their adsorption energies and thermodynamic parameters (the enthalpy and the Gibbs free energy of adsorption) were evaluated using the full optimization followed by the frequency calculations. Additionally, the different modes of incorporation of trace gas molecules into the ice particles were considered and the corresponding structural and energetic parameters were evaluated. The transition states for the possible hydration were located and the influence of the water cluster surrounding on the barrier heights was studied as well.

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