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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces" *by* Roope Halonen et al.

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We thank referee #2 for the favourable review of our manuscript.

Regarding the general comment on the effect of collision rate enhancement on new particle formation rates, we note that in cluster dynamics codes such as ACDC (McGrath et al., 2012) detailed balance is assumed, and therefore global changes to the collision rates obtained by application of an enhancement factor are compensated by the corresponding changes in evaporation rates. However, in complex systems, individually changing collision rates for reactions that are close to the kinetic limit can change the preferred pathway for cluster growth, leading to different cluster distributions and

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particle formation rates.

We will add the following paragraph to the conclusions. "However, before we can quantitatively assess the influence of collision rate enhancement on atmospherical new particle formation rates obtained from cluster dynamics models (for example ACDC, McGrath et al., 2012), it is necessary to obtain the enhancement factors for all the relevant collisions between clusters of different sizes and composition, as the pathway for growth may change–a formidable task, even if only the simplest acid-base clusters were considered. Future work therefore should also be aimed at finding simple models for predicting approximate rate enhancements, based on just a few physico-chemical properties, such as molecular structures, dipole moments or charge distributions, of the interacting molecules and/or clusters."

ad 1.
We will add the following clarification in the introduction: "[...] the impact parameter i.e. the perpendicular distance between the spheres' trajectories [...]"

ad 2.
We propose the following change to the sentence in the manuscript: "In fact, systematic discrepancies have been found between experimental particle formation rates and values predicted from kinetic modelling and cluster dynamics simulations, where hard-sphere collisions are assumed. Kürten et al. (2014) measured the kinetic formation rate of sulphuric acid dimers and found that an enhancement factor of 2.3 needed to be applied to the formation rate obtained from a kinetic model. Lehtipalo et al. (2016) and Kürten et al. (2018) have studied particle formation rates in systems containing sulphuric acid, dimethylamine and water and concluded that an enhancement factor of 2.7 and 2.3, respectively, was needed to match experimental particle formation rates."

ad 3.
We apologize for the lack of clarity regarding the difference between collision and capture. We will add the following paragraph to section 2.4: "As the collision rate in the

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context of atomistic simulations is defined as the reaction rate of hydrogen bonding, the related theoretical models are often based on the assumption that if the trajectory of the colliding molecules is able to surmount a centrifugal barrier the reaction is certain. This is known as the capture approximation; to emphasise this conceptual difference between simulations and theoretical models, we use the word *capture* instead of *collision* to refer to theory-based results."

ad 4.
We have added the following description of the functional forms of the inter- and intramolecular potentials to the methods section: "In both force fields intermolecular interactions are described by the sum of Lennard-Jones potentials between atoms i and j with distance and energy parameters σ_{ij} and ε_{ij}, and Coulomb interactions between the partial charges q_i and q_j,

$$\begin{aligned} U_{\text{inter}} &= \sum_{i=1}^{N_1}\sum_{j=1}^{N_2} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \\ &+ \sum_{i=1}^{N_1}\sum_{j=1}^{N_2} \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}. \qquad (1) \end{aligned}$$

However, in the force field by Ding et al., the geometry of the individual molecule is simply constrained by harmonic potentials with force constants k_{ij} between all pairs of atoms,

$$U_{\text{intra}}^{\text{Ding}} = \sum_{i=1}^{N_1-1}\sum_{j=i+1}^{N_1} \frac{k_{ij}}{2}\left(r_{ij} - r_{ij}^0\right)^2, \qquad (2)$$

while in OPLS the intramolecular interactions consist of the usual sum of two, three, and four-body potentials, i.e. harmonic bonds between covalently bonded atoms, harmonic angles between atoms separated by two covalent bonds, and torsions (dihedral angles) between atoms separated by three covalent bonds,

$$
\begin{aligned}
U_{\text{intra}}^{\text{OPLS}} &= \sum_{i=1}^{N_{\text{bonds}}} \frac{k_i^b}{2}\left(r_i - r_i^0\right)^2 + \sum_{j=1}^{N_{\text{angles}}} \frac{k_j^\theta}{2}\left(\theta_j - \theta_j^0\right)^2 \\
&+ \sum_{k=1}^{N_{\text{dihedrals}}} \sum_{n=1}^{4} \frac{V_n}{2}\left[1 + \cos(n\phi^k - \phi_n^k)\right] .\text{”} \qquad (3)
\end{aligned}
$$

ad 5.
We have numbered the hydrogen bonds for dimer structures a-d in Fig. 1 and added the corresponding hydrogen bond number to the hydrogen bond distance values in the table.

ad 6.
The paper by Temelso et al. (2012) is to our knowledge the only reference that contains detailed information on potential/electronic energies and hydrogen bond geometries for different conformers of the H_2SO_4 dimer, as well as the binding free energy. For the binding free energies, we found reasonable agreement between the study by Temelso et al. (2012) and more recent work by Elm et al. (2016) and Myllys et al. (2017), which we do mention in the manuscript. Note that Temelso et al. have obtained the binding free energy from Boltzmann-averaging over the four minimum energy dimer structures, while in the newer references only the global minimum energy structure has been considered.

ad 7.
In computational physics and chemistry, commonly used units of energy are eV, kJ/mol, kcal/mol, or $k_\mathrm{B}T$. The unit used in the LAMMPS simulation in/output was eV, which is why this was the most natural choice for the manuscript. Since none of the important quantities we report, such as the collision rate coefficients, or enhancement factors, have the unit of energy, we think this should not be a major concern. However, to

accomodate all audiences, we will add the conversion factors to the manuscript: 1 eV ≈ 96.49 kJ/mol ≈ 23.06 kcal/mol $\approx 38.68 k_\mathrm{B} T$ at $T = 300$ K.

ad 8.
The values cited in our manuscript indeed correspond to the values given in the paper by Chan and Mozurkewich (2001), both in the abstract and in Fig. 5.

Full figure captions:

Figure 1: Four minimum energy structures for the sulfuric acid dimer (a–d) used to benchmark the force fields by Ding et al. (2003) and Loukonen et al. (2010) against ab initio calculations by Temelso et al. (2012) Sulfur atoms are yellow, oxygens red and hydrogens white. Hydrogen bonds are indicated by dotted lines and enumerated according to Tab. 1.

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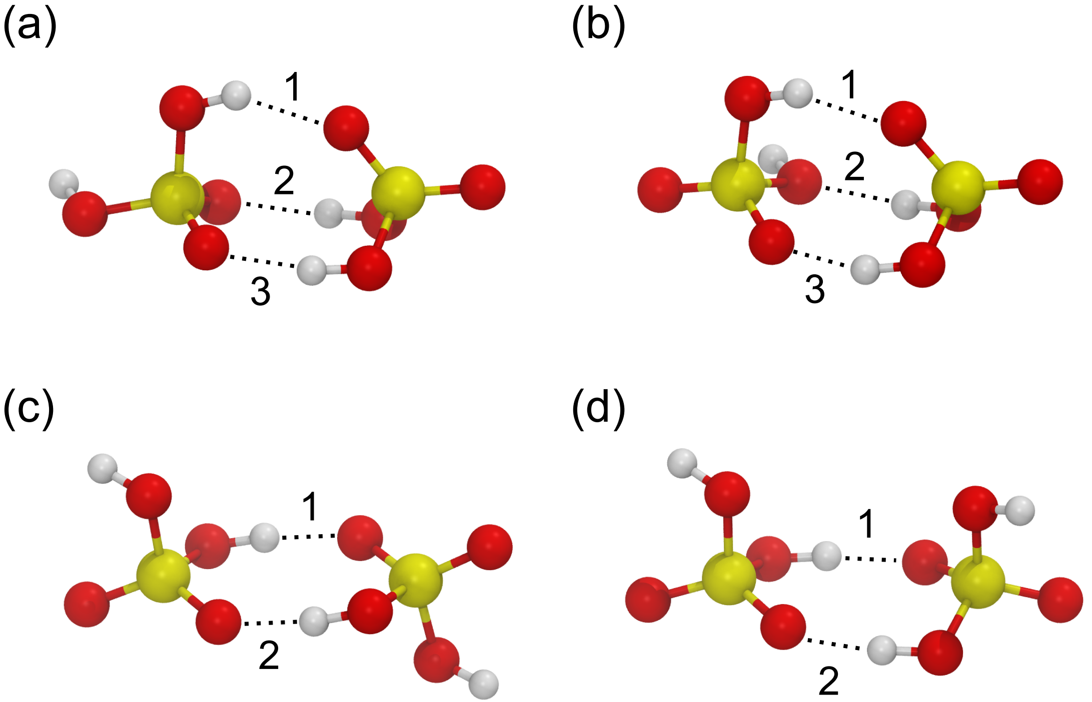

Fig. 1. Four minimum energy structures for the sulfuric acid dimer (a–d) used to benchmark the force fields by Ding et al. (2003) and Loukonen et al. (2010) against ab initio calculations by Temelso et al. (2

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