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NMR Evidence of Cage-to-Cage Diffusion of H_2 in H_2-Clathrates

LASITHA SENADHEERA, MARK CONRADI, Washington University — H_2 and heavy-ice at P>1 kbar and T ∼250 K form H_2-D_2O clathrate; four and one H_2 may occupy each large (L) and small (S) cage, respectively. In H_2-THF-H_2O clathrate, H_2 occupies singly and only S cages. Previous electronic-structure calculations estimate the barriers for H_2 passage though hexagonal and pentagonal faces of cages as ∼6 and ∼25 kcal/mol, respectively. Our H_2 NMR linewidth data reflect random crystal fields from frozen cage-wall D_2O orientations. We find dramatic reductions in linewidth starting at 120 K (175 K) for H_2-D_2O (H_2-TDF-D_2O) indicating time-averaging of the crystal fields. Assuming Arrhenius behavior, our data imply energies for escape from L (S) cages of about ∼4 (∼6) kcal/mol. For L cages, the agreement with the calculated (cages were treated as rigid) barrier is reasonable. For H_2 in S cages, in H_2-TDF-D_2O, the extreme disagreement with theory points to another mechanism of time-averaging, reorientations of the cage-wall D_2O molecules, as suggested by previous work in TDH-H_2O clathrate. Our limited NMR spectra at high T ∼145 K in H_2-D_2O show evidence of distinct resonances from diffusionally mobile and immobile H_2 molecules, as expected.

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