

a. PRF# 56192-DNI6

b. Project Title: Molecular Determinants of Favorable Clathrate - Surface Interactions

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Introduction: At low temperatures and high pressures, small guest molecules, such as CH₄ or CO₂, stabilize ice-like structures called clathrate (or gas) hydrates. On one hand, clathrate hydrates represent a bounty of oceanic natural gas reserves that are estimated to exceed the natural gas in all the other hydrocarbon reserves combined by a factor of two; on the other hand, gas hydrates are a source of great frustration due to their tendency to form plugs in oil and natural gas pipelines [1]. Thus, understanding the principles that govern clathrate formation is important. Under realistic conditions, the formation of hydrates occurs through heterogeneous nucleation, i.e., hydrate formation is catalyzed by surfaces [2]; however, what enables surfaces to facilitate (or inhibit) clathrate nucleation remains poorly understood. In this project, we seek to understand the molecular characteristics of surfaces that enable them to have favorable interactions with clathrate hydrates.

Progress made during the present reporting period:

Our first order of business was to uncover the molecular signatures of surface “clathrate-philicity”, i.e., the affinity of a surface for clathrate hydrates. We hypothesized that clues into whether a surface has favorable or unfavorable interactions with clathrate hydrates are present in certain properties of the supersaturated solution in the vicinity of a surface. To uncover such molecular signatures of surface clathrate-philicity, we made use of specialized molecular dynamics simulations.

Our first challenge was to use using molecular simulations to characterize interfacial waters, and to quantify their resemblance to water molecules in clathrate hydrates. However, the structure of clathrates (and of ice) resembles that of liquid water, both of which feature a tetrahedral network of hydrogen bonds; consequently, order parameters capable of teasing out the subtle differences between the two phases tend to be complex functions of the atomic positions. For example, the Steinhardt- Nelson-Ronchetti bond orientational order parameter, Q₆, which employs spherical harmonics to tease out the differences in orientational structure, has been used to discriminate between liquid water and ice. While hydrates are ice-like, they possess a somewhat different symmetry, so that Q₆ does not differentiate between the liquid and clathrate phases well [3]. To distinguish between water molecules belonging to clathrate hydrates, liquid water, hexagonal ice, and cubic ice, Nguyen and Molinero proposed a novel algorithm, which they called CHILL+ [4]. Thus, to discriminate between interfacial waters that are clathrate-like and those that are not, we chose as our order parameter, the number, λ_v, of waters in an interfacial volume, v, that are classified by CHILL+ as belonging to clathrates.

Although the CHILL+ algorithm makes it possible to identify clathrate-like interfacial waters, the corresponding order parameter is a highly complex and non-trivial function of atomic co-ordinates; see

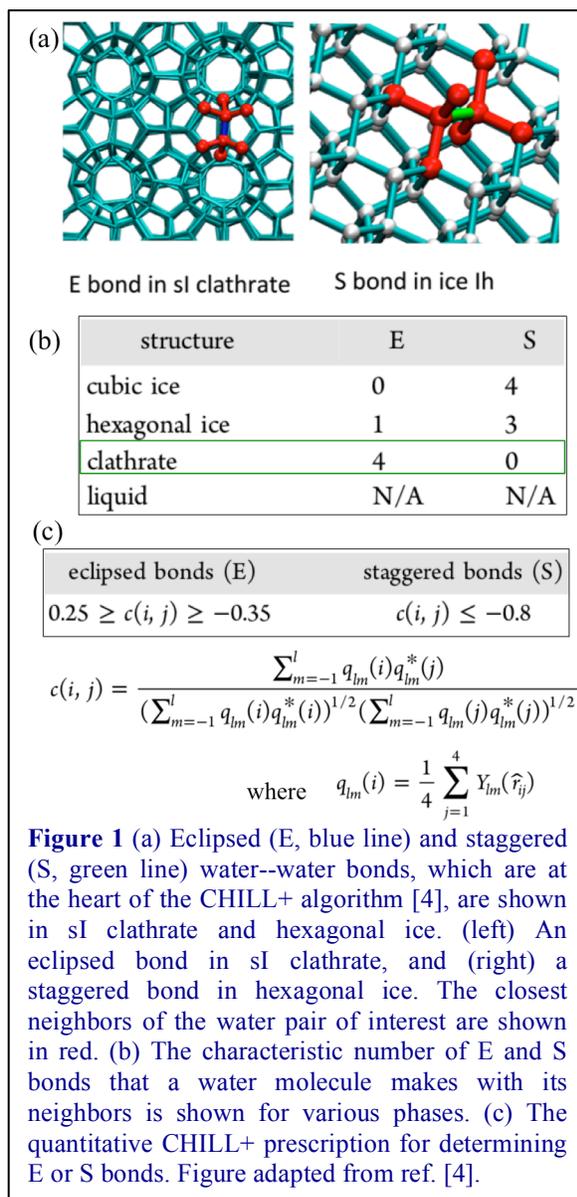
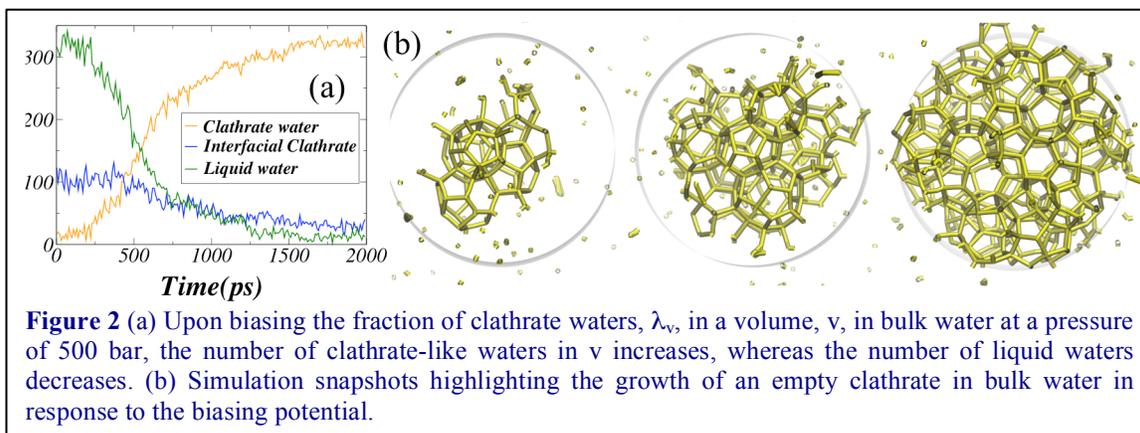


Figure 1. This complexity means that using enhanced sampling simulations to bias λ_v and stimulate clathrate nucleation is challenging. In this reporting period, we chose to undertake this challenge. Although extensive studies are needed to validate our results, our preliminary attempts to stimulate the formation of empty clathrates suggest that we are able to successfully use enhanced sampling to nucleate clathrate hydrates; see Figure 2.



Impact of the research on our research group: This Doctoral New Investigator Grant from the ACS Petroleum Research Fund has opened a new direction for our research group, and in addition to this project aimed at understanding the nucleation of gas hydrates, it has also facilitated related projects how antifreeze proteins inhibit ice nucleation. Funding to continue and expand the research on clathrate hydrates is being sought from the Department of Energy.

Facilitated in part by our work on this project: (i) Sean Mark's, a graduate student in the Patel group, was awarded the prestigious 4-year DOE CSGF fellowship, and (ii) the PI was awarded the 2018 Sloan Research Fellowship in Chemistry from the Alfred P. Sloan Foundation. The PI was also invited to present his work at the 2017 Berkeley Mini-Statistical Mechanics Meeting, and the 2017 Gordon Research Conference on the Chemistry and Physics of Liquids. One publication was submitted in the present reporting period [5].

References:

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