

Acceleration of xenon kick-out exchange in a cryptophane host explained by ab initio simulation

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Supporting information

1 Optimization of the Xe pseudopotential

We have designed a new ultrasoft pseudopotential¹ for xenon which is an improved version of the one used in our previous simulations.² The valence space includes 18 electrons, namely $4d^{10}5s^25p^6$. During its construction, the PBE density functional approximation³ was used and scalar relativistic effects included. The tests in this supplemental material and simulations in the article were performed with dispersion corrections according to the D3 scheme with zero-damping.⁴ The corresponding pseudopotential file is available on Zenodo at the following address: <https://doi.org/10.5281/zenodo.11127120>.

2 Test on the Xe-Xe dimer

The xenon dimer was considered because of the degenerate exchange reaction to be studied. Tests reported in Table S1 show that the PBE-D3 calculation with the new ultrasoft pseudopotential can accurately predict the interaction energy E_{int} but slightly overestimates the equilibrium distance R_e .

Table S1: Data optimized with the new Xe pseudopotential at a plane-wave cutoff of 35 Ry compared with PBE-D3⁵ and CCSD(T)⁶ reference calculations as well as experiment⁷

	R_e (Å)	E_{int} (kcal/mol)
PBE-D3 (35 Ry)	4.48	-0.566
PBE-D3 (ECP28MDF)	4.50	-0.546
CCSD(T)	4.41	-0.528
Exp.	4.36	-0.561

3 Tests on Xe-H₂O complexes

Interaction between xenon and water was considered because of the degenerate exchange reaction occurs in aqueous solution. Tests reported in Table S2 show that the PBE-D3 calculation with the new ultrasoft pseudopotential can accurately predict the energetic order between three geometries of the Xe-H₂O dimer, namely G5 (one H pointing toward Xe) < G2 (O pointing away from Xe) < G1 (O pointing toward Xe), with accurate distances as well.

Table S2: Data optimized with the new Xe pseudopotential at a plane-wave cutoff of 35 Ry for three geometries denoted as G5, G2 and G1. Corresponding CCSD(T) values⁸ are given in parentheses.

	R_e (Å)	E_{int} (kcal/mol)
G5	4.03 (4.00)	-0.910 (-0.548)
G2	4.00 (3.95)	-0.787 (-0.483)
G1	3.74 (3.85)	-0.527 (-0.462)

4 Tests on Xe-CH₄ complexes

Tests reported in Table S3 show that the PBE-D3 calculation with the new ultrasoft pseudopotential can also accurately predict the energetic difference between two geometries of the Xe-CH₄ dimer, corresponding to vertex (along the vertex of the CH₄ tetrahedron) and facial (perpendicular to one of the faces of the CH₄ tetrahedron) approaches, with accurate distances as well.

Table S3: Data optimized with the new Xe pseudopotential at a plane-wave cutoff of 35 Ry for two geometries denoted as vertex and facial. Corresponding complete basis set CCSD(T) values⁹ are given in parentheses.

	R_e (Å)	E_{int} (kcal/mol)
vertex	4.47 (4.50)	-0.529 (-0.387)
facial	4.07 (4.05)	-0.690 (-0.584)

5 Water distribution around free Xe

Radial distribution function of water molecules around the free xenon atom for the initial configuration, prior to the degenerate exchange, is shown in Figure S1. Integration under the first peak provides a hydration number of approximately 20.

6 Configurations during degenerate exchange

Configurations labelled A, B, C, D, and E on the free-energy profile included in the article are shown in figure S2.

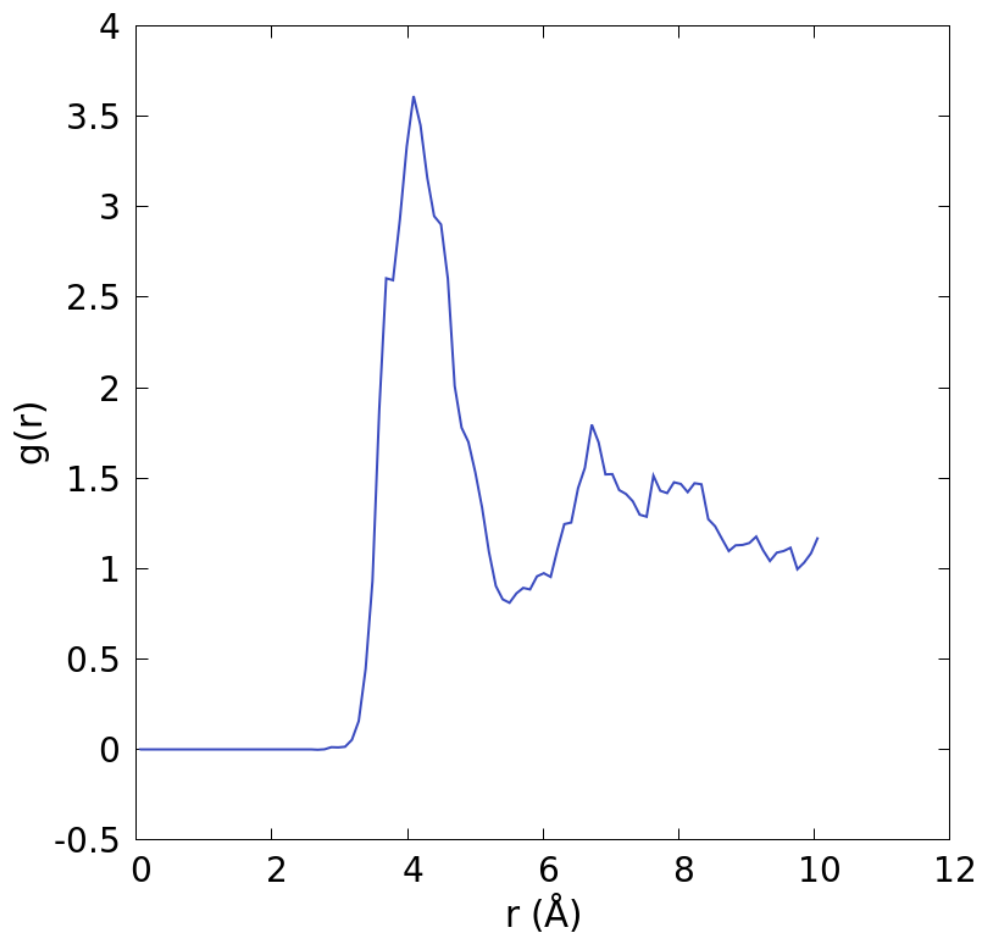


Figure S1: Radial distribution function of water oxygen atoms with respect to free Xe in the bulk

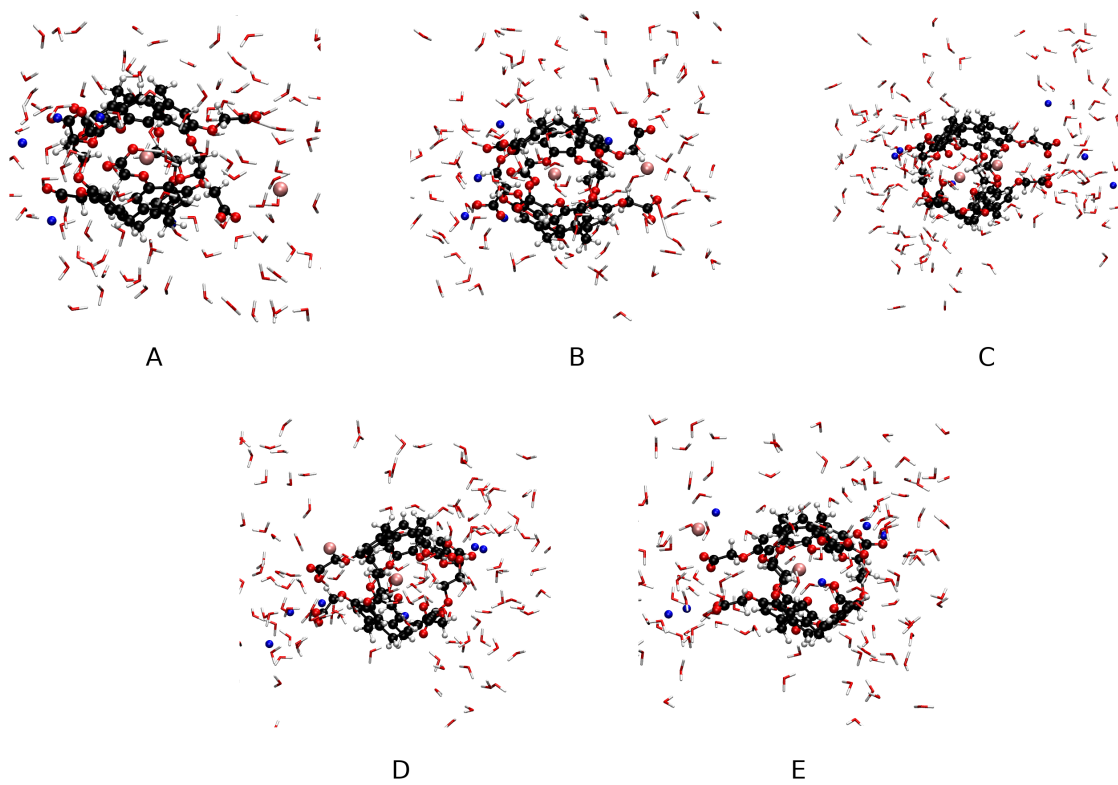


Figure S2: Representative configurations along the degenerate exchange reaction

References

- (1) Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895.
- (2) Pollet, R.; Dognon, J.-P.; Berthault, P. Isomer-Dependent Escape Rate of Xenon from a Water-Soluble Cryptophane Cage Studied by Ab Initio Molecular Dynamics. *ChemPhysChem* **2023**, *n/a*, e202300509.
- (3) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868, Erratum: (1997) Phys Rev Lett 78:1396.
- (4) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, *132*, 154104.
- (5) Kovács, A.; Cz. Dobrowolski, J.; Ostrowski, S.; Rode, J. E. Benchmarking density functionals in conjunction with Grimme’s dispersion correction for noble gas dimers (Ne₂, Ar₂, Kr₂, Xe₂, Rn₂). *International Journal of Quantum Chemistry* **2017**, *117*, e25358.
- (6) Rościszewski, K.; Paulus, B.; Fulde, P.; Stoll, H. Ab initio calculation of ground-state properties of rare-gas crystals. *Physical Review B* **1999**, *60*, 7905.
- (7) Ogilvie, J.; Wang, F. Y. Potential-energy functions of diatomic molecules of the noble gases I. Like nuclear species. *Journal of molecular structure* **1992**, *273*, 277–290.
- (8) Wen, Q.; Jäger, W. Rotational Spectroscopic and ab Initio Studies of the Xe- H₂O van der Waals Dimer. *The Journal of Physical Chemistry A* **2006**, *110*, 7560–7567.
- (9) Alexander, W. A.; Troya, D. Theoretical Study of the Ar-, Kr-, and Xe- CH₄,- CF₄ Intermolecular Potential-Energy Surfaces. *The Journal of Physical Chemistry A* **2006**, *110*, 10834–10843.