Sum Frequency Generation Spectroscopy and Molecular Dynamics Simulations Reveal A Rotationally Fluid Adsorption State of α-Pinene on Silica

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SUPPORTING INFORMATION

Table S1. Intramolecular parameters based on the CWCA force field.[a]

Bond parameters			Angle parameters		
Bond	K_b	R_o	Angle	K_a	R_o
Si-O_b	885.1	1.61	Si-O_b-Si	4.66	174.22
Si-O_h	438.0	1.61	O_b-Si-O_b	159.57	110.93
O_h-H	545.0	0.96	O_h-Si-O_b	153.26	111.09
			H-O_h-Si	57.50	106.0

[a]O_b and O_h refers to bulk and silanol oxygen atoms respectively. Bond and angle function is harmonic with force constant K_b and K_a (kcal/mol.Å) respectively. R_o refers to equilibrium bond distance (Å) and angle (°).

Table S2. **Intermolecular parameters based on the CWCA force field.**[a]

Atom	q ($\|e\|$)	ε (kcal/mol)	r^{min} (Å)
Si	0.90	0.3000	4.2950
O_b	-0.45	0.1500	2.500
O_h	-0.66	0.1521	3.5400
H	0.43	0.0460	0.4490

[a]O_b and O_h refers to bulk and silanol oxygen atoms respectively.

Table S3. Atomic charges for the various atom types in α-pinene.

Atom	Atom type	Charge
C1	CG2D1	0.184
C2	CG2D1	–0.303
C3	CG321	–0.146
C4	CG3RC1	–0.119
C5	CG3C41	0.102
C6	CG3RC1	–0.155
C7	CG331	–0.297
C8	CG331	–0.297
C9	CG3C41	–0.159
C10	CG331	–0.310
H11	HGA4	0.150
H12	HGA2	0.090
H13	HGA2	0.090
H14	HGA1	0.090
H15	HGA1	0.090
H16	HGA3	0.090
H17	HGA3	0.090
H18	HGA3	0.090
H19	HGA3	0.090
H20	HGA3	0.090
H21	HGA3	0.090
H22	HGA2	0.090
H23	HGA2	0.090
H24	HGA3	0.090
H25	HGA3	0.090
H26	HGA3	0.090

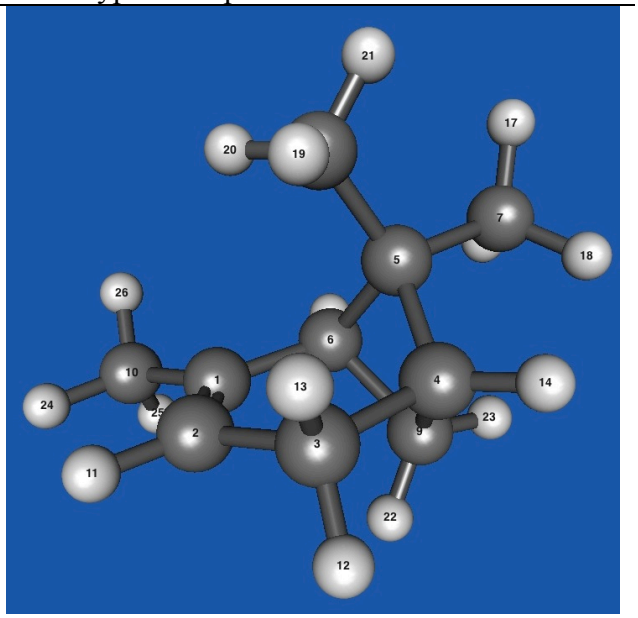


Figure S1. Contour plot of the normalized error (top) between the calculated (without accounting for Fermi resonance) and experimental spectra based on rotation angles θ and ψ.

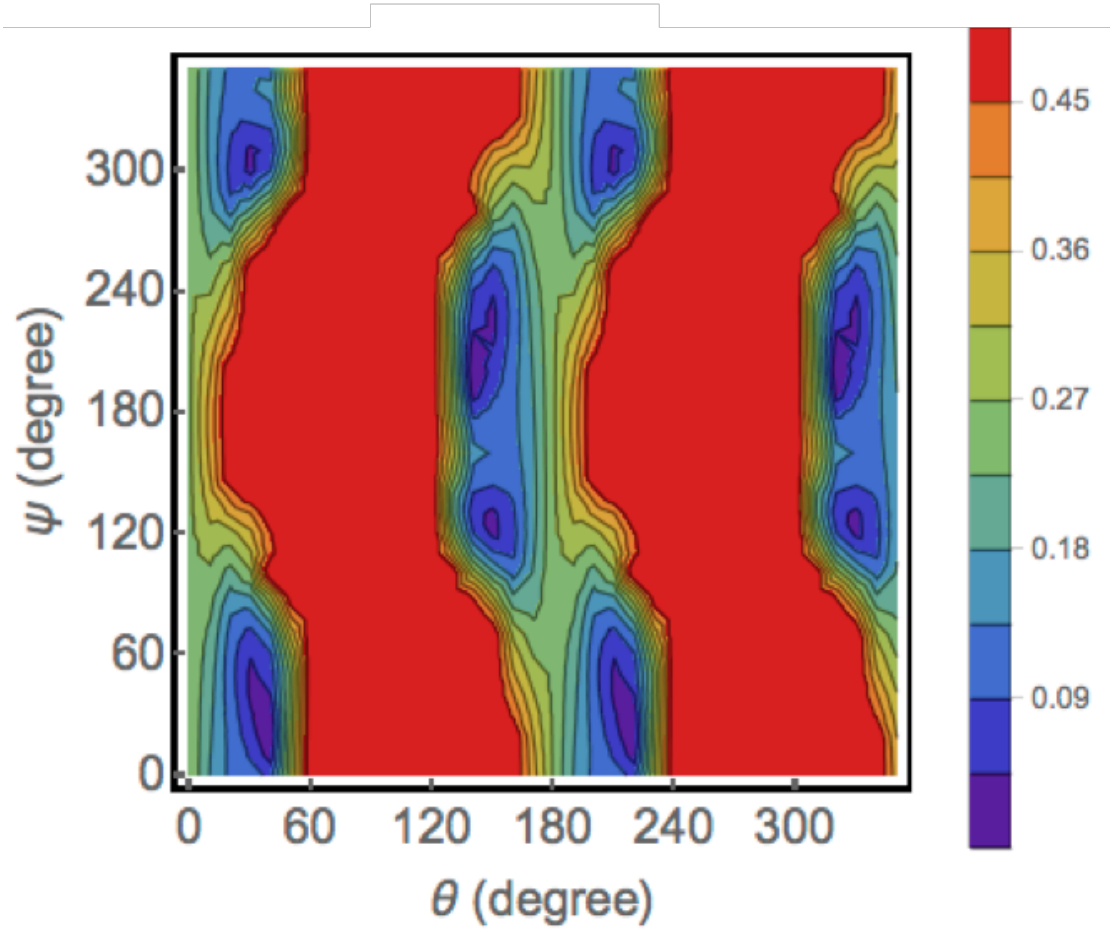
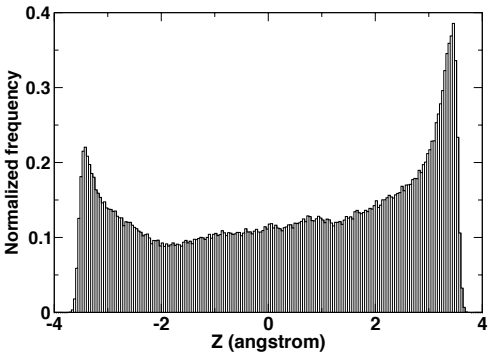
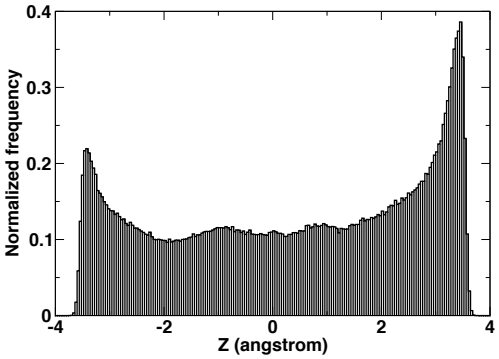


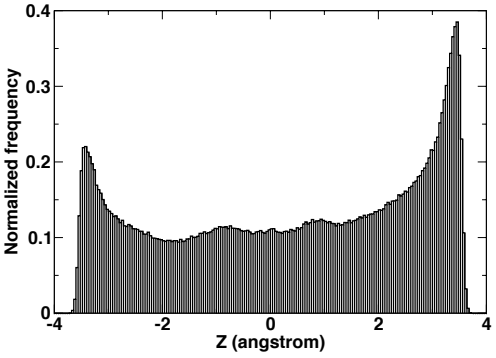
Figure S2. The histograms of z-values for 130 pinene molecules on fused silica surface computed as a function of simulation time.



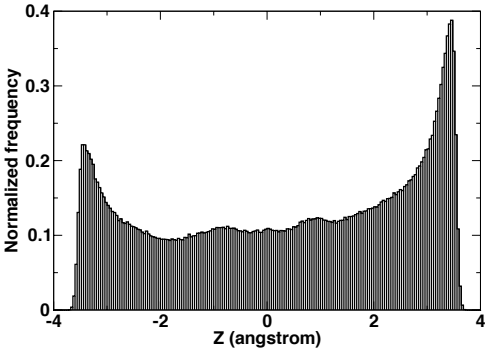
3ns



5ns



8ns



10 ns

Figure S3. The histogram of z-values for a pinene molecule on a cluster model of fused silica surface derived from a 120 ps DFTB trajectory.

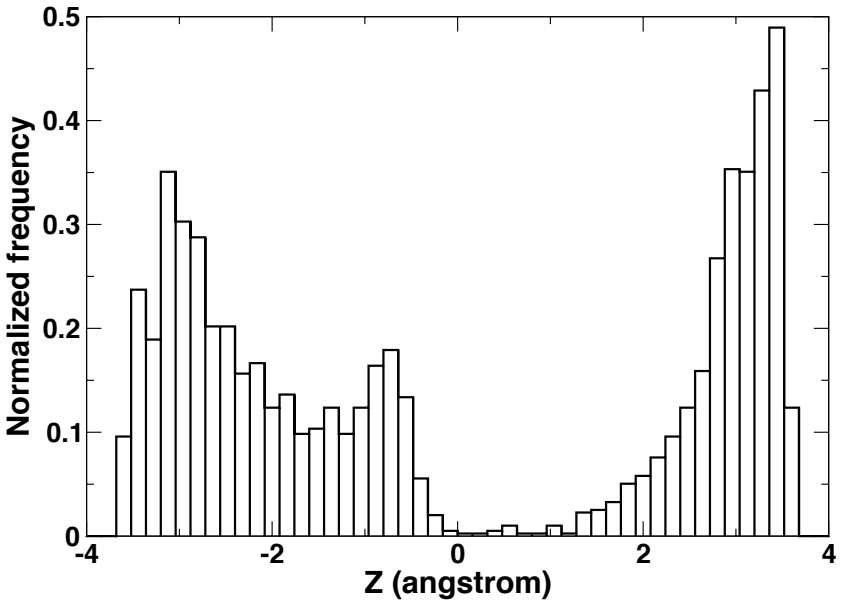


Figure S4. Single exponential fit (red dotted line) to the reorientational autocorrelation function. $C(t) = 0.409\exp\left(-t/1284.2\right)$