Supplementary Information

S.1 AIMC Working Equations

A brief overview and explanation of the working equations of the AIMC method is presented below; the derivation of these presented elsewhere.^{1,2} The wavefunction ansatz for AIMC is the same as that for MCE,^{3,4} where the wavefunction $|\Psi\rangle$ is composed of a trajectory guided basis $|\varphi_k\rangle$ coupled to timedependent amplitudes D_k and summed over K configurations

$$|\Psi\rangle = \sum_{k=1}^{K} D_k(t) |\varphi_k\rangle.$$
(S.1)

The trajectory guided basis $|\varphi_k\rangle$ is comprised of a product of nuclear and electronic parts

$$|\varphi_k\rangle = \left[\sum_{i=1}^J a_{ik}(t) |\phi_i\rangle\right] |\mathbf{z}_k(t)\rangle, \qquad (S.2)$$

where $|\phi_i\rangle$ represents the *i*th electronic state of a total of J electronic states with corresponding timedependent amplitude $a_{ik}(t)$, and $|\mathbf{z}_k(t)\rangle$ is the trajectory guided Gaussian basis vector centred at coordinates and momenta $(\mathbf{q}_k, \mathbf{p}_k)$:

$$\mathbf{z}_{k} = \left(\frac{\gamma}{2}\right)^{1/2} \mathbf{q}_{k} + \frac{i}{\hbar} \left(\frac{1}{2\gamma}\right)^{1/2} \mathbf{p}_{k}$$
(S.3)

$$\langle \mathbf{q} | \mathbf{z}_k \rangle = \left(\frac{\gamma}{\pi}\right)^{M/4} \exp\left(-\frac{\gamma}{2}(\mathbf{q} - \mathbf{q}_k)^2 + \frac{i}{\hbar}\mathbf{p}_k(\mathbf{q} - \mathbf{q}_k) + \frac{i\mathbf{p}_k\mathbf{q}_k}{2\hbar}\right).$$
(S.4)

The Gaussian basis vector is multidimensional, and is the product of M Gaussian basis functions for M atoms, $|\mathbf{z}_k\rangle = \prod_{m=1}^{M} |z_k^{(m)}\rangle$, whilst γ is a width parameter that takes a different value for different atoms.

The phase space centres $(\mathbf{q}_k, \mathbf{p}_k)$ of the Gaussians are guided by Ehrenfest trajectories that resemble Newton's equations of motion, but include quantum and nonadiabatic effects from electronic structure information

$$\dot{\mathbf{q}}_k = \mathbf{p}_k \mathbf{m}^{-1} \tag{S.5a}$$

$$\dot{\mathbf{p}}_k = \mathbf{F}_k \tag{S.5b}$$

$$\mathbf{F}_{k} = \sum_{i=1}^{J} a_{ik}^{*} a_{ik} \nabla_{q} V_{i}(\mathbf{q}_{k}) + \sum_{j \neq i} a_{ik}^{*} a_{jk} \mathbf{d}_{ij}(\mathbf{q}_{k}) \left[V_{i}(\mathbf{q}_{k}) - V_{j}(\mathbf{q}_{k}) \right].$$
(S.5c)

In the above, **m** are the atomic masses, \mathbf{F}_k is the Ehrenfest force, ∇_q is the gradient, $V_i(\mathbf{q}_k)$ is the adiabatic electronic energy, and $\mathbf{d}_{ij}(\mathbf{q}_k)$ is the nonadiabatic coupling vector that couples the *i*th and *j*th electronic

states in the adiabatic representation via

$$\mathbf{d}_{ij}(\mathbf{q}_k) = \langle \phi_i | \nabla_q | \phi_j \rangle \,. \tag{S.6}$$

The time-dependence of the electronic state amplitudes a_{ik} is given by

$$\dot{a}_{ik} = -\frac{i}{\hbar} \sum_{j=1}^{J} H_{ij}^{\text{el}}(\mathbf{z}_k) a_{jk}$$
(S.7)

where the elements of the electronic Hamiltonian $H_{ij}^{\text{el}}(\mathbf{z}_k)$, evaluated at the phase space centres of \mathbf{z}_k , are

$$H_{ij}^{\text{el}}(\mathbf{z}_k) = \begin{cases} V_i(\mathbf{q}_k) & i = j \\ -i\hbar \mathbf{p}_k \mathbf{d}_{ij}(\mathbf{q}_k) \mathbf{m}^{-1} & i \neq j \end{cases}.$$
 (S.8)

The time-dependence of the multiconfigurational amplitudes D_k is given by

$$\sum_{l=1}^{K} \langle \varphi_k | \varphi_l \rangle \dot{D}_l = -\frac{i}{\hbar} \sum_{l=1}^{K} \left[\langle \varphi_k | \hat{H} | \varphi_l \rangle - i\hbar \langle \varphi_k | \dot{\varphi}_l \rangle \right] D_l.$$
(S.9)

The entire Hamiltonian matrix elements $\langle \varphi_k | \hat{H} | \varphi_l \rangle$ are the sum of kinetic energy and potential energy components as well as a nonadiabatic coupling term

$$\langle \varphi_k | \hat{H} | \varphi_l \rangle = \sum_{i,j=1}^J a_{ik}^* a_{jl} \langle \mathbf{z}_k \phi_i | \hat{H} | \phi_j \mathbf{z}_l \rangle$$

$$= \sum_{i,j=1}^J a_{ik}^* a_{jl} \left[\delta_{ij} \langle \mathbf{z}_k | \hat{T} | \mathbf{z}_l \rangle + \delta_{ij} \langle \mathbf{z}_k | V_i(\mathbf{q}) | \mathbf{z}_l \rangle - \hbar^2 \langle \mathbf{z}_k | \mathbf{d}_{ij}(\mathbf{q}) \dot{\mathbf{q}} | \mathbf{z}_l \rangle \right].$$
(S.10)

While the kinetic energy component may be calculated analytically, the potential energy and matrix elements of nonadiabatic coupling must be calculated approximately. A bra-ket averaged Taylor (BAT) expansion is utilised that takes the average of two Taylor expansions centred around the maximum of one of the basis functions involved in the matrix element.¹ For the potential energy term, expansion to first order gives

$$\langle \mathbf{z}_{k} | V_{i}(\mathbf{q}) | \mathbf{z}_{l} \rangle \approx \langle \mathbf{z}_{k} | \mathbf{z}_{l} \rangle \left(\frac{V_{i}(\mathbf{q}_{k}) + V_{i}(\mathbf{q}_{l})}{2} \right) + \left(\frac{\langle \mathbf{z}_{k} | (\mathbf{q} - \mathbf{q}_{k}) | \mathbf{z}_{l} \rangle \nabla_{q} V_{i}(\mathbf{q}_{k}) + \langle \mathbf{z}_{k} | (\mathbf{q} - \mathbf{q}_{l}) | \mathbf{z}_{l} \rangle \nabla_{q} V_{i}(\mathbf{q}_{l})}{2} \right).$$
(S.11)

The potential energy and its derivative has already been evaluated at coordinates \mathbf{q}_k and \mathbf{q}_l for the trajectories in Eq. (S.5), therefore no additional electronic structure calculations are required to evaluate the potential energy matrix element.

The matrix elements of nonadiabatic coupling are approximated by a zeroth order BAT expansion to

give

$$\langle \mathbf{z}_k | \mathbf{d}_{ij}(\mathbf{q}) \dot{\mathbf{q}} | \mathbf{z}_l \rangle \approx \frac{i}{2\hbar} \langle \mathbf{z}_k | \mathbf{z}_l \rangle \left(\dot{\mathbf{q}}_k \mathbf{d}_{ij}(\mathbf{q}_k) + \dot{\mathbf{q}}_l \mathbf{d}_{ij}(\mathbf{q}_l) \right)$$
(S.12)

As with the potential energy matrix element, the matrix elements of nonadiabatic coupling require no extra electronic structure calculations to evaluate the BAT expansion. Each trajectory may also be propagated individually and then combined via the time-dependence of the multiconfigurational D amplitudes after the calculations have taken place, provided that the electronic structure information is saved at each time step.

S.1.1 Cloning Procedure

The previous section presented the working equations and matrix element evaluation for the AIMC method, and this present section describes the cloning procedure that expands the basis by wavepacket splitting. The cloning procedure is applied when a trajectory $|\varphi_k\rangle$ has significant population, or equivalently significant amplitude, on multiple electronic states with differing forces. In this circumstance, the Ehrenfest force guiding the trajectory would be an unphysical average of the different forces and will lead to a poor reproduction of the dynamics occurring. The difference between the force on the *i*th state and the Ehrenfest average force is given by

$$\Delta \mathbf{F}_{ik} = \nabla_q V_i(\mathbf{q}) - \sum_{j=1}^J a_{jk}^* a_{jk} \nabla_q V_j(\mathbf{q}).$$
(S.13)

The "breaking force" which triggers cloning is then defined as

$$\mathbf{F}_{ik}^{\mathrm{br}} = a_{ik}^* a_{ik} \Delta \mathbf{F}_{ik}.$$
(S.14)

When $|\mathbf{F}_{ik}^{br}\mathbf{m}^{-1}| > \xi_{clon}$ and the nonadiabatic coupling vector is small $|\mathbf{d}_{ij}(\mathbf{q}_k)| < \xi_{nac}$ cloning occurs. The thresholds ξ_{clon} and ξ_{nac} are determined empirically. For the former, ξ_{clon} needs to be large enough to limit the rate of basis set expansion so that it does not rise exponentially and cause the calculation to become intractable, but small enough to allow cloning to take place at all. The latter threshold, ξ_{nac} is utilised to ensure that cloning does not take place in regions of large population transfer, again to limit the size of the basis expansion.

When the cloning procedure is applied, one trajectory $|\varphi_k\rangle$ becomes two: $|\varphi'_k\rangle$ and $|\varphi''_k\rangle$. The amplitudes of the electronic states are adjusted to ensure that $|\varphi'_k\rangle$ has population on the *i*th electronic state with zero on the rest, whilst $|\varphi''_k\rangle$ is the opposite - zero population on the *i*th electronic state, and nonzero on the rest

$$|\varphi_k'\rangle = \left(\frac{a_{ik}}{|a_{ik}|} |\phi_i\rangle + \sum_{j \neq i} 0 \times |\phi_j\rangle\right) |\mathbf{z}_k\rangle \tag{S.15}$$

$$|\varphi_k''\rangle = \left(0 \times |\phi_i\rangle + \frac{1}{\sqrt{1 - |a_{ik}|^2}} \sum_{j \neq i} a_{jk} |\phi_j\rangle\right) |\mathbf{z}_k\rangle.$$
(S.16)

The multiconfigurational amplitudes are then adjusted to ensure that the wavefunction remains unchanged as a result of the cloning procedure

$$D'_k = D_k |a_{ik}| \tag{S.17}$$

$$D_k'' = D_k \sqrt{1 - |a_{ik}|^2}.$$
 (S.18)

S.2 Supporting Figures for Dissociation Kinetics

S.2.1 Initial N-H Stretch Energy vs Dissociation Time



Figure S.1: Initial vibrational energy in the N-H stretch coordinate for each trajectory (calculated using the harmonic approximation, and as sampled by the Wigner distribution in the harmonic approximation) versus the trajectories dissociation time.

S.2.2 Example Dynamic Trajectory Potential Energies



Figure S.2: Dynamic potential energy of a trajectory that (a) has sufficient energy to dissociate quickly over the barrier, and (b) samples more of the potential energy surface in the quasi-bound region before finding a way around the barrier, as a function of N-H distance (note that the trajectory is dynamic, so all other atoms are also moving). Static potential energy curves of the S_0 , S_1 , and S_2 states at the trajectories initial geometries are shown as a reference, generated by holding all atoms fixed except the hydrogen attached to the nitrogen, which is extended. All electronic structure is at the SA3-CAS(8,7)-SCF level with aug-cc-PVDZ basis set, as with the dynamics calculations.

References

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