Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Information

Efficient Kr/Xe separation from triangular g-C_3N_4 nanopore

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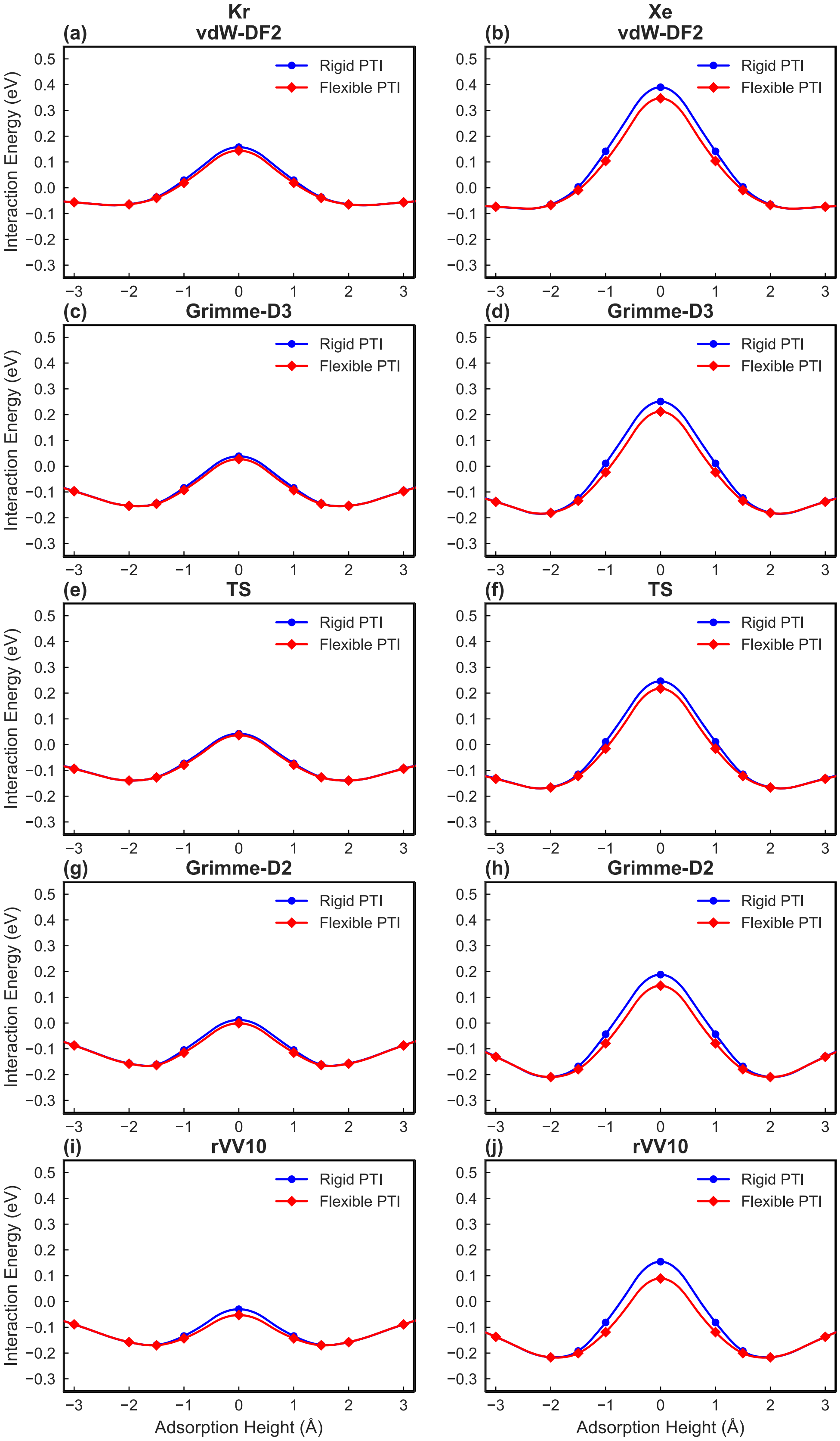

Figure S1. Potential energy surface (PES) of Kr (left) and Xe (right) on a rigid or flexible PTI monolayer using different van-der-Waals approximations: vdW-DF2, Grimme-D2, Grimme-D3, rVV10, and TS. PES data are obtained by constrained relaxation. A height of 0 Å corresponds to the plane of PTI monolayer.

RPA theory

The adiabatic connection fluctuation dissipation theorem (ACFDT) can be used as a framework to construct an exact expression for the exchange-correlation energy. All ACFD methods treat the exchange energy exactly, and the correlation in a consistent way. Moreover, it provides a framework for a systematic improvement of the exchange-correlation functional. The ACFDT also offers other advantages, such as:

- The self-interaction error which is present in Hartree energies exactly cancelled out by the exact-exchange energy.
- The correlation is purely non-local and van der Waals interactions are included automatically.

Based on Hohenberg-Kohn theory, the electron density can be obtained by solving the Kohn-Sham equations self-consistently:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{KS}[n](r) \right]\varphi_i(r) = \epsilon_i \varphi_i(r)$$

$$n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2$$

$$v_{KS}[n](r) = v_{ext}(r) + v_H[n](r) + v_{xc}[n](r)$$

It should be mentioned that if the exact xc functional were known, the self-consistent solution of Kohn-Sham equations would give the correct ground state density and energy of the interacting system. There are a lot of approximations for the xc functional, which can be classified in Local density approximation (LDA), Generalized Gradient approximation (GGAs), and hybrid functionals. Within the ACFDT novel functionals can be constructed.

The adiabatic connection theory originates from introducing a continuous set of coupling-strength (λ) dependent Hamiltonians $\hat{H}(\lambda)$ which connect a non-interacting Hamiltonian $\hat{H}_0 = \hat{H}(\lambda = 0)$ with the many-body Hamiltonian $\hat{H} = \hat{H}(\lambda = 1)$ describing the coulomb-interacting electronic system. This is done with a smooth turning-on of the electron-electron interaction controlled by the coupling-strength parameter λ. When the electron-electron interaction is turned-on, a non-trivial λ-dependent local potential $v_\lambda(r)$ is introduced in such a way to keep the density constant along the path. The local potential is such that at $\lambda = 1$, it is equal to the external potential of the fully interacting system while at $\lambda = 0$ it coincides with the Kohn-Sham potential $v_{KS}(r)$.

In the framework of ACFD, the exact expression of the exchange-correlation energy (E_{xc}) can be written as:[1,2]

$$E_{xc} =- \frac{1}{2}\int_0^1 d\lambda \int dr dr' \frac{e^2}{|r - r'|}\{\frac{\hbar}{\pi}\int_0^\infty \chi_\lambda(r,r';iu)du + \delta(r - r')n(r) \}$$

where $\chi_\lambda(r,r';iu)$ is the density-density response function of the λ-scaled interacting system evaluated for the imaginary frequencies.

The exchange-correlation energy consists of the KS exact-exchange energy E^{EXX}_x and the correlation energy E_c. The first one has the same expression as the Hartree-Fock exchange energy but it is evaluated with the KS orbitals $\phi_i(r)$,

$$E^{EXX}_{x} = -\frac{e^2}{2}\int drdr'\frac{\left|\sum_{v}^{occ}\phi^{*}_{v}(r)\phi_{v}(r')\right|^2}{|r-r'|}$$

The correlation energy is expressed as an integral over the coupling constant and over the imaginary frequency of the trace of the product of the Coulomb potential and the density-density response function. Using the RPA to approximate the latter the integral over the coupling constant can be done analytically, leading to the following expression for the correlation energy:

$$E^{RPA}_{c} = \frac{\hbar}{2\pi}\int_{0}^{\infty} duTr\{\ln\left[1-v_c\chi_0(iu)\right]+v_c\chi_0(iu)\}$$

where T_r stands for the integral with respect to r and r', and where the bare Coulomb interaction kernel v_c is defined as $v_c = e^2/|r-r'|$.

Therefore, the EXX/RPA total energy is defined as:

$$E^{EXX/RPA}_{tot} = T_s + E_{ext} + E_H + E^{EXX}_{x} + E^{RPA}_{c}$$

where T_s, E_{ext}, and E_H are the kinetic, external, and the Hartree energies of the KS system, respectively.

We refer the interested reader to ref. 3 and references therein for and exhaustive discussion of the RPA and its applications.

RPA convergence tests:

To carry out the EXX/RPA calculations and to find out the optimal parameters for RPA calculations, some general aspects were tested: first, the effects of molecule relaxation on the PES. Second, the influence of reducing the PTI supercell size. Third, effects of *k*-points sampling. Forth, the influence of using norm conserving pseudopotential instead of ultra-soft pseudopotential. And finally, the effects of reducing the cutoff as much as possible was studied:

With this convergence tests, it can be concluded that EXX/RPA calculations can be done with norm conserving pseudopotential, at the Γ point, on a small PTI supercell size (Figure S2).

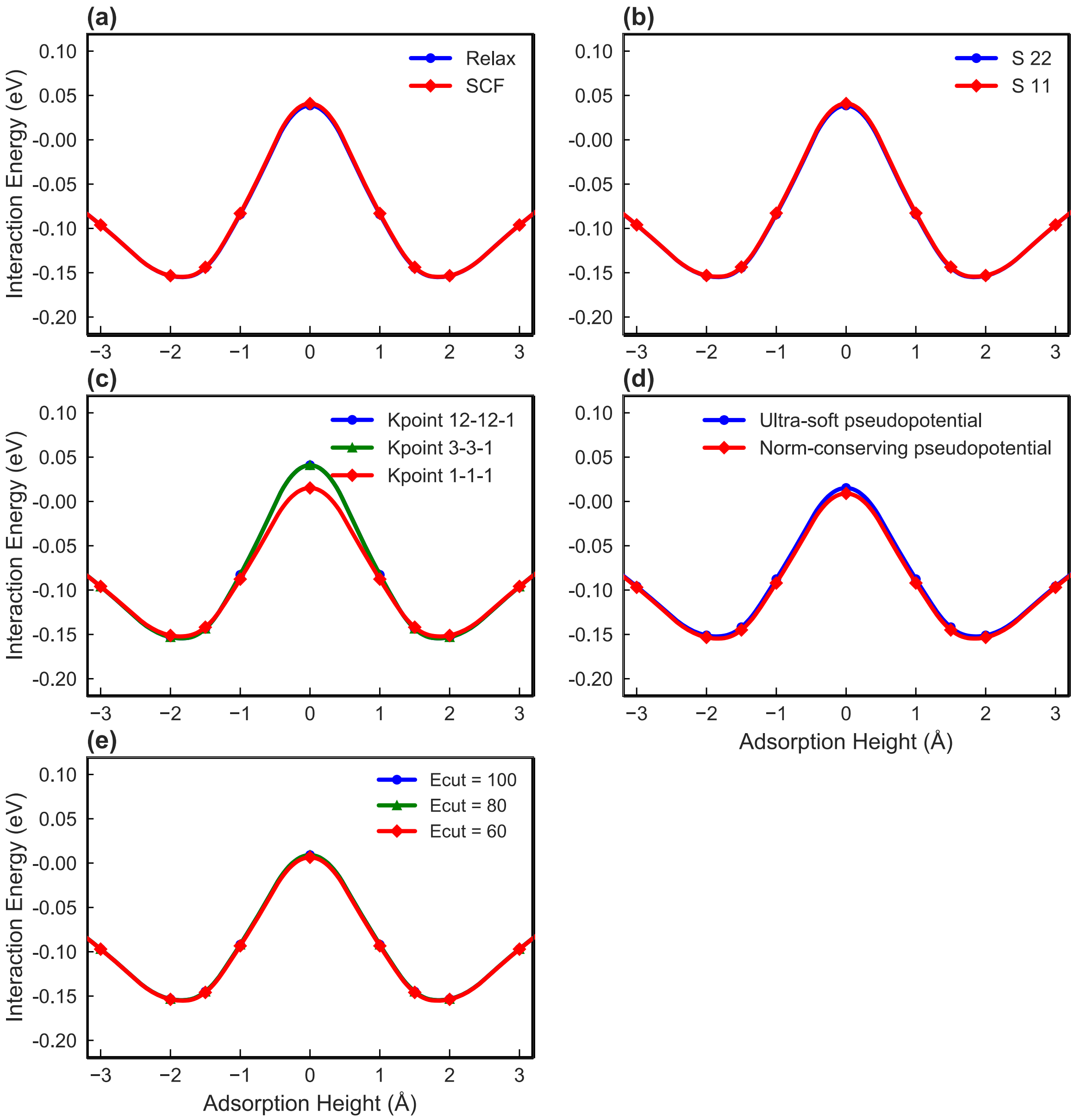

Figure S2. Potential energy surface (PES) of Kr molecule on PTI lattice a) with relaxation of molecule or just one snapshot energy calculation b) at different supercell size (2 × 2 supercell (S22) or 1 × 1 unit cell (S11)) c) at various *k*-points d) with ultra-soft or norm conserving pseudopotential e) at different cutoff values.

Force field parameters:

Supplementary Table 1. Force-field parameters employed in the classical MD simulations for the PTI monolayer.

Name	**Parameters**	**Energy (kcal/mol)**
Bond (C=NC)	$r_0 = 1.3298$ Å	498.0019
Bond (N-H)	$r_0 = 1.0156$ Å	404.6009
Bond (C-N_H)	$r_0 = 1.3813$ Å	478.0019
Bond (C-N)	$r_0 = 1.3532$ Å	488.0019
Angle (C-N-C)	$t_0 = 126.55$	72.6601
Angle (N-C-N)	$t_0 = 113.45$	68.3497
Angle (N-C-N_H)	$t_0 = 111.46$	68.3497
Angle (N-C-N_H)	$t_0 = 121.24$	70.9202
Angle (C-N_H-H)	$t_0 = 113.80$	68.3497
Angle (C-N_H-C)	$t_0 = 132.37$	70.9202

Supplementary Table 2. Non-bonded force-field parameters employed in the classical MD simulations.

Name	**Mass (1.66 * 10^{-27} Kg)**	**Charge (e)**	**LJ σ (Å)**	**LJ ε (kcal/mol)**
C	12.01	0.9494	3.3997	0.0860
H	1.008	0.4863	1.0691	0.0157
N(C-N_H-C)	14.01	-0.7855	3.2500	0.1700
N (C=N-C)	14.01	-0.8141	3.2500	0.1700
Kr	83.798	0.0	4.4590	0.1350
Xe	131.293	0.0	4.7730	0.1870

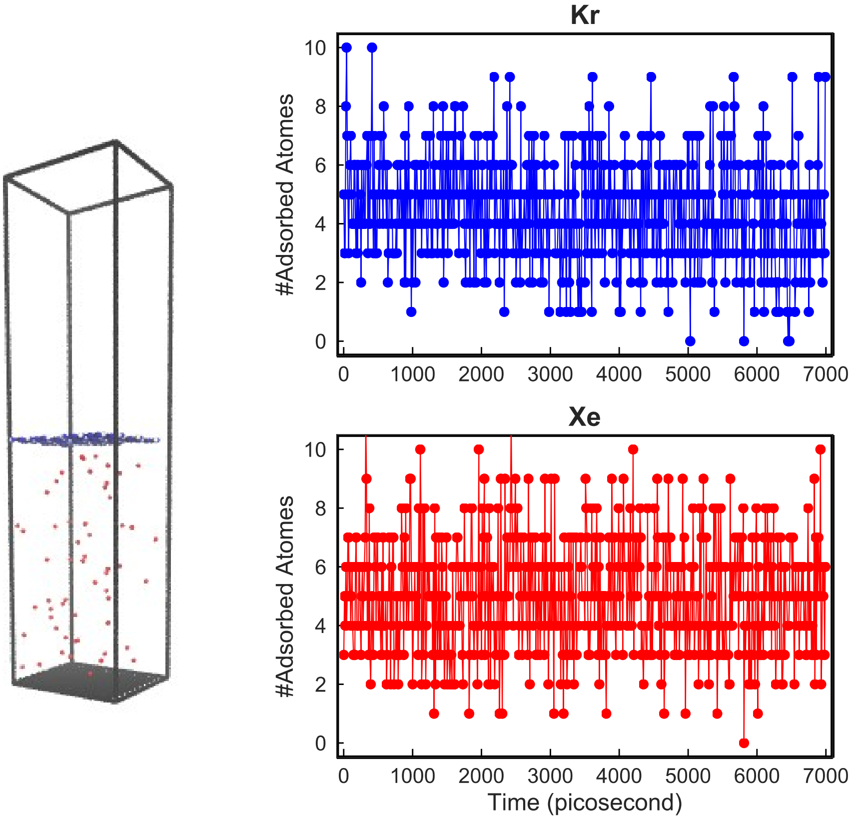

Figure S3. Left: Schematic of the simulation box consisting of a PTI sheet, graphene monolayer and Kr atoms (carbon in black, nitrogen in blue, hydrogen in white and krypton in red). Right: The number of adsorbed Kr and Xe atoms at different period of time.

References:

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