Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Solvent effects on the decarboxylation of trichloroacetic acid: insights from *ab initio* molecular dynamics simulations

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0.1 Methodological details of the classical molecular dynamics simulations

Classical molecular dynamics simulations were carried out for liquid DMSO using the LAMMPS[1] package along with the Strader and Feller[2] force field, which is based on CHARMM[3,4]. Both the Lennard-Jones and electrostatic interactions had an inner cutoff distance of 10 Å beyond which a switching function was applied up to an outer cutoff distance of 12 Å. Long-range dispersion corrections of the form given in Sun[5] were also added for the Lennard-Jones interaction. The particle-particle particle-mesh solver[6] was used to handle the long range contributions to the electrostatic interactions. The cross interactions parameters were obtained by using the Lorentz-Berthelot combining rules.

The initial configuration was built with the help of the PACKMOL package[7]. Simulations were carried out in the NPT ensemble with a reference temperature of 298.15 K and reference pressure of 1 atm. The system was simulated for 8 ns with a time step of 2 fs. The last 4 ns were considered for analysis.

0.2 Other results of the AIMD simulations

Figure S1 shows the density evolution for the AIMD simulation of bulk DMSO when no dispersions corrections were used. Note how the density values differ from the results obtained considering dispersion corrections. See Table 1 of the main text.

Figure S2 shows the comparison of the calculated PMF curves when the reactant is modeled with the aug-DZVP and MOLOPT basis sets. Note how the system overestimates the free energy barrier, in relation to the experimental value, when the MOLOPT basis set is employed.

The Figure S3 presents the results for the free energy curves obtained with the systems containing 32 and 68 DMSO molecules. Note the strange appearance of a valley in PMF obtained in the calculations using 32 DMSO molecules. As the result obtained with the bigger system shows only a smooth curve, it is likely that finite-size effects caused the artificial appearance of the minimum in the results of the smaller system.

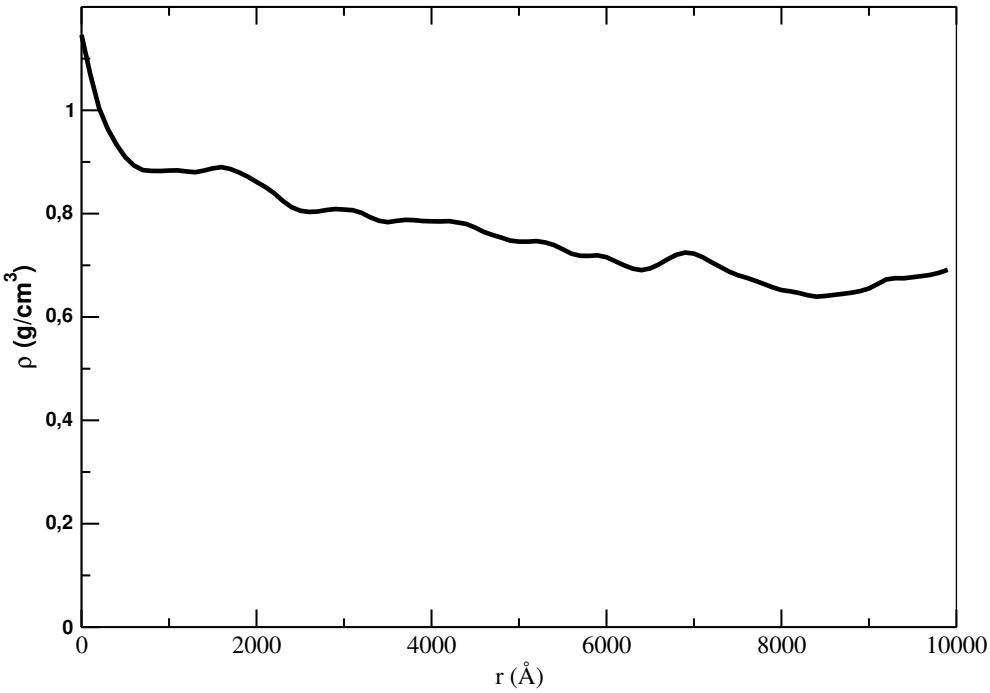

Fig. S1 Bulk density sampling of a 32 DMSO box when no dispersions corrections were added

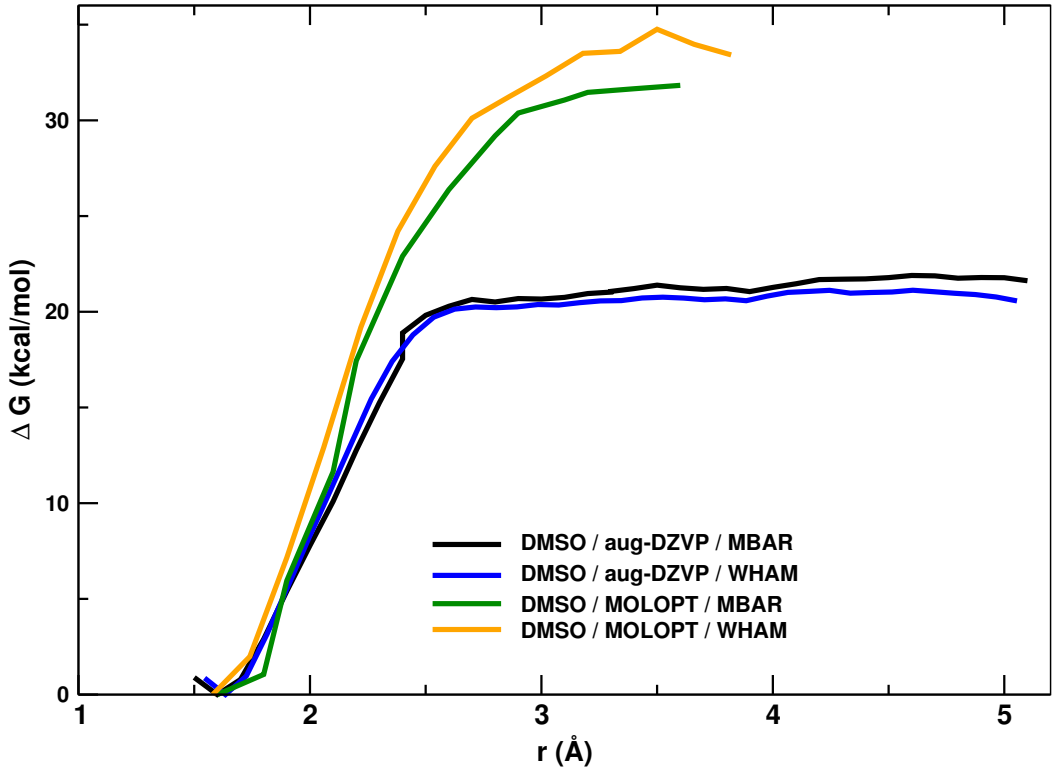

Fig. S2 Comparison between the PMF curves calculated with and without dispersion corrections

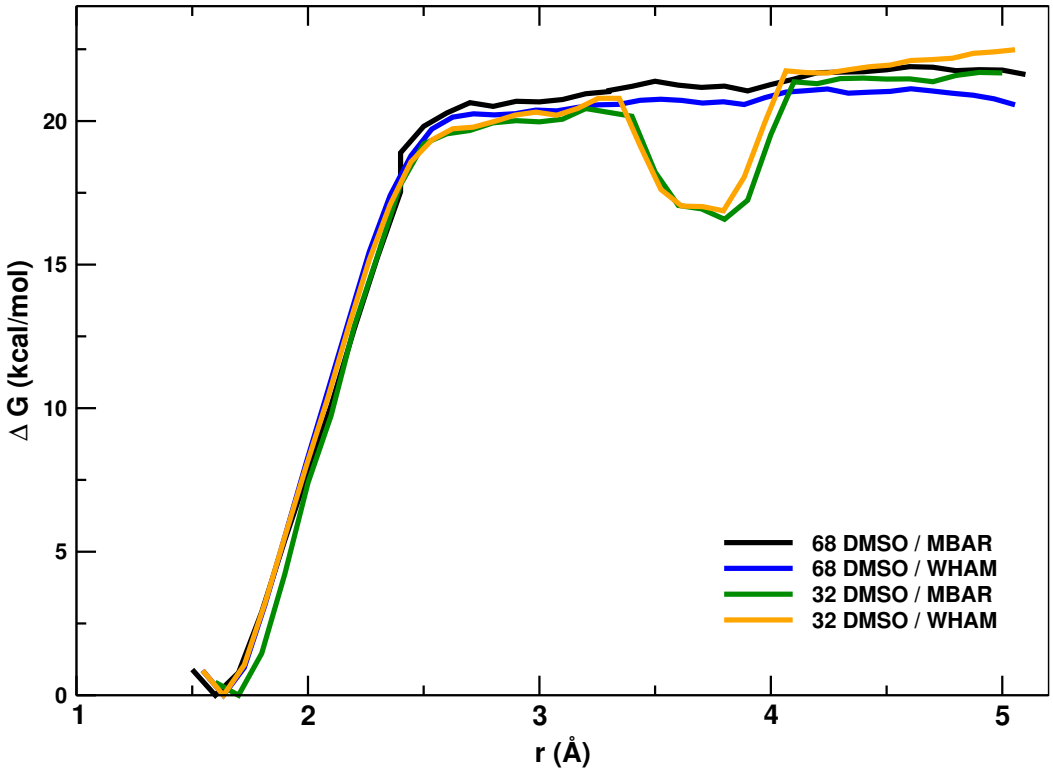

Fig. S3 Comparison between the PMF curves calculated with the systems containing 32 and 68 DMSO molecules

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