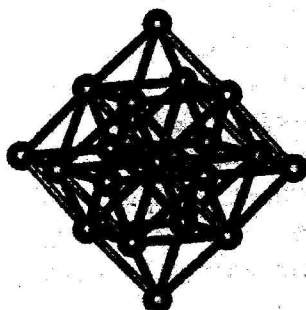


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BOOK OF ABSTRACTS

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Water-assisted proton transfer in formamide, thioformamide and selenoformamide

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The tautomerism in formamide and its thio and seleno analogs may occur by direct or water-assisted proton transfer. Water-assisted proton transfer was investigated in formamide at the MP2/6-31G(d,p) and MP2/6-31+G(d) levels. The influence of the intermolecular hydrogen bonds between solute and solvent molecules was taken into account including from one up to 3 water molecules. Water-assisted proton transfer decreasing two times the barrier of the chemical reaction compared with the direct proton transfer. The barriers with and without additional water molecules calculated at MP2/6-31G(d,p) level are 3–3.5 kcal/mol higher than the computed at the /6-31+G(d) level. When additional correlation effects [MP4/6-31+G(d)/MP2/6-31+G(d) and MP4/6-31G(d,p)/MP2/6-31G(d,p)] are taking into account, increasing of the barrier with about 3 kcal/mol is observed. The direct proton transfer is characterized by decreasing of the reaction barrier in the order: formamide, thioformamide and selenoformamide. The values for $\Delta H_{\text{a}}^{\ddagger}$ computed at the MP2/6-31G(d,p) level are 43.97, 38.75 и 35.58 kcal/mol, respectively. Similar tendency do not observed when water-assisted proton transfer is realizing by one water molecule. The predicted barriers are in the 19.3–19.9 kcal/mol range. The structural parameters of formamide and thioformamide, which were investigated, are in good agreement with available experimental data, obtained by microwave spectroscopy.