AN ACCURATE POTENTIAL ENERGY SURFACE FOR METHANE

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An accurate full dimensional methane potential energy surface (PES) will aid in assigning and understanding its complicated spectrum. Heretofore, there is no pure ab initio PES of methane on which rovibrational levels have errors less than one cm^{-1}. In this work, we obtain an accurate methane PES by starting with the ab initio PES of Schwenke and Partridge [Spectrochim. Acta A **57**, 887 (2001)] and adjusting 5 of their parameters to reproduce 39 reliable vibrational levels of CH_4. This reduces the rmsd from 4.3 cm^{-1} to 0.4 cm^{-1}. Since not all of the Tetradecad levels are certain, only 4, those confirmed by direct experimental transitions, are included in the fit. The new PES ought therefore to aid in the ongoing analysis of the Tetradecad polyad. To further test the accuracy of the new PES, vibrational and rovibrational levels are computed for CH_4, CH_3D, CHD_3 and CH_2D_2 and are compared with the extensive experimental data. The errors are all within about one cm^{-1}.

The fitting is made possible by a contracted-iterative method[a] for computing vibrational levels in a product of contracted stretch and bend functions. The fitting process is efficient because these contracted basis functions are not changed during the fitting cycles, which greatly reduces the time (to about 3 hours) to compute a new set of vibrational levels when the PES is slightly changed.

[a] X.-G. Wang and T. Carrington, Jr., J. Chem. Phys. **119**, 101 (2003).