Methyl-Group Rotational Tunneling Perturbations in Zeolitic Imidazolate Framework-8

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The framework-bonded methyl groups are oriented toward the large cavities of the nanoporous ZIF-8 structure and thus exhibit very rapid one-dimensional rotations. Indeed, the rotational potential was previously shown[1] to be primarily 3-fold in character with a very low rotational barrier of $\approx 7$ meV and a ground-state tunneling energy of $334 \, \mu$eV at 1.4 K. In this talk, we discuss the observed changes to this potential upon various perturbations to the ZIF-8 system, including Co substitution for Zn; site-specific adsorption of H$_2$, D$_2$, and CD$_4$; and high-pressure ($\leq 10$ kbar) He infiltration. Depending on the perturbation, the tunneling energy was found to vary by more than an order of magnitude, with values ranging from $408 \, \mu$eV to $<30 \, \mu$eV. [1] W. Zhou, H. Wu, T. J. Udovic, J. J. Rush, and T. Yildirim, J. Phys. Chem. A 112, 12602 (2008).