

Supporting information for:

Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study

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1 Details of molecular dynamics simulations

The purpose of the molecular dynamics (MD) simulations was to generate initial guess structures for the quantum chemistry geometry optimizations, i.e. to sample the configuration space. For this a simple three-step annealing algorithm was used with descending temperatures from 1500 K to 200 K to 0.1 K. Relaxed structures obtained after the last simulation were then used as initial guesses for optimizations performed at higher level of theory.

All MD simulations were performed in NVT ensemble with Nosé-Hoover (Evans and Holian, 1985) thermostat (relaxation time of 0.5 ps) in a cubic simulation cell of 20 Å (with periodic boundary conditions). The simulation time step was 0.2 fs and the potential cutoff 5 Å.

For water, SPC-E/F force field parameters (Berendsen et al., 1987) were used. For the other molecules, force field parameters were generated using the standard OPLS-AA doctrine

(Jorgensen et al., 1996). Briefly, this was done as follows. First, Lennard-Jones parameters were taken from the published literature (using the closest possible functional groups, see references given in Tables S1-S3). Next, partial charges were computed using the CHelpG (Gaussian 03, Revision C.02, 2004) electrostatic fit to MP2/cc-pVTZ densities computed at the HF/6-31G* minimum-energy geometries. For molecules with multiple minimum-energy geometries (conformers), some averaging over the different structures was done by hand. Harmonic stretching and bending force constants were computed by numerical differentiation at the HF/6-31G* level, with a scaling factor of 0.899. Finally, torsional parameters were computed by fitting the difference of HF/6-31G* and MD energies (computed at 15 degree intervals over all torsional angles) to a cosine series. All quantum chemical calculations for the force field fits were performed using the Gaussian 03 (Gaussian 03, Revision C.02, 2004) program suite.

2 Scaling factors

The scaling factors used for the vibrational frequencies were obtained by comparison between high-level (MP2/aug-cc-pV(D+d)Z) anharmonic vibrational frequencies (Kurtén et al., 2007) and the harmonic frequencies calculated with the SIESTA (Soler et al., 2002) program at the the BLYP/DZP level of theory. This comparison was done for the smallest clusters under study, namely the free water, free ammonia, free dimethylamine, free sulfuric acid and the mono- and dihydrate of sulfuric acid (for this purpose the anharmonic vibrational frequencies for free ammonia and free dimethylamine were explicitly calculated at the MP2/aug-cc-pVDZ level of theory using Gaussian 03).

For each molecule or complex, the ratios of anharmonic frequencies to the harmonic SIESTA-frequencies were calculated for all of the $(3N-6)$ individual vibrational degrees of freedom, where N is the number of atoms in the molecule or complex. The corresponding scaling factor for the structure in question was then obtained by taking the average of the ratios of the individual frequencies. The anharmonic and harmonic frequencies, ratios of these and the scaling factors for the mentioned structures are presented in the Tables S5a and S5b.

The scaling factors obtained as described above were used to estimate thermal contributions to the electronic binding energies calculated at zero Kelvin. However, to estimate the thermal contributions, one must also take into account the effect of zero-point vibrational energy.

Towards this end, we modified the scaling factor s used for other thermal contributions (i.e. for the entropy and the translational, rotational and vibrational parts of the enthalpy) to:

$$s_{ZPE} = 1 - 0.5x \quad (\text{S1}),$$

where x is the departure from unity of the scaling factor s ,

$$x = 1 - s \quad (\text{S2}),$$

thus yielding upon substitution

$$s_{ZPE} = 0.5(1 + s) \quad (\text{S3}).$$

The scaling factor s_{ZPE} for the zero-point vibrational energy contributions is slightly closer to unity than the one used for other contributions. This procedure seems to capture the general characteristics of the scaling factors often used to convert the calculated harmonic frequencies closer to observed, anharmonic ones (see for example Grev et al. (1991) and Scott and Radom (1996) for more discussion on the scaling factors). The scaling factors s_{ZPE} for the zero-point vibrational energy contributions are presented in the Table S6.

3 Coordinates

The coordinates of the structures corresponding to the minimum of electronic binding energy and the minimum of Gibbs free energy are presented in the Tables S7 and S8, respectively.

References for the supporting information

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