Decomposition of small protonated water clusters in humid air

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The study of plasma-chemical processes in humid air is relevant for the atmosphere physics, the meteorology and environmental safety. In this work, we calculated the rate constants for the decomposition of small protonated water clusters $H^+(H_2O)_n$ with numbers of water molecules $n = 2 \dots 6$. In accordance with the theory of unimolecular reactions, we assume that the decomposition can be initiated by collisions with the second body (N_2 molecules).
We performed the calculations using different models and assumptions. First, we applied the *ab initio* model to estimate the atomic positions and vibrational frequencies of the complexes, using the second order Møller-Plesset perturbation theory (MP2) for the electron correlation account. The unimolecular decomposition rate constants were estimated within the framework of Rice-Ramsperger-Kassel-Marcus theory (RRKM) [1]. Second, we applied the molecular dynamic simulations using the semi-empirical model from [2] for the calculation of energies and forces. The obtained results were compared with each others, and with the experimental data from [3].

[1] Robinson P J and Holbrook K A 1972 *Unimolecular reactions* (Wiley-interscience)
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[3] Sieck L W, Heron J T and Green D S 2000 *Plasma Chemistry and Plasma Processing* **20** 235–258