Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for "Diffusion Monte Carlo evaluation of disiloxane linearization barrier"

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Supplementary Information

Molecular geometry

Geometry information for the two disiloxane conformers as optimized by the MP2/cc-pVQZ level is given in Table 1.

Table 1: MP2/cc-pVQZ geometry optimization results of the two conformers of disiloxane molecule

Conformer	Si-O (Å)	∠ Si-O-Si (°)	Si-H* (Å)	∠ O-Si-H* (°)	∠ H-Si-H* (°)
Linear (straight)	1.630	180.0	1.475	109.6	109.3
Nonlinear (bent)	1.640	146.4	1.475	109.5	109.5
Experiment[1]	1.634	144.1	1.486	109.9	109.1

* Averaged values

Comparison of geometry optimization method

Comparison between two optimized geometries of non-liner disiloxane from at the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ level is shown in Table 2.

Table 2: Disiloxane molecular geometry with CCSD(T) and MP2 at the cc-pVTZ basis-set level

Method	Si-O (Å)	∠ Si-O-Si (°)	Si-H* (Å)	∠ O-Si-H* (°)	∠ H-Si-H* (°)
Non-linear					
MP2	1.646	147.0	1.477	109.5	109.4
CCSD(T)	1.644	146.5	1.482	109.6	109.3
Linear					
MP2	1.636	180.0	1.477	109.6	109.3
CCSD(T)	1.633	180.0	1.482	109.7	109.2

* Averaged values

Time-step bias in FNDMC

As outlined in main text, linear regression is usually utilized in DMC to obtain expectation values at timestep $\delta t \to 0$. In this work, quadratic regression is instead used in place of linear regression,

Table 3: Disiloxane linearization barrier with CCSD(T) and MP2 geometries at the cc-pVTZ basis-set level

Geometry	Linearization barrier (kcal/mol)	
	MP2	CCSD(T)
MP2	0.38602	0.42539
CCSD(T)	0.38618	0.42511
ΔE	-0.00016	0.00028

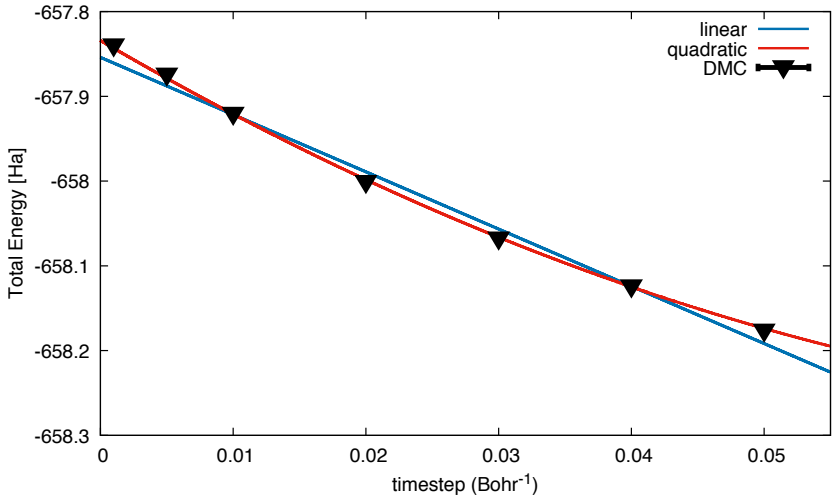

Figure 1: DMC calculation results at different timestep values for delinear disiloxane, using Slater orbitals derived from the cc-pVQZ basis set.

using 3 timestep values of 0.01, 0.005, and 0.001 $Bohr^{-1}$, all of which gives high acceptance ratio in the FNDMC algorithm (> 95%). From testing DMC calculations at various timestep values, a quadratic regression was found to be a better match for the general trend of the data instead of a linear regression, as shown in Figure 1 using the DMC calculation for the delinear structure of disiloxane with the cc-pVQZ basis set as an example.

References

(1) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. The molecular structure of disiloxane $(SiH_3)_2O$. *Acta Chem. Scand* **1963**, *17*, 2455–2460.