

# MNST: A code for multidimensional nonadiabatic statistical calculations of spin-forbidden kinetics

## Background

Existing methods for electronically nonadiabatic kinetics are significantly less well validated and less accurate than their electronically adiabatic counterparts. New methods are needed to enable predictive nonadiabatic kinetics calculations.

## New theory

- Our previously developed multistate trajectories methods (available in the code DiNT) are used to characterize the physics of spin-forbidden reactions, with the goal of identifying physics that is neglected in existing statistical models.
- The “missing physics” includes multidimensional effects in the nonadiabatic transition probability, nonlocal electronic coherences, and nonstatistical effects.
- New statistical-based methods are being developed that include these missing physics. Most notably, we have developed a multidimensional nonadiabatic statistical theory that includes static and dynamical multidimensional effects.

## Code

- Crossing seams are characterized via direct calls to electronic structure programs
- MNST calculations are based on multidimensional corrections calculated with DiNT
- Electronically nonadiabatic fluxes are produced for use as input to AITSTME
- Availability: Coming soon

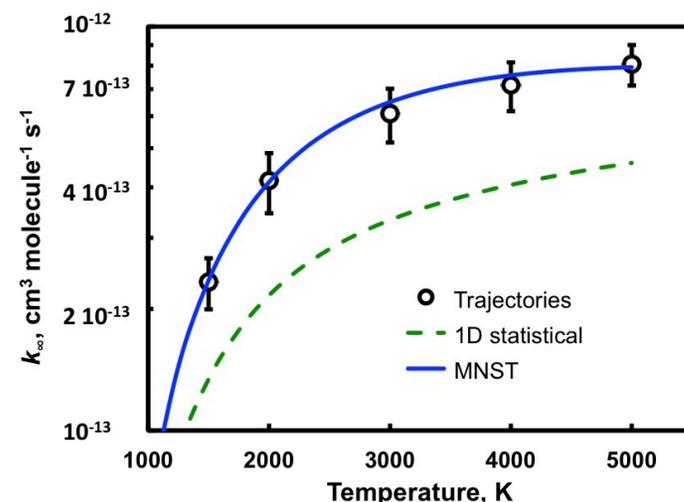


Fig 1. A comparison of spin-forbidden rates for  $O + CO \rightarrow CO_2$  calculated using: full-dimensional multistate trajectories (symbols), a simple one-dimensional statistical theory (green dotted line), and the new multidimensional statistical theory (blue solid line).

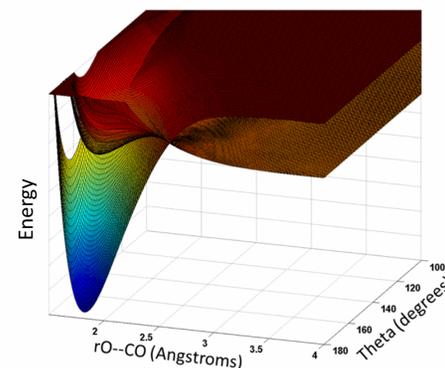


Fig 2. A representation of the 3 lowest-energy spin-orbit coupled potential energy surfaces of  $CO_2$  calculated via MRCI+Q/CBS and fit with IMLS. IMLS is an automated surface fitting strategy interfaced with DiNT and was used to obtain the multidimensional correction as input for MNST.