Micro-hydration in atmospheric chemistry of NO^+

Ivan Černušák[1], Pavel Jungwirth[2], Milan Uhlár[3]

[1]*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, SK-84215 Bratislava, Slovakia*

[2]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems, Flemingovo nám. 2, 16610 Prague 6, Czech Republic*

[3]*Institute of Physics, Faculty of Philosophy and Science, Silesian University, Bezručovo nám. 13, CZ-746 01 Opava 1, Czech Republic*

Ion clusters and ion-molecule complexes play an important role in many branches of physics, chemistry and biology because these processes are relevant to gas-phase solvation, acid-base equilibria, combustion, catalysis and atmospheric phenomena. They often include various types of intermolecular interactions that can become initial step of chemical reaction. Among them are of particular interest those ion-molecule interactions that are part of important gas-phase solvation processes in the stratosphere (altitudes 15-50 km) and ionosphere (altitudes above 50 km).

We have studied the complex $NO^+.H_2S$, which is assumed to be intermediate during acid rain formation, exhibits thermodynamic stability of ΔH^0_{300K} = -75.9kJ/mol, or ΔG^0_{300K} = -46.8kJ/mol. Its further transformation via H-transfer is connected with rather high barriers. One of the conceivable routes to lower the energy of the transition state is the action of the additional solvent molecule(s) that can mediate the proton transfer. Using DFT, MP2 and CCSD(T) techniques we have studied several $NO^+.H_2S$ structures with additional one, two and three water molecules and have found stable structures (local minima), intermediates and saddle points for the three-body, $NO^+.H_2S.H_2O$, and four-body, $NO^+.H_2S.(H_2O)_2$, clusters. Hydrogen bonds network in the four-body cluster plays crucial role in its conversion to thionitrous acid. Recently, our molecular ab initio calculations were supplemented by CP-molecular dynamics of microhydrated $NO^+.H_2S$ clusters at 200K.