NMR Evidence of Cage-to-Cage Diffusion of H₂ in H₂-Clathrates

LASITHA SENADHEERA, MARK CONRADI, Washington University — H₂ and heavy-ice at P>1 kbar and T ~250 K form H₂-D₂O clathrate; four and one H₂ may occupy each large (L) and small (S) cage, respectively. In H₂-THF-H₂O clathrate, H₂ occupies singly and only S cages. Previous electronic-structure calculations estimate the barriers for H₂ passage though hexagonal and pentagonal faces of cages as ~6 and ~25 kcal/mol, respectively. Our H₂ NMR linewidth data reflect random crystal fields from frozen cage-wall D₂O orientations. We find dramatic reductions in linewidth starting at 120 K (175 K) for H₂-D₂O (H₂-TDF-D₂O) 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 H₂ in S cages, in H₂-TDF-D₂O, the extreme disagreement with theory points to another mechanism of time-averaging, reorientations of the cage-wall D₂O molecules, as suggested by previous work in TDH-H₂O clathrate. Our limited NMR spectra at high T ~145 K in H₂-D₂O show evidence of distinct resonances from diffusionally mobile and immobile H₂ molecules, as expected.