



Supplement of

Collision-sticking rates of acid–base clusters in the gas phase determined from atomistic simulation and a novel analytical interacting hard-sphere model

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Calculated potential of mean force (PMF) curves for acid-base clusters

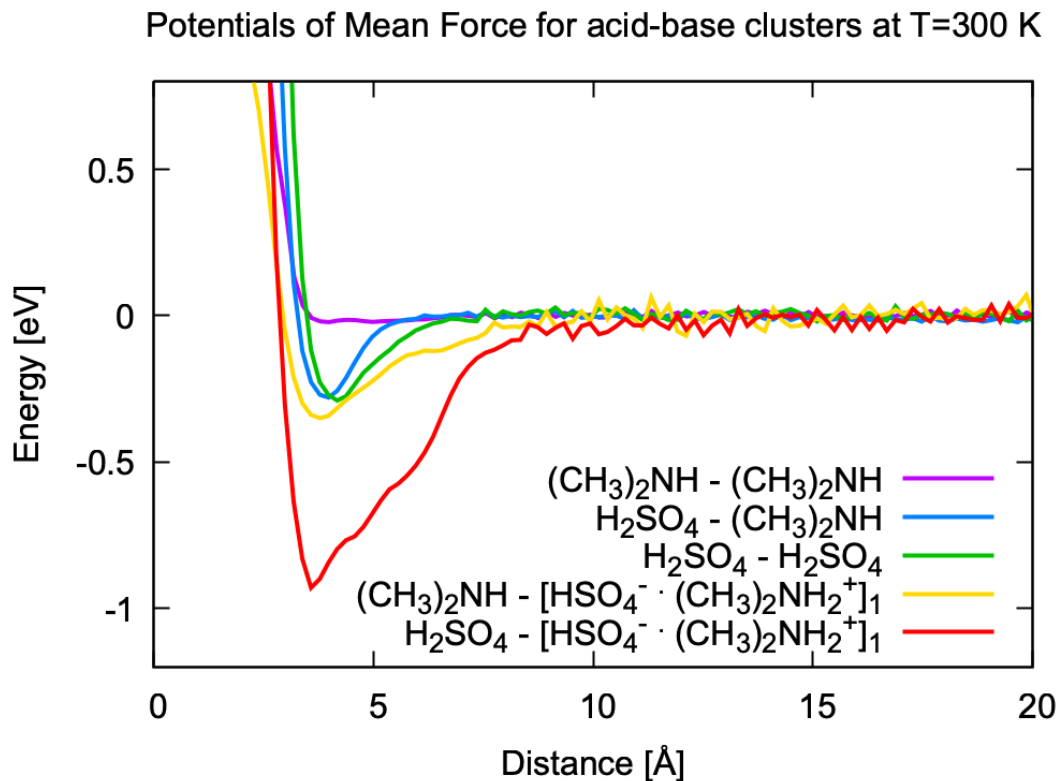


Figure S1. Potentials of Mean Force as a function of the center of mass distance between the investigated acid-base “monomers” in Hamaker’s approach, obtained from well-tempered metadynamics simulations at T=300 K using an OPLS-AA force field.

Extracted ϵ and σ values from the calculated PMF curves

Table S1. Extracted ϵ and σ values

	$(\text{CH}_3)_2\text{NH}$ & $(\text{CH}_3)_2\text{NH}$	H_2SO_4 & H_2SO_4	H_2SO_4 & $(\text{CH}_3)_2\text{NH}$	H_2SO_4 & $\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+$	$(\text{CH}_3)_2\text{NH}$ & $\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+$
ϵ [eV]	~0	0.29	0.26	0.93	0.35
σ [Å]	N/A	3.71	3.54	3.19	3.36

Two example cases where the interacting hard-sphere model and the central field approach result in significantly different critical impact parameters

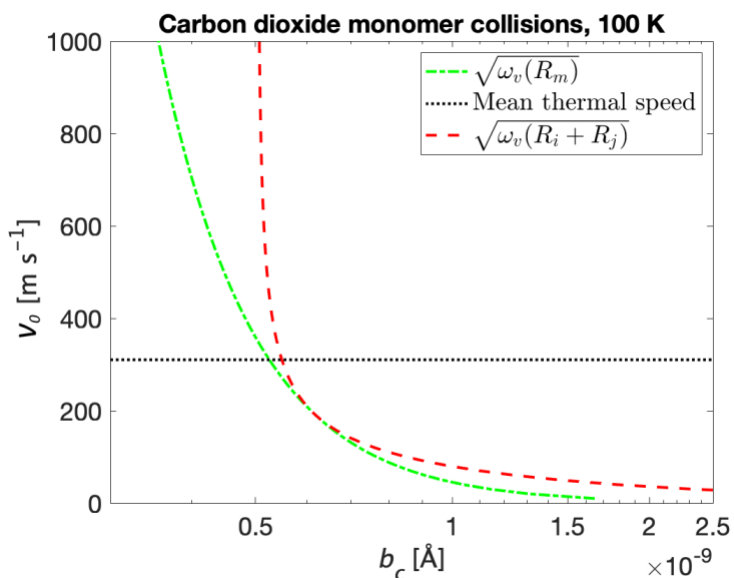


Figure S2. Critical impact parameter for collisions of carbon dioxide monomers at 100 K. The Lennard-Jones parameters are $\epsilon = 0.0108$ eV and $\sigma = 3.04 \text{ \AA}^1$.

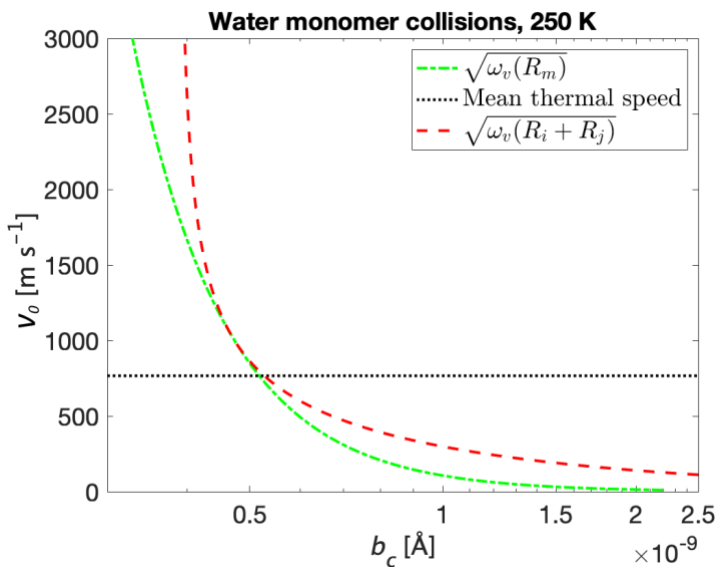


Figure S3. Critical impact parameter for collisions of water monomers at 250 K. The Lennard-Jones parameters are $\epsilon = 0.031$ eV and $\sigma = 2.928 \text{ \AA}^2$.

The root of Eq. 14 in the main text

In this part, we provide a reasoning to the statement that Eq. 14 in the main text always has exactly one real root that is larger than R_c , and we shall identify that root. Substitution of Eq. 13 in the main text into $\omega_v(r)$ yields:

$$\omega_v(r, U_{mc}) = r^2 \left[1 + \frac{8n_c \epsilon \sigma^6}{\mu v_0^2} \cdot \frac{1}{(r^2 - R_c^2)^3} \right]. \quad (\text{S1})$$

We take the derivative of Eq. S1 with respect to r and obtain:

$$\omega_v'(r, U_{mc}) = 2r \left[1 - \frac{8n_c \epsilon \sigma^6}{\mu v_0^2} \cdot \frac{2r^2 + R_c^2}{(r^2 - R_c^2)^4} \right] \equiv 2r[1 - \theta f(r)], \quad (\text{S2})$$

where, $\theta = \frac{8n_c \epsilon \sigma^6}{\mu v_0^2}$ is a positive constant and

$$f(r) = \frac{2r^2 + R_c^2}{(r^2 - R_c^2)^4} = \frac{2}{(r^2 - R_c^2)^3} + \frac{3R_c^2}{(r^2 - R_c^2)^4} \quad (\text{S3})$$

decreases monotonically from $+\infty$ to 0 as r increases from R_c to $+\infty$. Therefore, $\omega_v'(r, U_{mc}) = 0 \Leftrightarrow f(r) = \frac{1}{\theta}$ should have a single root for $r > R_c$. Note that $\omega_v'(r, U_{mc}) = 0$ is equivalent to Eq. 14 in the main text, so now it is safe to say that Eq. 14 has a single real root larger than R_c . This single real root R_m should correspond to the maximum of the four roots of the quartic function defined by Eq. 14, which is:

$$R_m^2 = -\frac{a_3}{4a_4} + M + \frac{1}{2} \sqrt{-4M^2 - 2p + \frac{q}{M}}, \quad (\text{S4})$$

where $p = \frac{8a_4 a_2 - 3a_3^2}{8a_4^2} = 0$, $q = \frac{a_3^3 - 4a_4 a_3 a_2 + 8a_4^2 a_1}{8a_4^3} = -2l_c^6$, $M = \frac{1}{2} \sqrt{-\frac{2}{3}p + \frac{1}{3a_4} \left(N + \frac{\Delta_0}{N} \right)}$,

$N = \sqrt[3]{\frac{\Delta_1 + \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2}}$, $\Delta_0 = a_2^2 - 3a_3 a_1 + 12a_4 a_0 = -36R_c^2 l_c^6$, and $\Delta_1 = 2a_2^3 - 9a_3 a_2 a_1 +$

$27a_3^2 a_0 + 27a_1^2 a_4 - 72a_4 a_2 a_0 = 108l_c^{12}$ with $l_c \equiv \left(\frac{8n_c \epsilon \sigma^6}{\mu v_0^2} \right)^{\frac{1}{6}}$. Substituting the expressions of coefficients a_i into Eq. S4 and rearranging leads to Eq. 15 in the main text.

Temperature dependence of collision and sticking rates for clusters of different sizes

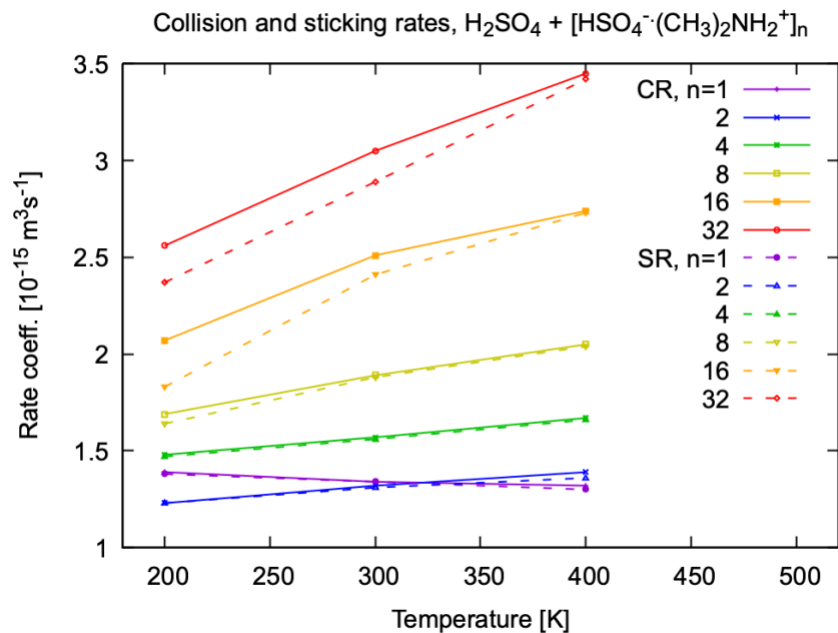


Figure S4. Temperature dependence of collision (CR) and sticking rates (SR) for $\text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions ($n = 1, 2, 4, 8, 16,$ and 32).

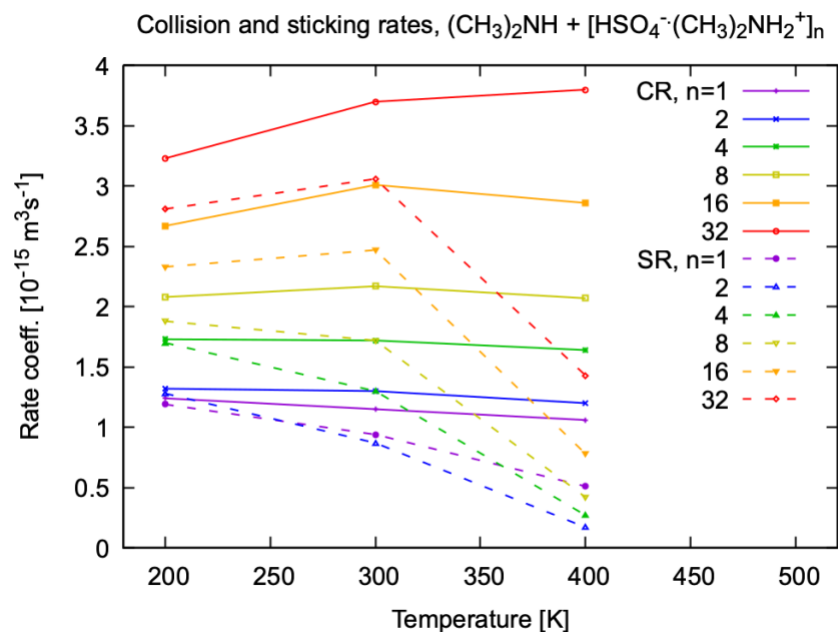


Figure S5. Temperature dependence of collision (CR) and sticking rates (SR) for $(\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions ($n = 1, 2, 4, 8, 16,$ and 32).

When the temperature is increased, the Maxwell Boltzmann distribution is shifted to higher speeds, which has two consequences: First, the monomer flux per unit collision cross section is increased due to higher average relative velocities. Second, the area of the collision cross section is decreased due to the diminished influence of the attractive forces at higher relative velocities. The rate of collision and sticking is hence the net effect of the above two competing factors. The second factor (i.e., decreased collision cross section due to increased temperature) is more significant for small clusters, as the attractive forces play a greater role (leading to higher collision enhancement factors). Therefore, the collision rate decreases with temperature for small clusters, while it increases with temperature for larger clusters.

For $\text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions, the temperature dependence of the collision and sticking rates are similar, as the mass accommodation coefficient is always close to 1 in the studied temperature range. For $(\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions, the mass accommodation coefficient decreases sharply with temperature, hence the sticking coefficient also drops sharply with temperature.

Step-by-step procedure for implementing the interacting hard-sphere model

Step 1. Input parameters to supply

As input parameters for the interacting hard-sphere model, we need the energy ε and length σ Lennard-Jones self-interaction parameters and the radius R for each molecule in the collision system. For a collision between two molecules, this means the ε , σ , and R of each of these molecules. For a collision between a molecule and a cluster, this means the ε , σ , and R of each type of monomer in the cluster, as well as the molecule colliding with the cluster.

The Lennard-Jones self-interaction parameters can be obtained from literature (e.g., the following references³⁻⁷), potential of mean force calculations (as is done in the main text) or fitting to experimental or quantum chemistry data.

The radii of the molecules can be obtained from literature, calculated from liquid bulk density, or taken as the radius of gyration.

The radius R_c of a cluster consisting of N_t different types of monomers can be roughly, but sufficiently, estimated from the density ρ_i and molecular mass m_i of each monomer type in the cluster by assuming spherical monomer volumes:

$$R_c = \left(\frac{3}{4\pi} \sum_i^{N_t} n_{c,i} m_i / \rho_i \right)^{1/3}, \quad (\text{S5})$$

where $n_{c,i}$ is the number of monomers of type i in the cluster.

Step 2. Calculating the collision cross section

Molecule-molecule collision

We first need to calculate the distance R_m .

$$R_m = \sigma \left(\frac{16\varepsilon}{\mu v_0^2} \right)^{1/6}, \quad (\text{S6})$$

where μ is the reduced mass of the collision system. Depending on the relative magnitude of R_m and the sum of hard-sphere radii of the two colliding molecules $R_i + R_j$, the collision cross section is calculated from one of the following equations:

$$\Omega(v_0) = \begin{cases} 3\pi\sigma^2 \left(\frac{2\varepsilon}{\mu v_0^2} \right)^{1/3}, & \text{if } R_m > R_i + R_j \\ \pi(R_i + R_j)^2 \left[1 + \frac{8\varepsilon}{\mu v_0^2} \left(\frac{R_i + R_j}{\sigma} \right)^{-6} \right], & \text{if } R_m \leq R_i + R_j \end{cases}. \quad (\text{S7})$$

Molecule-cluster collision

We consider collisions between a molecule and a cluster consisting of N_t different types of monomers. First, we need to calculate the distance R_m .

$$R_m^2 = R_c^2 + M + \sqrt{-M^2 - \frac{q}{4M}}, \quad (\text{S8a})$$

where

$$q = -2l_c^6, \quad (\text{S8b})$$

$$M = \frac{\sqrt{(N + \Delta_0/N)/3}}{2}, \quad (\text{S8c})$$

$$N = \left[\frac{\Delta_1 + \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2} \right]^{1/3}, \quad (\text{S8d})$$

$$\Delta_0 = -36R_c^2 l_c^6, \quad (\text{S8e})$$

$$\Delta_1 = 108l_c^{12}, \quad (\text{S8f})$$

$$l_c = \left(\frac{8}{\mu v_0^2} \sum_{i=1}^{N_t} \sigma_i^6 n_{c,i} \varepsilon_i \right)^{\frac{1}{6}}. \quad (\text{S8g})$$

Note that the equation of l_c simplifies to $l_c = (8n_c \varepsilon \sigma^6 / \mu v_0^2)^{1/6}$ as in the main text if the cluster consists of a single type of monomer.

Depending on the relative magnitude of R_m and the sum of hard-sphere radii of the colliding molecule and cluster $R_i + R_j$, the collision cross section is calculated from one of the following equations:

$$\Omega(v_0) = \begin{cases} \pi R_m^2 \left[1 + \frac{8}{\mu v_0^2 (R_m^2 - R_c^2)^3} \sum_{i=1}^{N_t} n_{c,i} \varepsilon_i \sigma_i^6 \right], & \text{if } R_m > R_i + R_j \\ \pi (R_i + R_j)^2 \left[1 + \frac{8}{\mu v_0^2 ((R_i + R_j)^2 - R_c^2)^3} \sum_{i=1}^{N_t} n_{c,i} \varepsilon_i \sigma_i^6 \right], & \text{if } R_m \leq R_i + R_j \end{cases} \quad (\text{S9})$$

Step 3. Calculating the collision rate coefficient

The collision rate coefficient is given by

$$k_{\text{IHS}} = \int_0^\infty v_0 f_{\text{MB}}(v_0) \Omega(v_0) dv_0 \approx \sum_{v_0=0} v_0 f_{\text{MB}}(v_0) \Omega(v_0) \Delta v_0. \quad (\text{S10})$$

where $\Omega(v_0)$ is either the molecule-molecule or molecule-cluster collision cross section calculated in step 2, and $f_{\text{MB}}(v_0)$ the Maxwell-Boltzmann relative speed distribution

$$f_{\text{MB}} = 4\pi v_0^2 \left(\frac{\mu}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{\mu v_0^2}{2k_B T}}. \quad (\text{S11})$$

Here, k_B is the Boltzmann constant. When approximating k_{IHS} as a sum, the sum should run over a relative range of v_0 according to the Maxwell-Boltzmann relative speed distribution (e.g., for collisions between H_2SO_4 with $[\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_3^+]_1$, the range $v_0 = 0\text{-}850 \text{ ms}^{-1}$ covers more than 99.9% of the Maxwell-Boltzmann relative speed distribution at 300 K). Practically, the sum can be calculated numerically with an *if* statement in the code to distinguish between the two cases $R_m > R_i + R_j$ and $R_m \leq R_i + R_j$.

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