SUPPLEMENTARY INFORMATION

Unravelling Mn_4Ca Cluster Vibrations in the S_1, S_2 and S_3 states of the Kok-Joliot cycle of Photosystem II

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1 Convergence of IR Spectra

In order to assess the reliability of the reported data, we present here an evaluation of the theoretical spectra over the simulation timescale. We conducted this evaluation on the total IR spectrum for one of the reported metastable states of the cycle, i.e., the S_1 state, and on the S_2-minus-S_1 differential IR spectrum. For robust band assignment, it is mandatory to sample each vibrational mode a sufficient number of times. As an example, the C=O bonds in the ligands of the cluster, which are characterized by a high frequency of vibration, oscillate $\sim$50 times in 1 ps. In contrast, sampling the same number of vibrations for modes vibrating at low frequencies, such as Mn-O bonds, requires $\sim$5 ps. Thus, the convergence of the spectra is not reached at the same time for all frequency windows. Particularly, the low-frequency region will be the last to converge. We therefore conducted the theoretical spectrum calculation, as reported in the methods section, on increasing timescales of the system dipole sampled over the MD-QMMM simulation. To include all vibrations from the cluster and its ligands, we selected a 5 ps step increase to analyze the convergence in the range from 0 up to 1800 cm^{-1}. As shown in Fig.S1, after 15 ps of simulation, the shape of the spectra is globally conserved (cyan line), and after 20 ps (orange line), only minor deviations are observed. Additionally, we report the convergence for three specific sub-systems: Mn_4CaO_5 cluster, Diamond1 (Mn1-O1-Mn2-O2) and Mn1-O1. In the partitioning of the Mn cluster core we can observe with increased detail that after 20 ps the DCFT has also converged in the band positioning and relative intensities. Thus, all the assignments of each mode done in the discussion section can be considered as reliable and robust. Eventually, we report the same convergence analysis, but carried out on the differential spectrum of S_2-minus-S_1 (Fig.S5). Here, we can still observe some changes in the differential spectrum between the 25 and 30 ps trajectory trunk, but as with the total spectrum, after 20 ps (orange line), all the band positions are fixed, and only the relative intensity is slightly affected. In balancing the computational cost and analysis effectiveness, we considered the results converged after 30 ps of sampling for all the states.

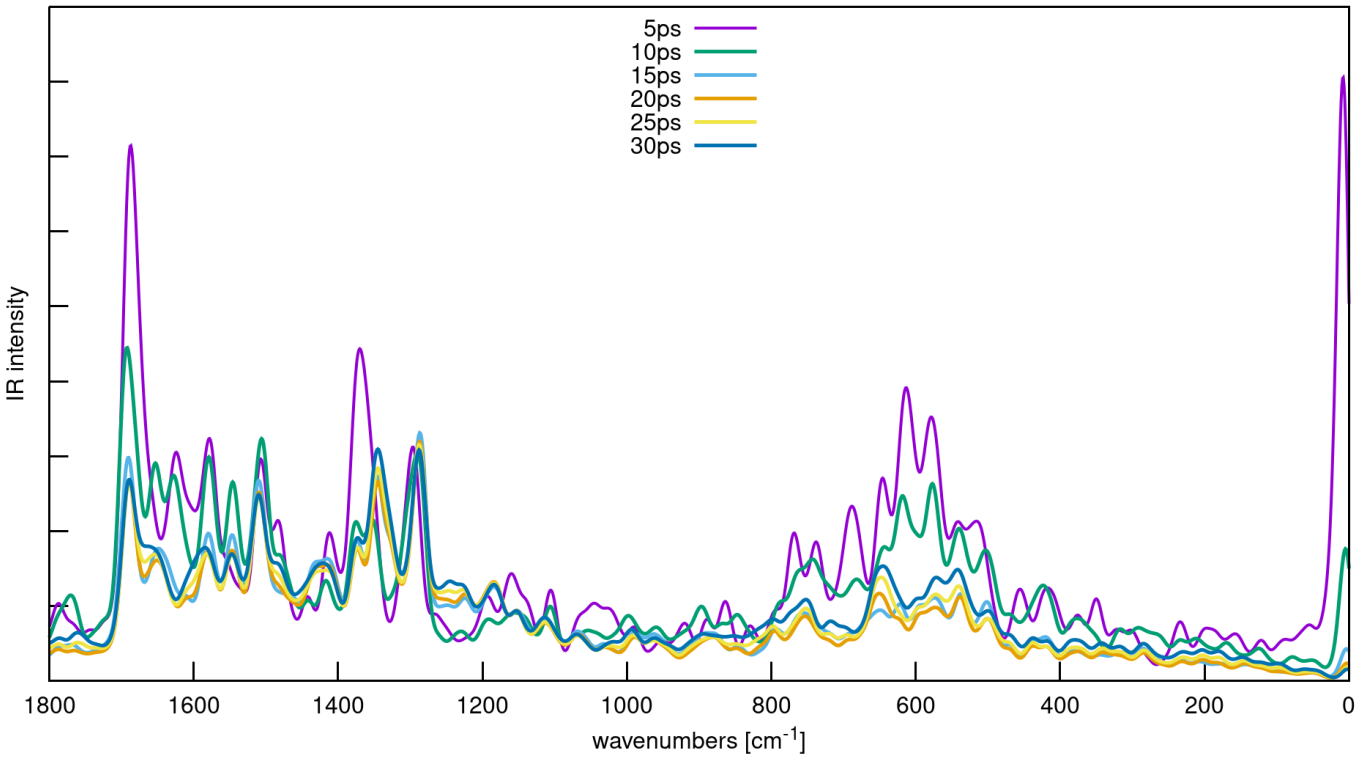

Fig. S1 Convergence of the S_1 infrared spectra with increasing simulation time.

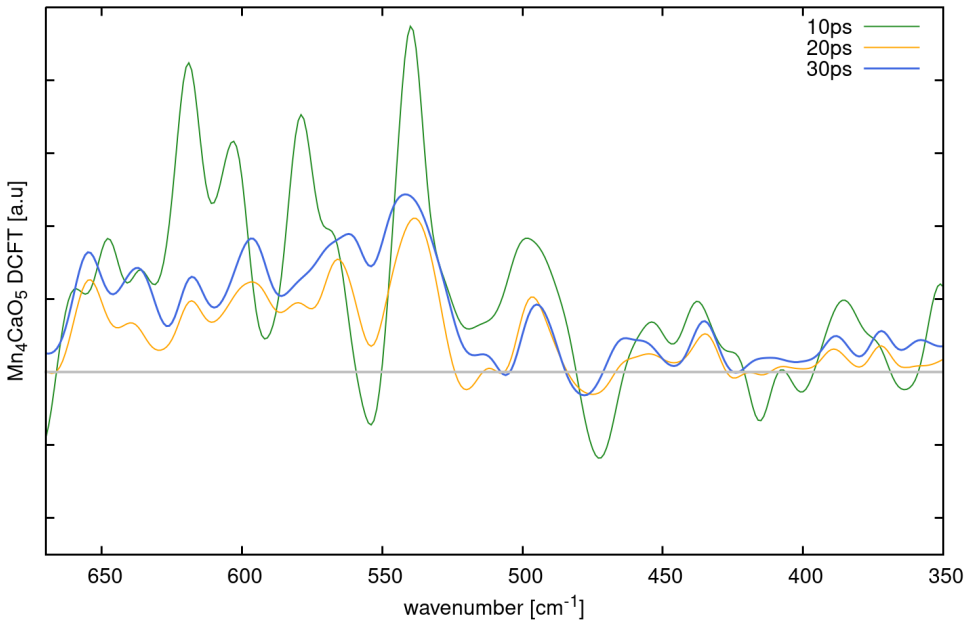

Fig. S2 Convergence of Mn_4CaO_5 portion in the S_1 state with increasing simulation time.

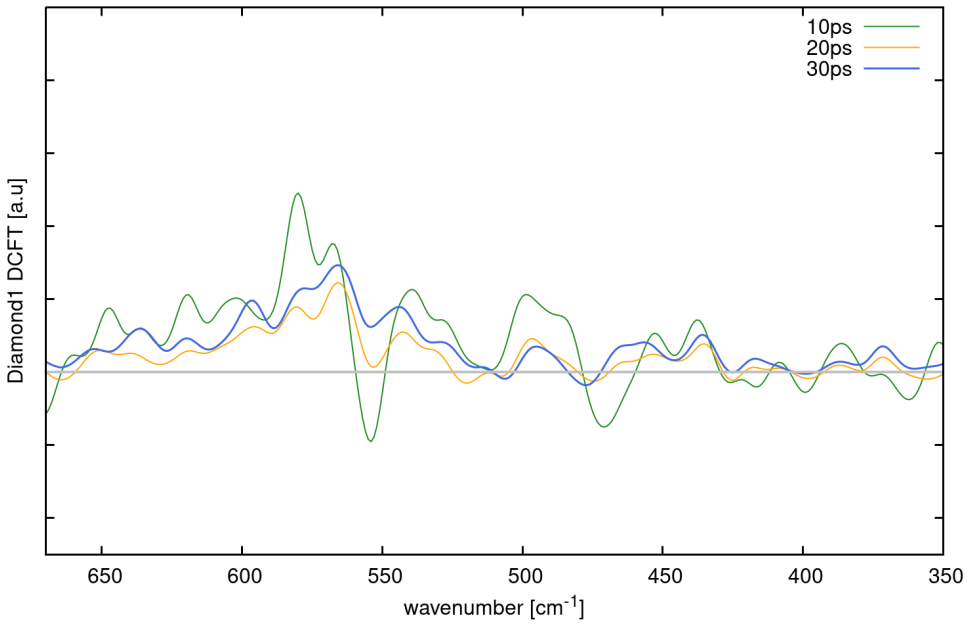

Fig. S3 Convergence of Diamond1 (Mn1-O1-Mn2-O2) portion in the S_1 state with increasing simulation time.

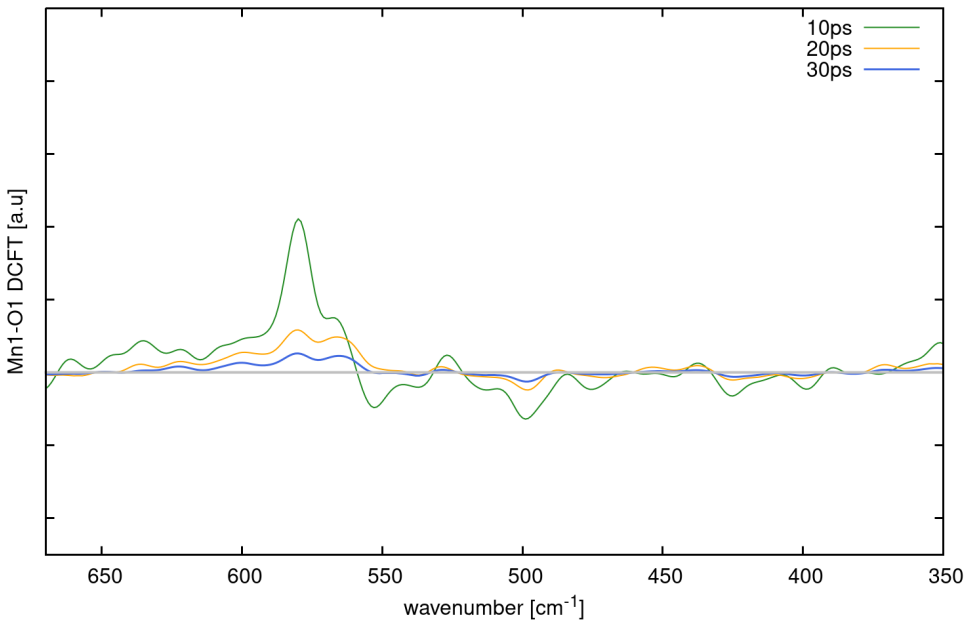

Fig. S4 Convergence of Mn1-O1 portion in the S_1 state with increasing simulation time.

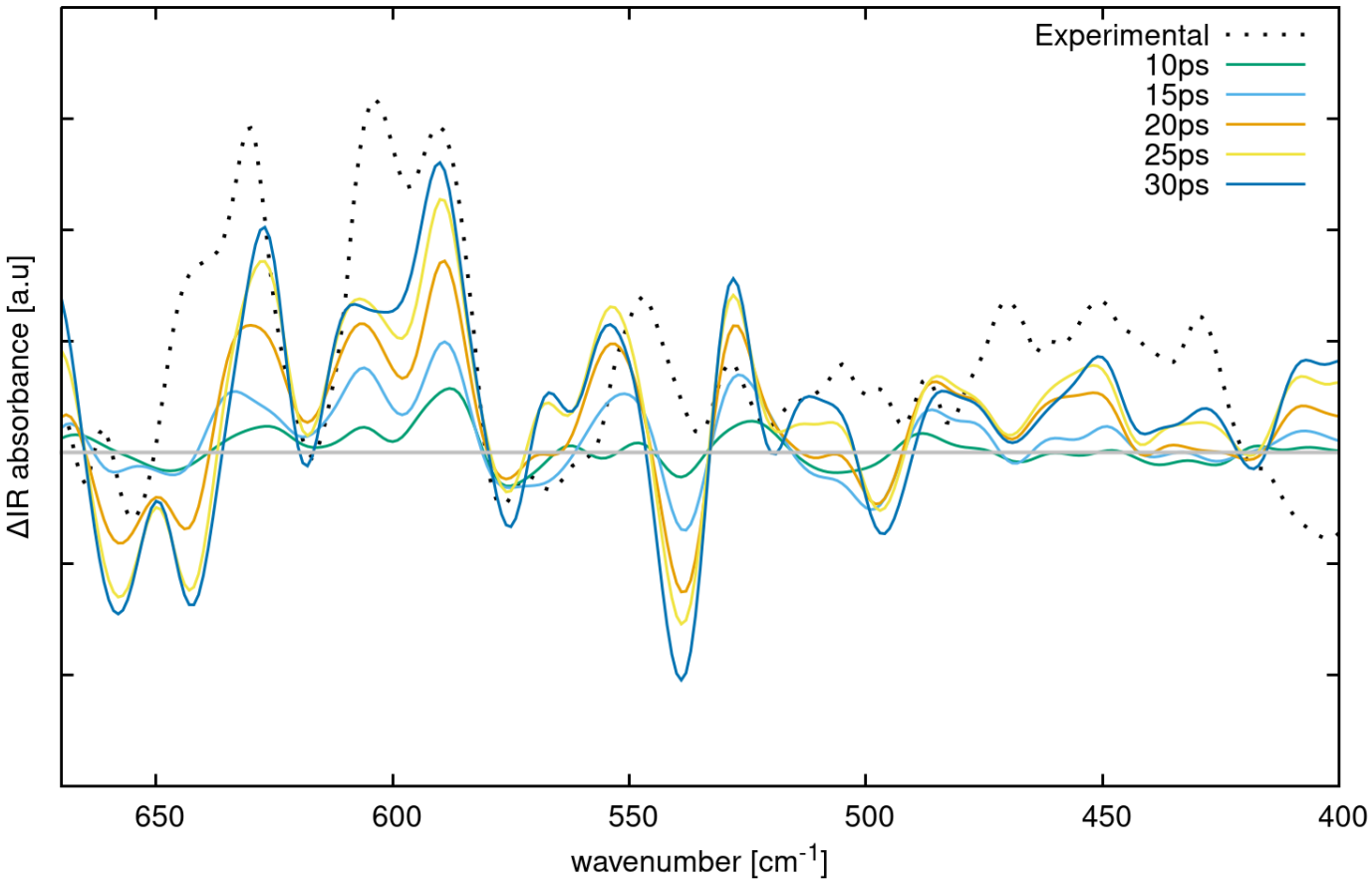

Fig. S5 Convergence of S_2-minus-S_1 differential IR-spectra in the low frequency region.

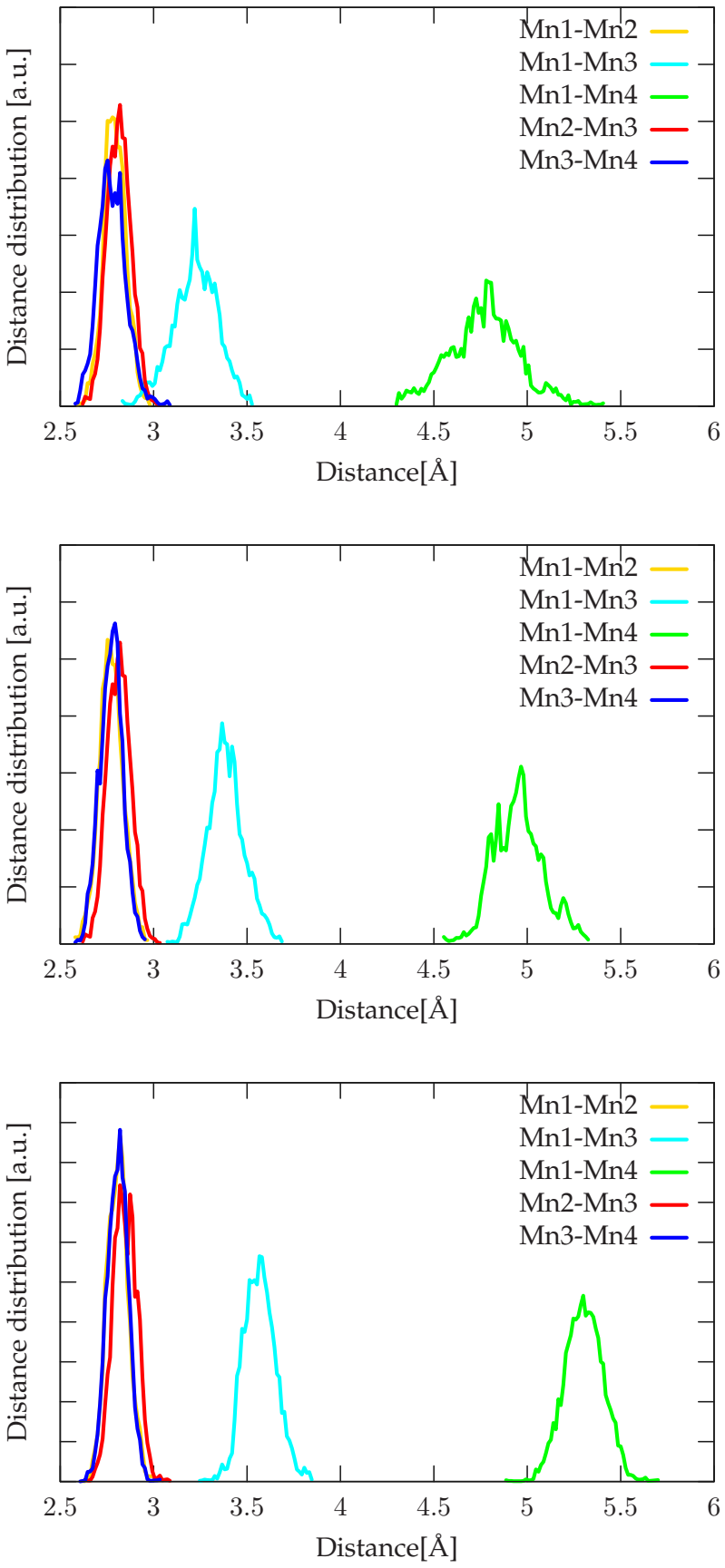

Fig. S6 Distribution of the Mn-Mn distances in S_1 (top), S_2 (middle), and S_3 (bottom) states sampled along the respective QM/MM MD simulations.

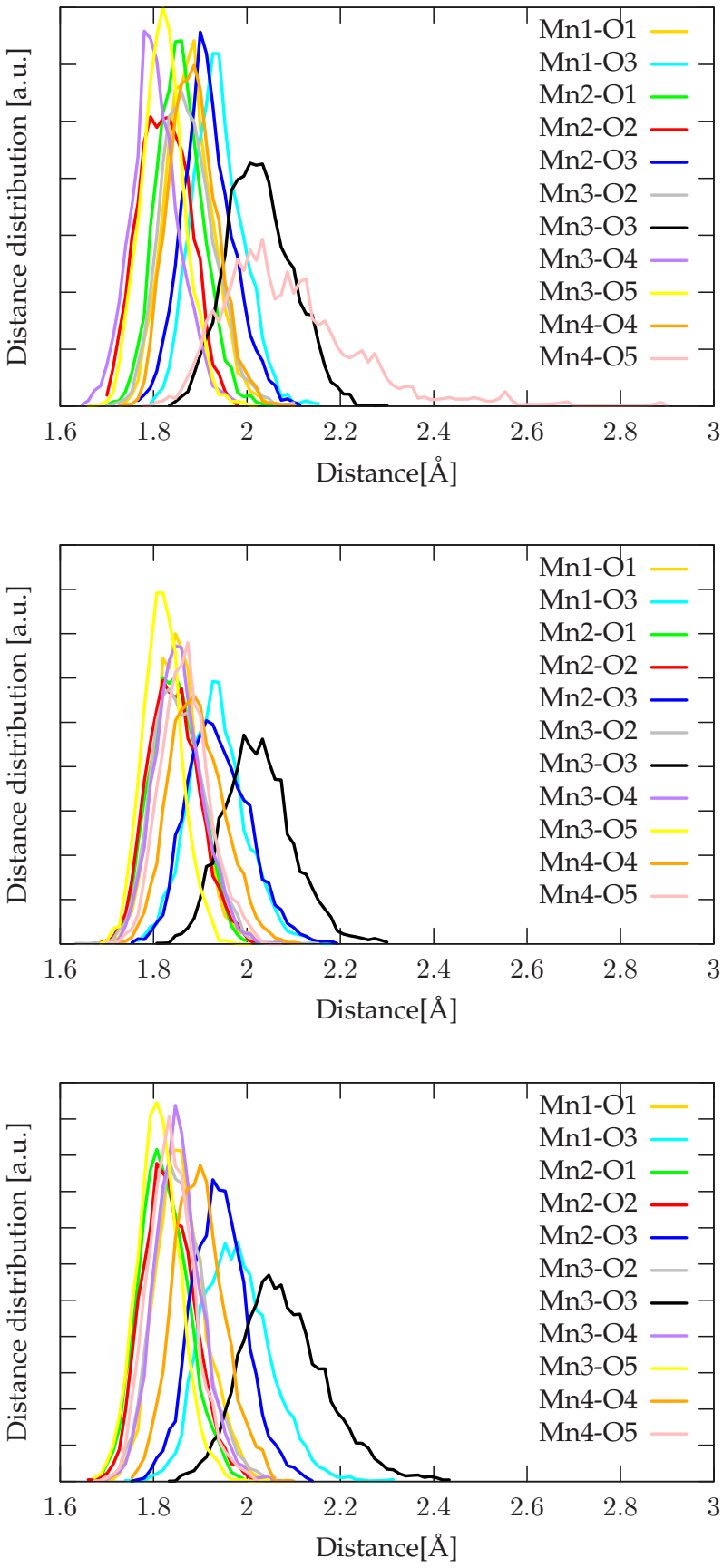

Fig. S7 Distribution of the Mn-O distances in S_1 (top), S_2 (middle), and S_3 (bottom) states sampled along the respective QM/MM MD simulations.