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 $\sim$250 K form H$_2$-D$_2$O clathrate; four and one H$_2$ may occupy each large (L) and small (S) cage, respectively. In H$_2$-THF-H$_2$O 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 $\sim$6 and $\sim$25 kcal/mol, respectively. Our H$_2$ NMR linewidth data reflect random crystal fields from frozen cage-wall D$_2$O orientations. We find dramatic reductions in linewidth starting at 120 K (175 K) for H$_2$-D$_2$O (H$_2$-TDF-D$_2$O) indicating time-averaging of the crystal fields. Assuming Arrhenius behavior, our data imply energies for escape from L (S) cages of about $\sim$4 ($\sim$6) kcal/mol. For L cages, the agreement with the calculated (cages were treated as rigid) barrier is reasonable. For H$_2$ in S cages, in H$_2$-TDF-D$_2$O, the extreme disagreement with theory points to another mechanism of time-averaging, reorientations of the cage-wall D$_2$O molecules, as suggested by previous work in TDH-H$_2$O clathrate. Our limited NMR spectra at high T $\sim$145 K in H$_2$-D$_2$O show evidence of distinct resonances from diffusionally mobile and immobile H$_2$ molecules, as expected.

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