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Quantum instanton evaluation of the kinetic isotope effects JIRI VANICEK, Institute for Advanced Study, Princeton, WILLIAM H. MILLER, Department of Chemistry, University of California, Berkeley — The quantum instanton approximation is used to compute kinetic isotope effects for intramolecular hydrogen transfer in *cis*-1,3-pentadiene. Due to the importance of skeleton motions, this system with 13 atoms is a simple prototype for hydrogen transfer in enzymatic reactions. The calculation is carried out using thermodynamic integration with respect to the mass of the isotopes and a path integral Monte Carlo evaluation of relevant thermodynamic quantities. Efficient "virial" estimators are derived for the logarithmic derivatives of the partition function and the delta-delta correlation functions. These estimators require significantly fewer Monte Carlo samples since their statistical error does not increase with the number of discrete time slices in the path integral. The calculation treats all 39 degrees of freedom quantum-mechanically and uses an empirical valence bond potential based on a modified general AMBER force field. The importance of quantum effects due to the skeleton motion is demonstrated by comparison with a mixed quantum-classical calculation.

Jiri Vanicek
Institute for Advanced Study, Princeton

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