Supplementary Materials for

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

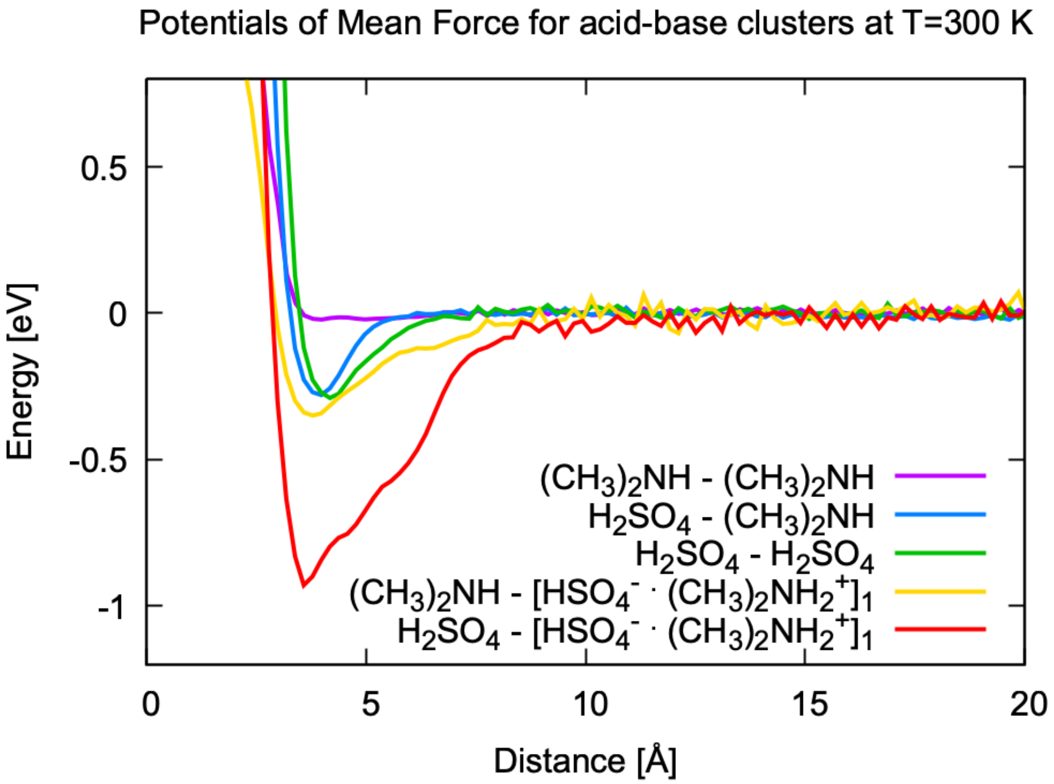

Figure S1. Potentials of Mean Force as a function of the center of mass distance between the investigated acid-base "monomers" in the Hamaker approach, obtained from well-tempered metadynamics simulations at T=300 K using an OPLS-AA force field.

Extracted ϵ and σ values from the calculated PMF curves

Table S1. Extracted ϵ and σ values

	$(CH_3)_2NH$ & $(CH_3)_2NH$	H_2SO_4 & H_2SO_4	H_2SO_4 & $(CH_3)_2NH$	H_2SO_4 & $HSO_4^- \cdot (CH_3)_2NH_2^+$	$(CH_3)_2NH$ & $HSO_4^- \cdot (CH_3)_2NH_2^+$
ϵ [eV]	$\sim$0	0.29	0.26	0.93	0.35
σ [Å]	N/A	3.71	3.54	3.19	3.36
r_ϵ [Å]	N/A	4.17	3.97	3.58	3.77

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

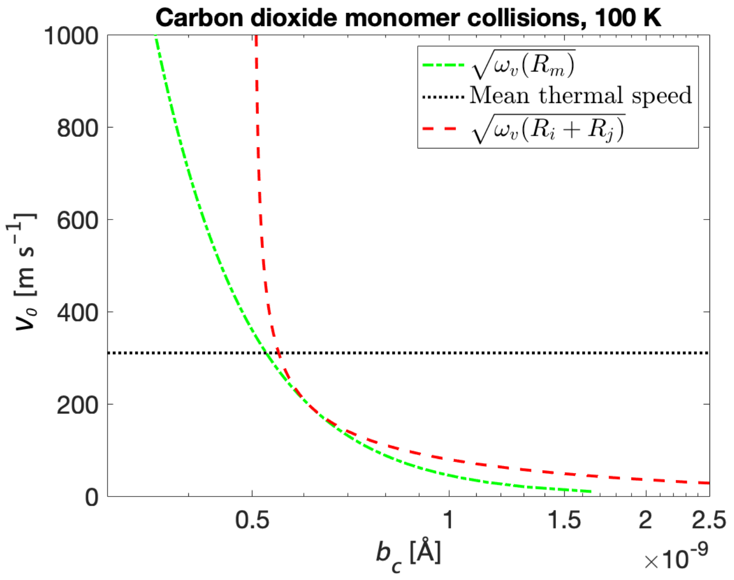

Figure S2. Critical impact parameter for collisions of carbon dioxide monomers at 100 K. The Lennard-Jones parameters are $\epsilon = 0.0108$ eV and $\sigma = 3.04$ Å [1].

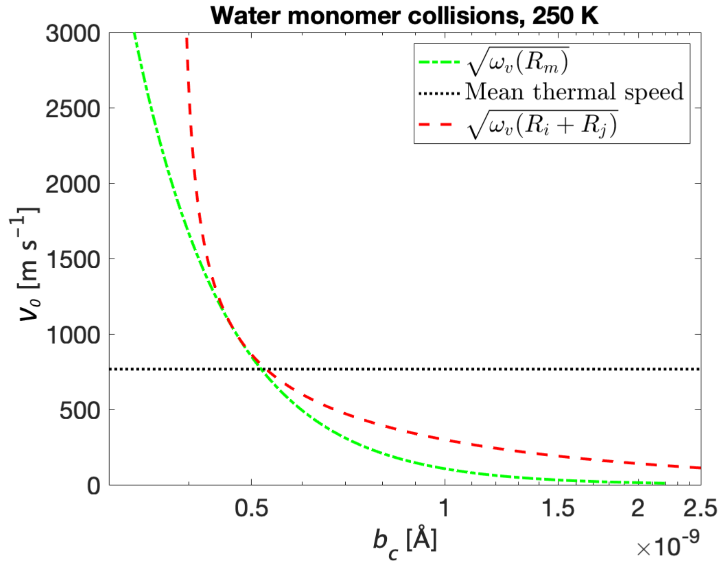

Figure S3. Critical impact parameter for collisions of water monomers at 250 K. The Lennard-Jones parameters are $\epsilon = 0.031$ eV and $\sigma = 2.928$ Å [2].

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 exact 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:

$$\omega_v(r, U_{\mathrm{mc}}) = r^2 \left[1 + \frac{8n_{\mathrm{c}}\epsilon\sigma^6}{\mu {v_0}^2} \cdot \frac{1}{(r^2 - {R_{\mathrm{c}}}^2)^3}\right]. \tag{S1}$$

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

$$\omega_v'(r, U_{\mathrm{mc}}) = 2r \left[1 - \frac{8n_{\mathrm{c}}\epsilon\sigma^6}{\mu {v_0}^2} \cdot \frac{2r^2 + {R_{\mathrm{c}}}^2}{(r^2 - {R_{\mathrm{c}}}^2)^4}\right] \equiv 2r[1 - \theta f(r)], \tag{S2}$$

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

$$f(r) = \frac{2r^2 + {R_{\mathrm{c}}}^2}{(r^2 - {R_{\mathrm{c}}}^2)^4} = \frac{2}{(r^2 - {R_{\mathrm{c}}}^2)^3} + \frac{3{R_{\mathrm{c}}}^2}{(r^2 - {R_{\mathrm{c}}}^2)^4} \tag{S3}$$

decreases monotonically from $+\infty$ to 0 as r increases from R_{c} to $+\infty$. Therefore, $\omega_v'(r, U_{\mathrm{mc}}) = 0 \Leftrightarrow f(r) = \frac{1}{\theta}$ should have a single root for $r > R_{\mathrm{c}}$. Note that $\omega_v'(r, U_{\mathrm{mc}}) = 0$ 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:

$${R_{\mathrm{m}}}^2 = -\frac{a_3}{4a_4} + M + \frac{1}{2}\sqrt{-4M^2 - 2p + \frac{q}{M}}, \tag{S4}$$

where $p = \frac{8a_4a_2 - 3{a_3}^2}{8{a_4}^2} = 0$, $q = \frac{{a_3}^3 - 4a_4a_3a_2 + 8{a_4}^2a_1}{8{a_4}^3} = -2{l_c}^6$, $M = \frac{1}{2}\sqrt{-\frac{2}{3}p + \frac{1}{3a_4}(N + \frac{\Delta_0}{N})}$, $N = \sqrt[3]{\frac{\Delta_1 + \sqrt{{\Delta_1}^2 - 4{\Delta_0}^3}}{2}}$, $\Delta_0 = {a_2}^2 - 3a_3a_1 + 12a_4a_0 = -36{R_{\mathrm{c}}}^2{l_{\mathrm{c}}}^6$, and $\Delta_1 = 2{a_2}^3 - 9a_3a_2a_1 + 27{a_3}^2a_0 + 27{a_1}^2a_4 - 72a_4a_2a_0 = 108{l_{\mathrm{c}}}^{12}$ with $l_{\mathrm{c}} \equiv \left(\frac{8n_{\mathrm{c}}\epsilon\sigma^6}{\mu {v_0}^2}\right)^{\frac{1}{6}}$. Substituting the expressions of coefficients a_i into Eq. **S4** and rearranging leads to Eq. **15** in the main text.

References

[1] Manos, G., Dunne, L., Jalili, S., Furgani, A., Neville, T.: Monte Carlo Simulation and Exact Statistical Mechanical Lattice Models as a Development Tool for Zeolite Multi-Component Adsorption Isotherm Derivation, Adsorption Science & Technology 30, 503-519, 2012.

[2] Hirschfelder, J. O., Curtiss, C. F., Bird, R. B.: *Molecular theory of gases and liquids,* 1964.