# Supplementary Material

## TECHNICAL VALIDATION

Central to the HEOM approach is the assumption that the bath correlation function $C_a(t)$ for site $a$ can be represented by an infinite sum of exponentially decaying terms $C_a(t) = \sum_k^\infty c_{ak} \exp(-\nu_{ak} t)$, where $\nu_{ak} = 2\pi k/\beta\hbar$ are Matsubara frequencies. Further, each exponential term leads to a set of auxiliary density matrices which take into account the non-Markovian evolution of the system's RDM under the influence of bath. In practice, the summation must be truncated at a finite level, $K$, which is called Matsubara cut-off and the set of auxiliary density matrices needs to be truncated at a finite number $M$. In the truncated set of auxiliary matrices are indexed by $\mathbf{n} = (n_{10}, \ldots, n_{1K}, n_{M0}, \ldots, n_{MK})$. The hierarchy truncation level is given by $L = \sum_{a=1}^{M} \sum_{k=0}^{K} n_{ak}$, where $n_{ak}$ is the index of an auxiliary density matrix. The computational cost of the HEOM method rises steeply with the hierarchy level $L$ (Strümpfer and Schulten (2012)).

The hierarchy truncation level $L$ depends on how non-Markovian the system is. Although, there is some guidance on how to choose the Matsubara cut-off and hierarchy truncation level based on bath and spectral density parameters, (Tanimura (2020); Ishizaki and Fleming (2009)) in practice, the values of $M$ and $K$ have to be chosen by requiring the convergence of the RDM to acceptable accuracy level. In this work HEOM calculations for the SB model were performed by setting $L = 30$ for all temperatures. The Matsubara cut-off was chosen depending on the temperature as follows: for $\beta$ = 0.1 $K$ was set to 2; for $\beta = 0.25, K = 3$, for $\beta = 0.5, K = 3$, for $\beta = 0.75, K = 4$, and for $\beta = 1.0, K = 5$. These values are chosen sufficiently high to ensure the convergence of the populations with respect to $K$ and $L$. Choosing high truncation levels in the HEOM calculations of a TLS does not present a problem given the presently available computational resources.

Similar approach of taking excessively large values of $K$ and $L$, however, is infeasible in the FMO calculations because the computational cost of HEOM grows steeply with the size of the quantum system. Therefore, the following approach was adopted for the HEOM calculations of the 8-site FMO model (FMO-VI data set). Starting from $K = 0$ and $L = 1$, $K$ was increased until the maximum difference in the populations between calculations with $K$ and $K + 1$ falls below a threshold $\Delta$, i.e.,

$$\delta = \max_{\substack{n=1,\ldots,N_{el} \\ t=0,\ldots,t_{max}}} \left| \rho_{n,n}^{K,L}(t) - \rho_{n,n}^{K+1,L}(t) \right| < \Delta. \tag{S1}$$

When Eq.S1 is satisfied for a given $\Delta$ the convergence with respect to Matsubara cut-off is deemed to have been achieved. Then, for a fixed $K$ a series of calculations were performed with increasing values of $L$ until the maximum difference in populations between two consecutive calculations becomes less than the same threshold value $\Delta$. When this condition is satisfied the convergence with respect to hierarchy truncation level as well as the overall convergence is declared. These steps were performed in the HEOM calculations for each parameter set for an 8-site FMO model until either the overall convergence is achieved or $K$ and/or $L$ become large enough so the calculation becomes intractable exceeding RAM available on our machines (1 TB).

In this work we set the threshold $\Delta = 0.01$. This threshold was chosen such that the population errors would be almost imperceptible which is illustrated in Figure S1. This data set is converged enough to be helpful in benchmarks of approximate methods describing quantum dynamics because the errors of these methods often exceed the threshold used in this work. Figures S2 and S3 show the number of Matsubara terms and the hierarchy truncation level required for achieving the overall convergence depending on spectral density parameters and temperature.

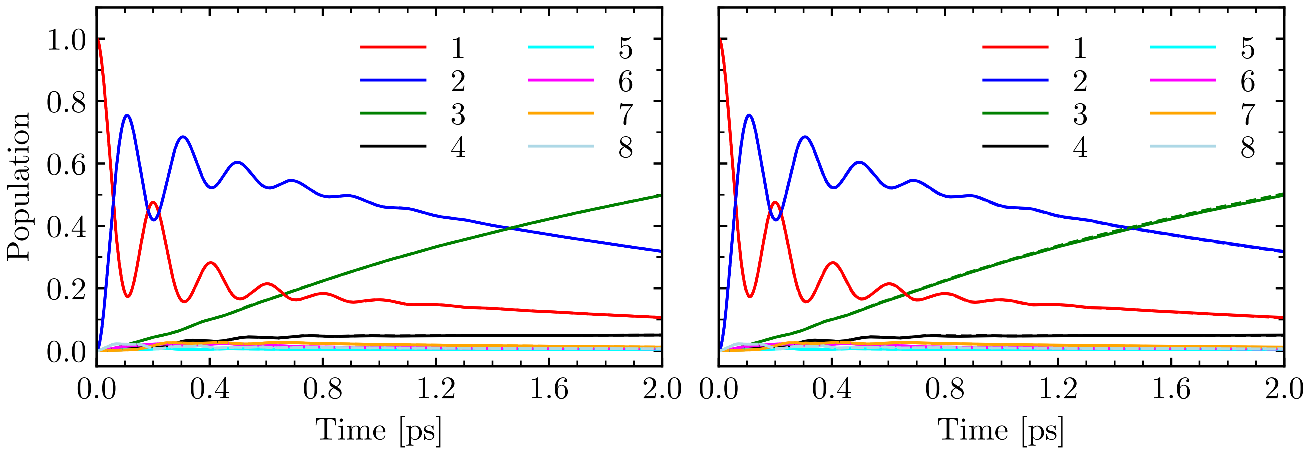


**Figure S1.** Example of the technical validation of the convergence of HEOM calculations for the following parameters $T = 30$ K, $\lambda = 70$ cm$^{-1}$, $\gamma = 500$ cm$^{-1}$ calculated using the Hamiltonian given by Eq. 14 (in the main text). The convergence within $\Delta = 0.01$ threshold was achieved for $K = 7$ and $L = 4$. Left plot shows the populations obtained with $K = 7$ and $L = 4$ (solid lines) compared to populations obtained with $K = 7$ and $L = 5$ (dashed lines) for all 8 sites. The largest population difference is $\delta = 3.14 \cdot 10^{-4}$. The right plot shows the populations obtained with $K = 7$ and $L = 4$ (solid lines) compared to the populations obtained with $K = 8$ and $L = 4$. The largest population difference is $\delta = 4.62 \cdot 10^{-3}$. In both cases the difference is very small illustrating the validity of the chosen threshold.

Here we will also comment on the computational cost of HEOM. While the computational cost of LTLME is relatively low, the computational cost of HEOM is much higher. For example, for an 8-site FMO model with the Hamiltonian given by Eq. 14 (see main text), $T = 370$ K, $\lambda = 520$ cm$^{-1}$, and $\gamma = 75$ cm$^{-1}$ to achieve the desired accuracy of $\Delta = 0.01$ such calculation would require $L = 13$ and $K = 1$. This calculation using adaptive integration uses 310 Gb of RAM and takes 48 hours to complete. The same calculation without an adaptive integrator exceeds seven days.

## REFERENCES

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Strümpfer, J. and Schulten, K. (2012). Open Quantum Dynamics Calculations with the Hierarchy Equations of Motion on Parallel Computers. *Journal of Chemical Theory and Computation* 8, 2808–2816. doi:10.1021/ct3003833

Tanimura, Y. (2020). Numerically “exact” approach to open quantum dynamics: The hierarchical equations of motion (HEOM). *J. Chem. Phys.* 153, 020901. doi:10.1063/5.0011599

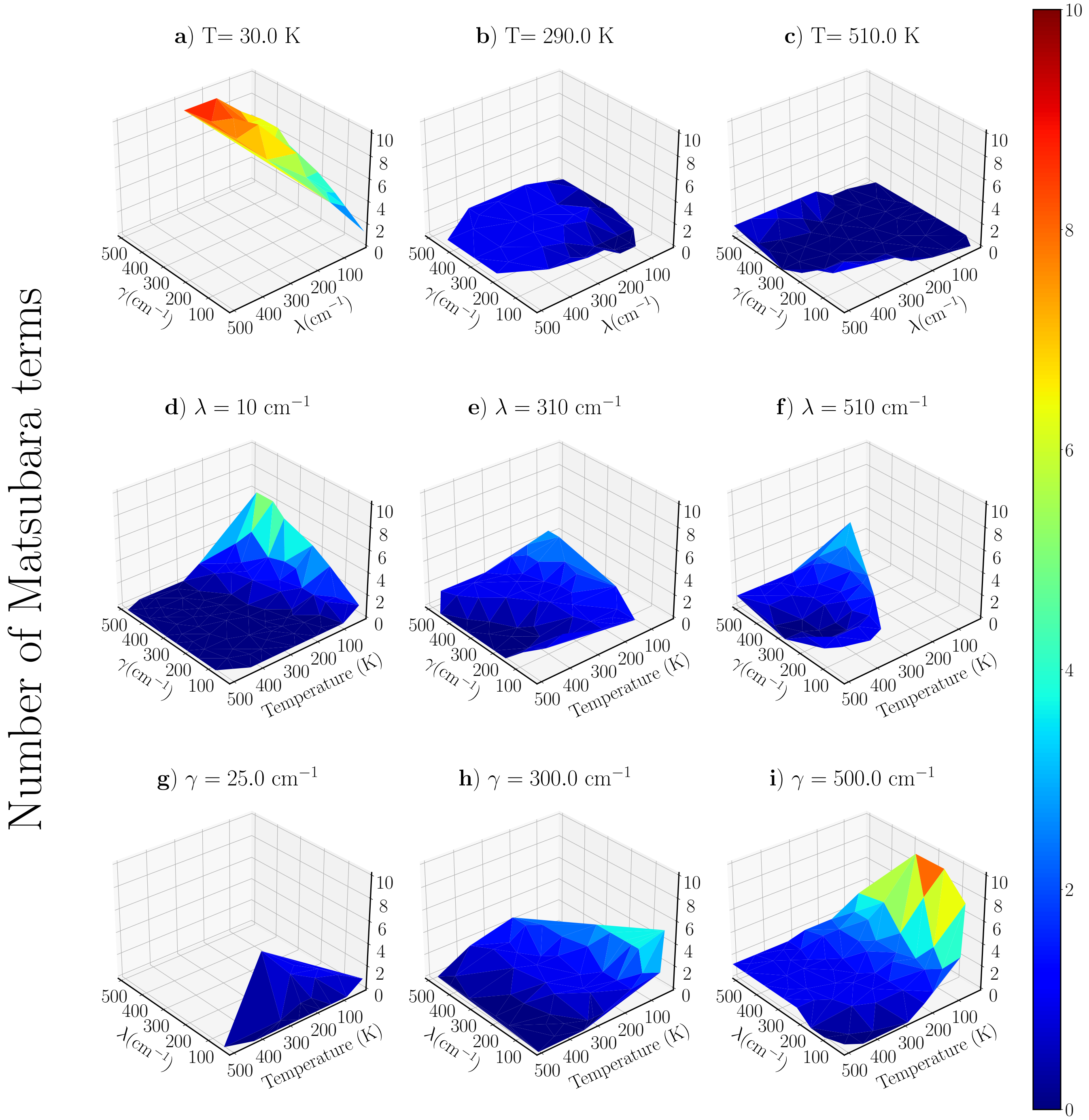


**Figure S2.** Number of Matsubara terms (Matsubara cut-off, $M$) required for converging populations of an 8-site FMO model with the system Hamiltonian given by Eq. 14 (in the main text) for three selected temperatures ($T$), reorganization energies ($\lambda$), and bath cut-off frequencies ($\gamma$). The unfilled spaces on the plots show the regions that we were not able to converge to the set accuracy $\Delta = 0.01$.

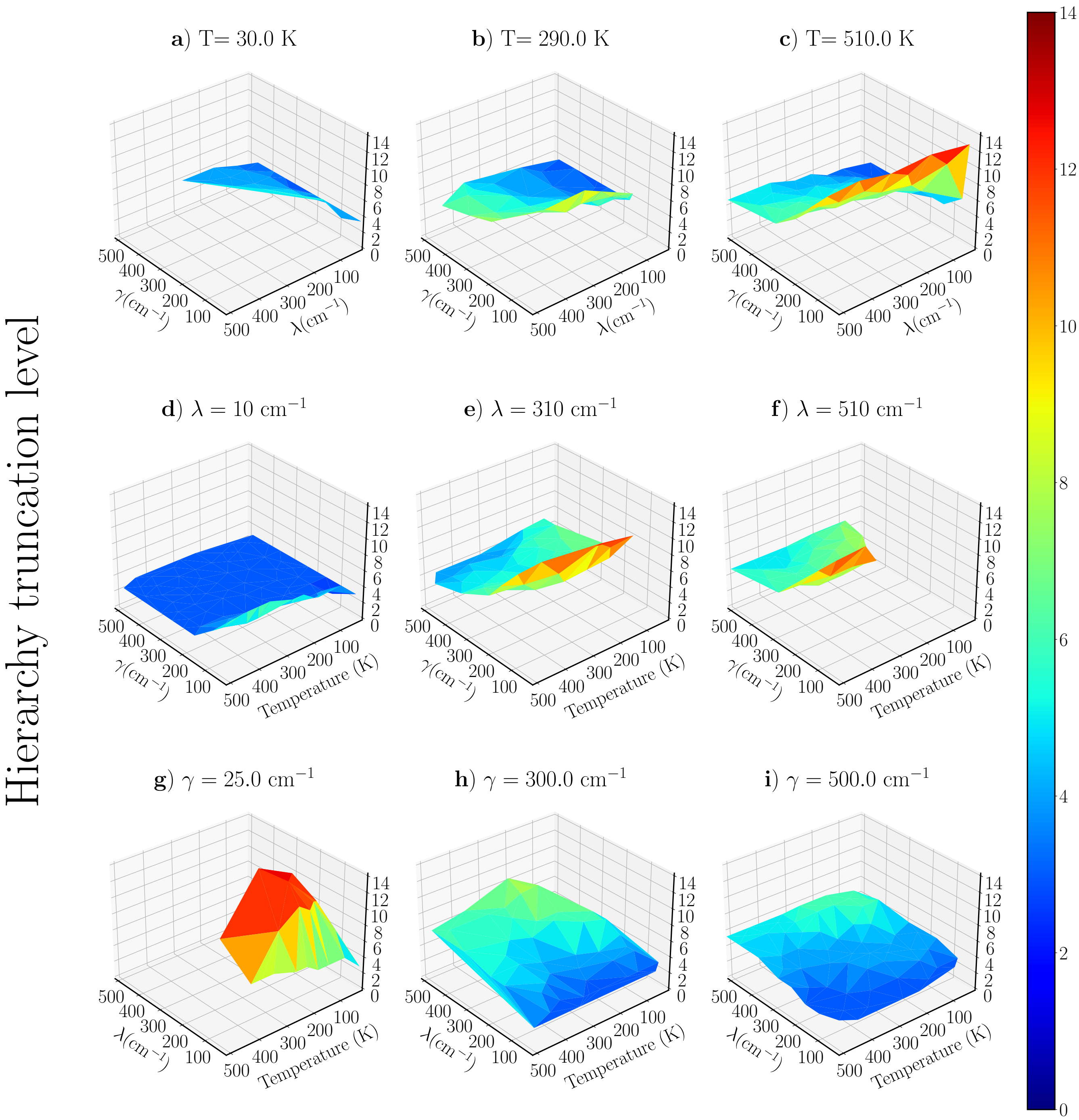


**Figure S3.** Hierarchy truncation level $L$ required for converging populations of an 8-site FMO model with the system Hamiltonian given by Eq. 14 (in the main text) for three selected temperatures ($T$), reorganization energies ($\lambda$), and bath cut-off frequencies ($\gamma$). The unfilled spaces on the plots show the regions that we were not able to converge to the set accuracy $\Delta = 0.01$.