To compute the wire potential for a particular configuration, positions of protons in the hydrogen bond wire are first quenched dynamically with all other degrees of freedom held fixed:

$$m_{\mathrm{H}}\ddot{\mathbf{r}}_i = -\nabla_i E(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_\ell; \mathbf{r}^{N-\ell}), \qquad i = 1, 2, ..., \ell. \tag{1}$$

Here, $\mathbf{r}_i$ denotes the positions of wire proton i, and $\mathbf{r}^{N-\ell}$ represents the positions of the $N-\ell$ remaining atoms, which are fixed parameters in the energy E. As the wire protons evolve in time according to Eq. 1, the influence of a low-temperature heat bath is simulated by occasionally removing kinetic energy. Specifically, if the kinetic energy exceeds a threshold K_{t}, velocities are rescaled to be consistent with the temperature of the bath, T_{b}:

$$\mathbf{v}_i'(t) = \alpha^{-1/2}\mathbf{v}_i(t), \qquad \text{if } K > K_{\mathrm{t}}, \tag{2}$$

$$\alpha = m_{\mathrm{H}} \sum_{i=1}^{\ell} |\mathbf{v}_i|^2 / 3\ell k_{\mathrm{B}} T_{\mathrm{b}} . \tag{3}$$

In Eqs. 2 and 3, $\mathbf{v}_i$ and $\mathbf{v}_i'$ are the proton velocities before and after rescaling, respectively. The bath temperature is taken to be 100 K initially, and is then lowered over about 100 fs until the minimum energy observed in the dynamics varies by less than ~ 0.1 kcal/mol. The resulting energy, $E^{(0)}$, is locally minimum with respect to the wire proton positions:

$$\nabla_i E(\mathbf{r}_1^{(0)}, \mathbf{r}_2^{(0)}, ..., \mathbf{r}_\ell^{(0)}; \mathbf{r}^{N-\ell}) \approx 0, \qquad i = 1, 2, ..., \ell. \tag{4}$$

In the presence of a strong, solvent-generated electric field opposing recombination of the ions, charges remain separated during this quenching procedure. For this case, $E_{\mathrm{ion}} \equiv E^{(0)}$ is thus the energy of a metastable ionic configuration with proton positions $\mathbf{r}^{(0)}$.

We determine the energy of the corresponding neutral system by displacing the wire protons along hydrogen bonds:

$$\mathbf{r}_i' = \mathbf{R}_{i+1} + d\frac{\mathbf{R}_i - \mathbf{R}_{i+1}}{|\mathbf{R}_i - \mathbf{R}_{i+1}|}. \tag{5}$$

Here, $\mathbf{R}_i$ is the position of the oxygen atom to which the ith wire proton is initially bound, and d is a typical O–H bond distance, 1 Å. Using Eq. 5, we effectively transfer protons along the hydrogen bond wire, so that neutral water molecules are formed. From this artificially constructed, neutral configuration, we again quench the positions of the wire protons via low-temperature *ab initio* molecular dynamics, with all other nuclear degrees of freedom held fixed, until a locally minimum energy $E^{(1)}$ is obtained:

$$\nabla_i E(\mathbf{r}_1^{(1)}, \mathbf{r}_2^{(1)}, ..., \mathbf{r}_\ell^{(1)}; \mathbf{r}^{N-\ell}) \approx 0, \qquad i = 1, 2, ..., \ell. \tag{6}$$

Here, $\mathbf{r}_1^{(1)}$ is the position of wire proton i in the neutral configuration with energy $E_{\text{neut}} \equiv E^{(1)}$.

We define ΔE as the energy difference between the ionic and neutral configurations identified above, i.e., $\Delta E \equiv E_{\text{ion}} - E_{\text{neut}}$. The energy of configuration space between these two minima is then probed by interpolating between their structures:

$$E(q) = E(\mathbf{r}_1(q), \mathbf{r}_2(q), ..., \mathbf{r}_\ell(q); \mathbf{r}^{N-\ell}), \tag{7}$$

$$\mathbf{r}_i(q) = (1 - q)\mathbf{r}_i^{(0)} + q\,\mathbf{r}_i^{(1)}. \tag{8}$$