ELECTRONIC SUPPORTING INFORMATION FOR *CHEMICAL SCIENCE*

Army Ants Tunneling for Classical Simulations

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Details of the tunneling calculation

Because the tunneling path is along an internal coordinate, the Cartesian coordinates along the path are generated by Wilson's **A** matrix using eq. 1 and then converted to isoinertial coordinates. The end of the tunneling path is the geometry at which $[V(\mathbf{q})-V(\mathbf{q_0})]$ becomes zero again (it is zero at the beginning of the tunneling path, then positive, then comes back to zero).

Before calculating a tunneling path, its length is unknown. To calculate the imaginary action integral efficiently in the general case, we predefine a long enough tunneling path (longer than all the tunneling paths in the trajectories) and divide this predefined path into segments; in the current studies, the predefined path is 3.6 bohrs for bond length and 180 degrees for torsion angle, and the whole path is divided into 18 segments. The relative potential energy of the end point of each segment relative to the starting point of the tunneling path is calculated, and if the relative potential energy is positive, the segment should be fully included in the real tunneling path; if segment *M* is the first segment whose end point has negative energy, a small step (10^{-3} bohr for bond length and 0.1 degree for torsion angle) is used to search the precise ending point of the tunneling path. To calculate the distances ξ_i of points *i* from the start of a curved path in isoinertial coordinates, an evenly spaced fine grid is created in internal coordinates along the tunneling path and the distance $\xi_i^{\mathbf{int}}$ in internal coordinates is calculated for each grid point. Then ξ_i in isoinertial coordinates is approximated as a sum of small chord lengths, i.e. $\xi_i = \sum_{j=1}^{i} \left|\mathbf{q}_j - \mathbf{q}_{j-1}\right|$. Gauss-Legendre quadrature with 6 or more nodes is applied to the

whole tunneling path. For a given Gauss-Legendre node ξ_k that falls between ξ_i and ξ_{i-1}, we use linear interpolation to calculate the corresponding length in internal coordinate ξ_k^{int}, i.e., $\xi_k^{\text{int}} = \frac{(\xi_k - \xi_{i-1})\xi_i^{\text{int}} + (\xi_i - \xi_k)\xi_{i-1}^{\text{int}}}{\xi_i - \xi_{i-1}}$. If more than one internal coordinate is used in the definition of the tunneling direction, this expression is used for each internal coordinate. Once all ξ_k^{int} are known, the Cartesian coordinates of node *k* are calculated using Wilson's A matrix iteratively, and then the potential energy is calculated for that Cartesian geometry.

To conserve total energy and total angular momentum at the end of the tunneling path, the new momentum is adjusted to satisfy

$$\sum_j \mathbf{x}_{\text{end},j} \times \mathbf{p}_{\text{end},j} = \sum_j \mathbf{x}_{0,j} \times \mathbf{p}_{0,j} \tag{3}$$

$$\left|\mathbf{p}_{\text{end},j}\right| = \left|\mathbf{p}_{0,j}\right| \tag{4}$$

where $\mathbf{x}_j$ and $\mathbf{p}_j$ denote respectively the position vector of atom *j* in the unscaled Cartesian coordinates and the momentum of atom *j*. Since total angular momentum is zero in this study, both sides of eq. (3) are zero, and the momentum after tunneling is adjusted to $\mathbf{p}_{\text{end},j} = \left|\mathbf{p}_{0,j}\right| \frac{\mathbf{x}_{\text{end},j}}{\left|\mathbf{x}_{\text{end},j}\right|}$.

Illustration of the effect of varying the parameter η

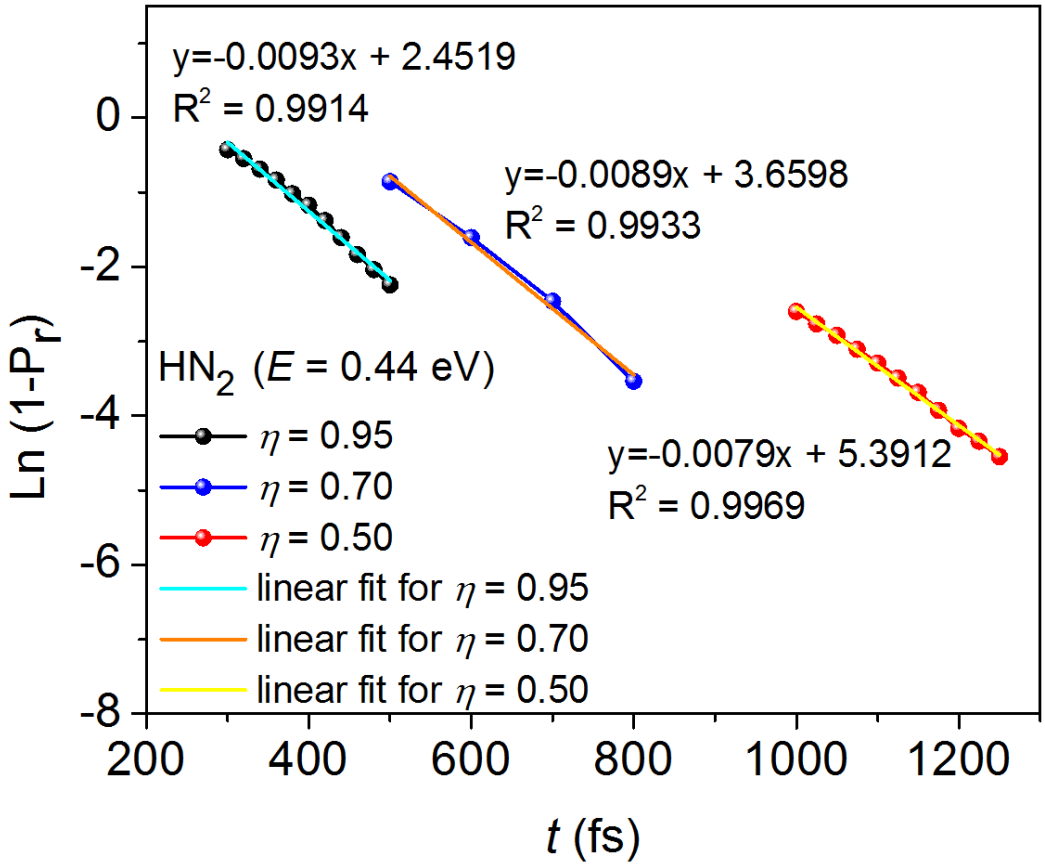

Figure S1. Linearity of the decay curves after induction time for various η values and the linear fitting results for obtaining rate constant.