electronic supplementary information (ESI) 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 displacements of Cartesian coordinates along the path are generated by Wilson's **A** matrix using eq. 1

$$\Delta \mathbf{x} = \mathbf{A}(\mathbf{x})\Delta \mathbf{R} \qquad \text{(S1)}$$

where $\mathbf{A}(\mathbf{x})$ is a generalized inverse matrix of Wilson **B** matrix at the current geometry **x** (where **x** is a vector of $3N$ Cartesian coordinates, where N is the number of atoms), and $\Delta \mathbf{R}$ is a column vector of internal coordinate displacements. Then the Cartesian coordinates are converted to isoinertial coordinates **q** by eq 2 of the main text. The end of the tunneling path is the geometry $\mathbf{q}'$ at which $\left[V(\mathbf{q}') - V(\mathbf{q}_0)\right]$ becomes zero again (it is zero at the beginning of the tunneling path, with coordinates $\mathbf{q}_0$, then positive, then comes back to zero). The location of the center of mass is unchanged by the tunneling process because it is carried out in internal coordinates, and in the presentation here we place the center of mass at the origin.

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 ξ_i^{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 angular momentum and total energy at the end of the tunneling path, the final atomic momenta are adjusted to satisfy

$$\sum_{i=1}^{N} \mathbf{x}'_i \times \mathbf{p}'_i = \sum_{i=1}^{N} \mathbf{x}_{0,i} \times \mathbf{p}_{0,i} \tag{S2}$$

$$\left| \mathbf{p}'_i \right| = \left| \mathbf{p}_{0,i} \right| \qquad i = 1, \ldots, N \tag{S3}$$

where $\mathbf{x}_{0,i}$ and $\mathbf{p}_{0,i}$ denote respectively the initial position vector of atom *i* in the unscaled Cartesian coordinates and the initial momentum of atom *i*. (Note that $\mathbf{x}_0$ in the

main text is a vector of length 3*N* obtained by joining the three components of all *N* $\mathbf{x}_{0,i}$ into a single vector.) The primed variables in eqs. S2 and S3 denote the same quantities as $\mathbf{x}_{0,i}$ and $\mathbf{p}_{0,i}$ but at the end of the tunneling step. The adjustment is accomplished as follows.

The total angular momentum **J**, which must be conserved, is

$$\mathbf{J} = \sum_{i=1}^{N} \mathbf{x}_i \times \mathbf{p}_i \tag{S4}$$

where $\mathbf{x}_i$ can be $\mathbf{x}_{0,i}$ or $\mathbf{x}'$ and where $\mathbf{p}_i$ can be $\mathbf{p}_{0,i}$ or $\mathbf{p}'_i$. The change of Cartesian coordinates for atom *i* along the whole tunneling path is $\Delta\mathbf{x}_i$ so that

$$\mathbf{x}'_i = \mathbf{x}_{0,i} + \Delta\mathbf{x}_i \qquad i = 1, \ldots, N \tag{S5}$$

Equation S3 conserves the magnitudes of the atomic momenta, but not their directions. We denote the initial and final atomic momenta as

$$\mathbf{p}_{0,i} = \left|\mathbf{p}_{0,i}\right| \mathbf{u}_{0,i} = p_{0,i}\mathbf{u}_{0,i} \qquad i = 1, \ldots, N \tag{S6}$$

$$\mathbf{p}'_i = \left|\mathbf{p}_{0,i}\right| \mathbf{u}'_i = p_{0,i}\mathbf{u}'_i \qquad i = 1, \ldots, N \tag{S7}$$

where we have used eq. S3, and where $\mathbf{u}_{0,i}$ and $\mathbf{u}'_i$ are unit vectors. We choose to minimize the changes in direction subject to the constraints of eqs. S2 and S3. Thus we minimize the quantity

$$\begin{aligned} f &= \sum_{i=1}^{N} \left|\mathbf{u}_{0,i} - \mathbf{u}'_i\right|^2 \\ &= \sum_{i=1}^{N} \sum_{\gamma=x,y,z} \left(u_{0,i\gamma} - u'_{i\gamma}\right)^2 \end{aligned} \tag{S8}$$

subject to the constraint of eq. S2. Note that $u_{0,i\gamma}$ and $u'_{i\gamma}$ are direction cosines. Adding three Lagrange multipliers ($\lambda_i, i = 1,2,3$) to enforce the constraint gives a new objective function:

$$g = \sum_i \sum_{\gamma=x,y,z} \left(u_{0,i\gamma} - u'_{i\gamma}\right)^2 + \lambda_1 \left[J_x - \sum_i p_{0,i}(x'_{iy}u'_{iz} - x'_{iz}u'_{iy}) \right] + \lambda_2 \left[J_y - \sum_i p_{0,i}(x'_{iz}u'_{ix} - x'_{ix}u'_{iz}) \right] + \lambda_3 \left[J_z - \sum_i p_{0,i}(x'_{ix}u'_{iy} - x'_{iy}u'_{ix}) \right] \quad \text{(S9)}$$

Then we combine all the final direction cosines into a single algebraic vector:

$$v_1 = u'_{1x,}\ v_2 = u'_{1y,}\ v_3 = u'_{1z,}\ v_4 = u'_{2x,}\ \text{etc.} \quad \text{(S10)}$$

Then the equations to be solved for the final direction cosines $u'_{i\gamma}$ are

$$\frac{\partial g}{\partial v_j} = 0, \qquad j = 1, \ldots, 3N \quad \text{(S11)}$$

$$\frac{\partial g}{\partial \lambda_k} = 0. \qquad k = 1, 2, 3 \quad \text{(S12)}$$

Equations S11 and S12 constitute $3N + 3$ nonlinear equations, and they can be solved iteratively by the Newton-Raphson method for the $3N$ component of $\mathbf{v}$ and the three components of $\boldsymbol{\lambda}$. Using the resulting $\mathbf{v}$ along with eqs. S7 and S10, one obtains the momentum components after the tunneling event.

Illustration of the effect of varying the parameter η

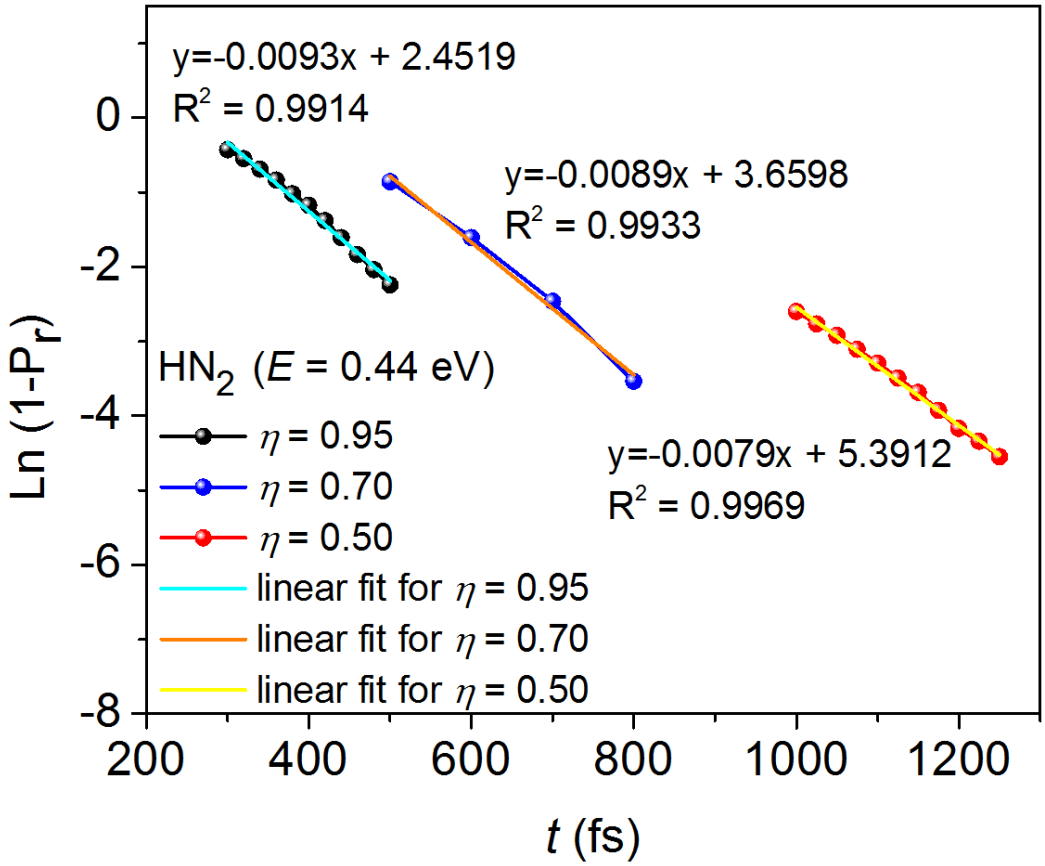

Figure S1. Linearity of the decay curves after induction time for various η values and the linear fitting results for obtaining rate constant.