Supplement of

Electron-induced chemistry in microhydrated sulfuric acid clusters

Jozef Lengyel[1,2], Andriy Pysanenko[1], Michal Fárník[1]

[1]J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Dolejškova 3, 18223 Prague, Czech Republic

[2]Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens-Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria

Correspondence to: Jozef Lengyel (jozef.lengyel@jh-inst.cas.cz), Michal Fárník (michal.farnik@jh-inst.cas.cz)

S1 Experimental setup

The experiments were performed on a versatile and unique experimental apparatus CLUB (cluster beam apparatus) which allows a variety of different experiments with a molecular beam of isolated clusters in vacuum. The apparatus and experiments have been described in numerous publications previously (e.g., mass spectrometry: (Lengyel et al., 2012; Kočišek et al., 2013a; Kočišek et al., 2013b); electron attachment: (Kočišek et al., 2016a; Kočišek et al., 2016b; Lengyel et al., 2016); etc.) and the details can be found in these references. The sketch of the CLUB apparatus is shown in Fig. S1 below. In the present work, the clusters were produced in the first vacuum chamber by supersonic expansion of the sulfuric acid vapor with buffer gas He, i.e. a mixture of H_2SO_4, H_2O and He gas phase molecules. The present mass spectrometry was performed in the 4th vacuum chamber TOFMS, where the cluster beam was crossed by a low-energy electron beam. Further details are given in the experimental section of the present paper. The other options and features of the CLUB apparatus shown in Fig. S1 were not exploited in the present experiments.

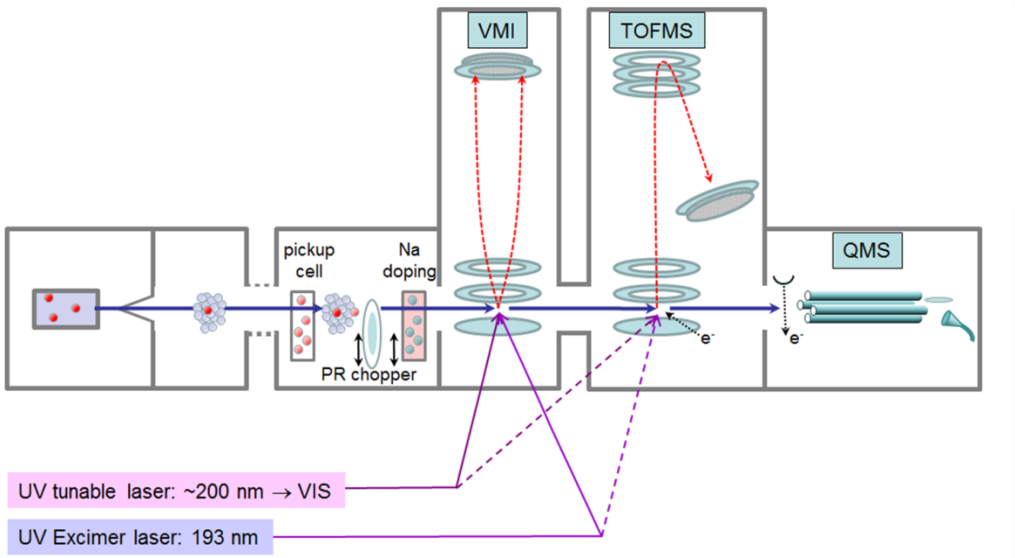

Figure S1: Schematic overview of the CLUB apparatus: VMI –velocity map imaging for photodissociation of molecules in clusters; TOFMS –reflectron time-of-flight mass spectrometer with various ionization methods, e.g., electron ionization, electron attachment, photoionization; QMS –quadrupole mass spectrometer with electron ionization.

S2 Thermochemistry

Table S1: Reaction energies (in kJ mol^{-1}) for the HSO_4^- dissociation channels after electron attachment to H_2SO_4/H_2O clusters optimized at the M06-2X/aug-cc-pVDZ level of theory.

N	$H_2SO_4(H_2O)_N$	$(H_2SO_4)_2(H_2O)_N$
0	–8.6	–132.2
1	–16.2	–117.2
2	–30.3	–120.5
3	–39.6	–110.6
4	–43.5	–108.9
5	–46.3	–89.2

Table S2: The standard Gibbs free energy (in kJ mol^{-1}) of binary nucleation of H_2O and H_2SO_4 to small $H_2SO_4(H_2O)_n$ clusters calculated at the M06-2X/aug-cc-pVDZ level of theory.

	H_2O	H_2SO_4
H_2SO_4	–11.2	–26.3
$H_2SO_4(H_2O)$	–7.2	–31.4
$H_2SO_4(H_2O)_2$	–3.4	–32.6
$H_2SO_4(H_2O)_3$	–9.7	–40.9
$H_2SO_4(H_2O)_4$	–4.8	–43.8

References

Kočišek, J., Grygoryeva, K., Lengyel, J., Fárník, M., and Fedor, J.: Effect of cluster environment on the electron attachment to 2-nitrophenol, Eur. Phys. J. D, 70, 98, doi:10.1140/epjd/e2016-70074-0, 2016a.

Kočišek, J., Lengyel, J., and Fárník, M.: Ionization of large homogeneous and heterogeneous clusters generated in acetylene-Ar expansions: Cluster ion polymerization, J. Chem. Phys., 138, 124306, doi:10.1063/1.4796262, 2013a.

Kočišek, J., Lengyel, J., Fárník, M., and Slavíček, P.: Energy and charge transfer in ionized argon coated water clusters, J. Chem. Phys., 139, 214308, doi:10.1063/1.4834715, 2013b.

Kočišek, J., Pysanenko, A., Fárník, M., and Fedor, J.: Microhydration prevents fragmentation of uracil and thymine by low-energy electrons, J. Phys. Chem. Lett., 7, 3401–3405, doi:10.1021/acs.jpclett.6b01601, 2016b.

Lengyel, J., Kočišek, J., Fárník, M., and Fedor, J.: Self-scavenging of electrons in $Fe(CO)_5$ aggregates deposited on argon nanoparticles, J. Phys. Chem. C, 120, 7397–7402, doi:10.1021/acs.jpcc.6b00901, 2016.

Lengyel, J., Pysanenko, A., Kočišek, J., Poterya, V., Pradzynski, C. C., Zeuch, T., Slavíček, P., and Fárník, M.: Nucleation of mixed nitric acid-water ice nanoparticles in molecular beams that starts with a HNO_3 molecule, J. Phys. Chem. Lett., 3, 3096–3101, doi:10.1021/jz3013886, 2012.