FULL DIMENSIONAL VIBRATIONAL CALCULATIONS FOR METHANE USING AN ACCURATE NEW AB INITIO BASED POTENTIAL ENERGY SURFACE

MOUMITA MAJUMDER, RICHARD DAWES, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA; XIAO-GANG WANG, TUCKER CARRINGTON, Department of Chemistry, Queen’s University, Kingston, ON, Canada; JUN LI, HUA GUO, Chemistry, University of New Mexico, Albuquerque, NM, USA; SERGEI MANZHOS, Department of Mechanical Engineering, National University of Singapore, Singapore, China.

New potential energy surfaces for methane were constructed, represented as analytic fits to about 100,000 individual high-level ab initio data. Explicitly-correlated multireference data (MRCI-F12(AE)/CVQZ-F12) were computed using Molpro [1] and fit using multiple strategies. Fits with small to negligible errors were obtained using adaptations of the permutation-invariant-polynomials (PIP) approach [2,3] based on neural-networks (PIP-NN) [4,5] and the interpolative moving least squares (IMLS) fitting method [6] (PIP-IMLS). The PESs were used in full-dimensional vibrational calculations with an exact kinetic energy operator by representing the Hamiltonian in a basis of products of contracted bend and stretch functions and using a symmetry adapted Lanczos method to obtain eigenvalues and eigenvectors. Very close agreement with experiment was produced from the purely ab initio PESs.