Quantum Balancing: Entropy and Intermolecular Dynamics of CO_2 Captured in Green Solvents

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Deep eutectic solvents (DES) such as reline are an emerging class of low-cost, environmentally friendly solvents with tunable properties that are potentially applicable for capture and separation of CO_2. Experimental measurements showed that a reline-based membrane contactor can capture and separate CO_2 via physisorption through a dissolution process with 96.7% purity from a mixed gas containing CO_2 and N_2 (50% : 50% molar ratio)[1]. We examine the nature of interaction of CO_2 and N_2 with reline employing quantum chemical methods[2]. We focus on explaining the mechanism by which CO_2 and N_2 bind to reline and the nature of high selectivity for absorption of CO_2 compared to N_2. We analyze the dynamics, energetics, and binding motifs for CO_2 and N_2 in reline employing Density Functional Theory (DFT), Density Functional Tight Binding (DFTB), and ab initio molecular dynamics (AIMD). We also investigate the effect of reline on vibrational spectra of CO_2 and reline. Our simulations indicate that the selective capture of CO_2 from the mixture of CO_2 and N_2 is due to the interplay between attractive electrostatic and charge polarization forces with the opposing entropic effects which shift the energetic balance and makes the N_2 absorption unfavorable in reline.

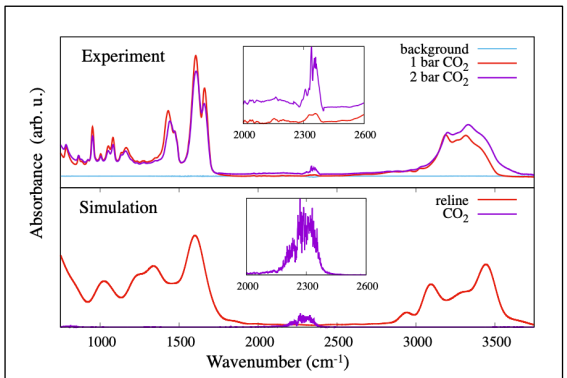

Figure 1. Comparison of experimental and theoretical vibrational spectrum of CO_2 in reline.

[1] S. Islam, A. Arifuzzaman, G. Rother, V. Bocharova, R. Sacci, J. Jakowski, J. Huang, I. N. Ivanov, R. R. Bhave, T. Saito, D. Sholl, *A Membrane Contactor Enabling Energy-efficient CO_2 Capture from Point Sources with Deep Eutectic Solvents*, Ind. & Eng. Chem. Res. (2023) 62, 10,4455-4465 [DOI: 10.1021/acs.iecr.3c00080]

[2] Jacek Jakowski, Jingsong Huang, Syed Z. Islam, David S. Sholl, "*Quantum Chemical Simulations of CO2 and N2 Capture in Reline, a Prototypical Deep Eutectic Solvent*", J. Phys. Chem. B, (2023), 127, 8888-8899 [doi: 10.1021/acs.jpcb.3c02174]