

QUANTUM MOLECULAR SIEVING IN CARBONS

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Introduction

The molecular sieving of isotopes has long been considered impossible, as they are of essentially identical size and shape. However, for light isotopes such as H₂ and D₂, quantum effects can lead to sufficiently large differences in de Broglie wavelengths at cryogenic conditions to make their molecular sieving possible in nanoporous materials having pores of molecular dimension. Whilst most of the attention [1,2] has focused on adsorption equilibrium, our recent simulations have shown remarkable counterintuitive effects, with the heavier deuterium diffusing faster than hydrogen at sufficiently low temperatures in nanoporous materials [3-5]. Here, we report the first *microscopic* experimental verification of this prediction, using quasi-elastic neutron scattering, along with extensive simulations of D₂/H₂ quantum separation in carbons. The results suggest suitable structures for facilitating the quantum effect, opening the door for carbon-based quantum effect-mediated kinetic separation of light isotopes.

Experimental

Our experiments were conducted using Takeda 3Å CMS. The micropore size distribution of the CMS was characterized by CO₂ adsorption at 273 K, with data interpretation by density functional theory. Quasi-elastic neutron scattering (QENS) measurements were performed at the Institut Laue Langevin, Grenoble, France, at very low loading (0.5 mmol/g) over the 30-140 K temperature range. The QENS spectra was fitted to a Lorentzian function of the energy to the experimental dynamical structure factor obtained at small values of the wave-vector transfer, and self-diffusivities obtained from the broadening [6].

Simulation

Adsorption simulations were performed for the adsorption of H₂/D₂ and H₂/HD mixtures in carbon slit pores, and in the Takeda 3Å CMS based on the PSD determined. We employed the Silvera-Goldman (SG) potential for adsorbate-adsorbate interactions, and the Steele 10-4-3 potential for adsorbate-adsorbent interactions. Quantum effects are incorporated into the simulations by the Feynman path integral (PI) formalism [7], modeling a single molecule as a ring of multiple interacting beads connected via harmonic springs. Adsorption

simulations were performed in the grand canonical ensemble, directly employing the PI formalism in grand canonical Monte Carlo (GCMC) simulations.

For interpreting the QENS spectra equilibrium molecular dynamics (EMD) simulations were performed to determine the self-diffusivities of H₂ and D₂ in a synthetic model carbon with defective slit-like pores. This model carbon comprises two parallel graphitic sheets separated by a carbon-carbon distance corresponding to pore size H_{cc} . Cage-window pairs are created by removal of carbon atoms such that the pore volume of the carbon model approximates that of the actual Takeda 3Å CMS of 0.17 cm³/gm. Hydrogen isotope molecules (H₂ and D₂) and carbon atoms are modeled as effective Lennard-Jones (LJ) spheres. The Lennard-Jones (12-6) potential is employed to model sorbate-sorbate and sorbate-carbon interactions, with the fourth order expansion [3] of the semi-classical Feynman-Hibbs potential representing quantum effects. For the H₂-H₂ and D₂-D₂ interactions we used the LJ parameters $\sigma_f = 0.2958$ nm and $\epsilon_f / k_B = 36.7$ K, and for the C-C interaction we used the flat surface parameters [8] $\sigma_c = 0.34$ nm and $\epsilon_c / k_B = 37.2$ K. LJ sorbate-carbon parameters were determined based on the Berthelot mixing rules. The EMD simulations used a 0.3 fs time step, with total run length typically 120 ns. Each run consists of 3 molecules in a unit cell which approximates the experimental loading of 0.5 mmol/g. The self-diffusivity is determined from the particle velocity autocorrelation function (VACF).

Results and Discussion

Figure 1 depicts the comparison of predicted and measured [9] isotherms of hydrogen and deuterium in the Takeda 3Å CMS at 77 K. Our predictions used the pore size distribution (shown in the inset) obtained by CO₂ adsorption at 273 K, using the PI technique to represent quantum effects. High pressure adsorption data for CO₂ were combined with our low pressure data in obtaining the PSD [8]. While showing excellent agreement of the predictions with data, the results clearly show the importance of the quantum effect, with D₂ having stronger adsorption than H₂.

We performed equilibrium simulations of mixture adsorption in carbon slit pores at temperatures of 40 K and 77 K, using the PI formalism. The molar ratio of the two components in the bulk phase was taken to be 1:1 for the simulations. The selectivity was calculated using $S_{21} = (x_2 / x_1) / (y_2 / y_1)$, where S_{21} is the selectivity of specie 2 over specie 1, x_i is the mole fraction of specie i in the adsorbed phase and y_i is the mole fraction of specie i in the bulk phase. The results showed that the lower temperature of 40 K is more favorable for selective adsorption of HD or D₂ over H₂, with pores of size 0.56-0.57 nm being optimal. In this pore size range the selectivity is rather weakly sensitive to pore size while the density increases remarkably with pore size at low pressure. At 0.57 nm pore size the selectivity is about 15-17 for D₂ compared to H₂ and about 5 for HD over the 0.1-10 bar pressure range.

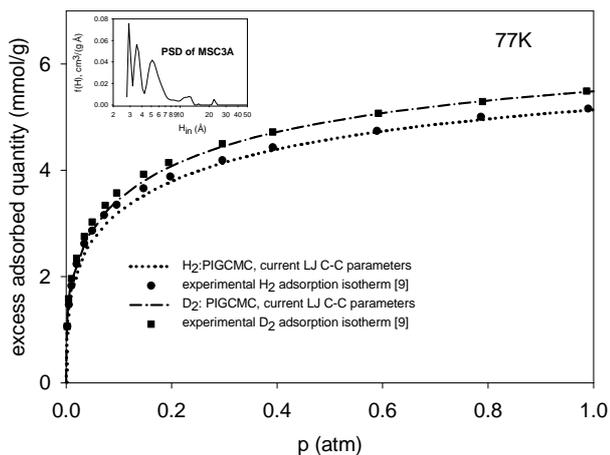


Figure 1. Comparison of experimental adsorption isotherms of H₂ (filled circles) and D₂ (filled squares) in Takeda 3 Å CMS at 77 K with those predicted using the PSD (inset).

Calculations were subsequently done for the mixture equilibrium in the Takeda 3 Å CMS at 40 K and 77 K, but yielded very low selectivity largely because of the wide PSD. However, narrow necks of the CMS may facilitate kinetic separation. Consequently, QENS experiments were conducted, and yielded a kinetic selectivity of about 3 for D₂ over H₂ at 40 K. To interpret the QENS measurements we used the Feynman-Hibbs approach with transition state theory for the barrier crossing across a pore neck, to obtain

$$\ln\left(\sqrt{2}\frac{D_s(D_2)}{D_s(H_2)}\right) = \frac{A}{T^2} \quad (2)$$

where A represents a *quantum separation factor*, dependent only on the intrinsic properties of an adsorption system. Equation (2) is a remarkable result, showing inverse *quadratic* temperature dependence due to quantum effects, distinct from the Arrhenius character of a classical activated barrier crossing process. Figure 2 validates the applicability of Eq. (2) to our QENS data, confirming the importance of the quantum effect.

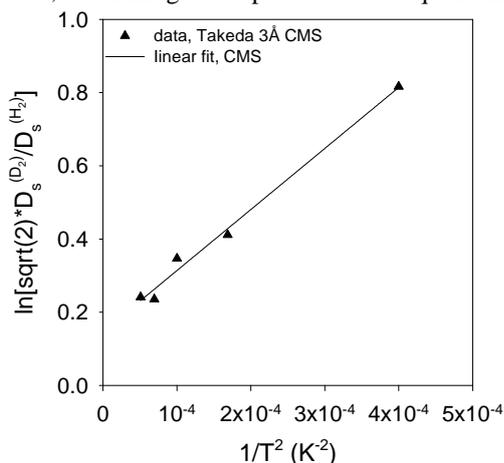


Figure 2. Variation of ratio of diffusivities of D₂ and H₂ in Takeda 3 Å CMS with inverse temperature squared.

Molecular dynamics simulations and transition state theory calculations were next conducted to estimate diffusion coefficients of D₂ and H₂ using synthetic model carbons. These comprised of slit-like pores in which cage-window pairs were created by removal of carbon atoms, and fullerenes with narrow windows. Cross-over of the diffusivities was observed below 100K, with larger pores contributing to the quantum effect as temperature is reduced. The QENS data could be explained quantitatively considering the range of pore sizes in the first peak of the PSD of the CMS to correspond to windows connecting slightly larger cages. The results highlight the importance of sufficiently narrow pore mouth size in facilitating the quantum kinetic sieving effect, with only slightly wider pore bodies to restrict the energy barrier.

Conclusions

Quantum effects on hydrogen isotopes in CMS are not sufficiently significant at equilibrium, but narrow necks can facilitate quantum kinetic sieving. Indeed, quantum kinetic sieving of H₂ and D₂ has been observed in Takeda 3 Å CMS at low temperatures, with the latter diffusing faster below 100 K. Our simulations and interpretations of the data indicate that carbonaceous molecular sieves hold promise as adsorbent materials for this separation. The key to an optimal material is to have both a small pore mouth, to provide a strong quantum effect, and small cage size, so as to achieve high flux by minimising the energy barrier. The design and synthesis of improved materials with these properties will lead to new adsorptive separation process for light isotopes.

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