

Efficient evaluation of anharmonic vibrational properties

Scientific Achievement

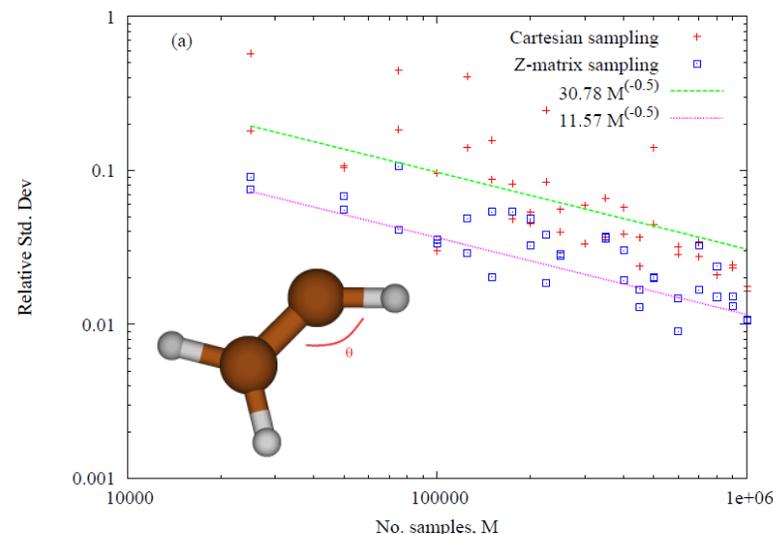
A new theoretical method and code (mcPSI) have been developed for evaluating fully anharmonic vibrational state counts and partition functions in generalized curvilinear coordinates.

Significance and Impact

Vibrational anharmonicity is typically neglected in practical rate calculations of combustion chemistry, which can result in significant errors. The present approach enables quantitative kinetics predictions, is demonstrated to accurately predict fully anharmonic vibrational properties, and is efficient enough to be applied to real systems.

Research Details

- State counts via classical Monte-Carlo integration of phase space, which are then quantum-corrected.
- Numerical evaluations of the Jacobian allow for optimal, problem specific coordinate systems, including “chemists coordinates” (stretches, bends, and torsions).
- Quantitatively, anharmonicity increases the reaction rate by factors of 2.0 and 1.4 for methane and vinyl radical dissociation.
- The algorithm uniquely allows for rovibrational coupling, which increases the methane partition function by 10% at 2500K.



An application of mcPSI for the vinyl radical in Cartesian normal mode and Z-matrix coordinates. Z-matrix coordinates show a 10x improvement in convergence rate which we attribute to the more natural description of the bending motion by the angle θ .

$$W(E) = 8\pi^2 h^{-(\alpha+3)} \int u[E - H(\mathbf{x}, \mathbf{p}, \mathbf{j})] \times \sqrt{I_1(\mathbf{x})I_2(\mathbf{x})I_3(\mathbf{x})} S^{\alpha+3}(\mathbf{p}(\mathbf{x})) d\mathbf{x}$$