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Gibbs free energies of carbon dioxide solvation predicted by ab initio/classical free energy perturbation method.

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The carbon dioxide - water binary system is one of the most studied systems relevant to geochemistry, biochemistry atmospheric chemistry and industrial processes. Despite obvious their importance, the thermodynamic properties of this system are only known to moderate temperatures and pressures less than 10 kbar. Empirical equations of state are not applicable outside the PVTx space covered experimentally. On the contrary, approaches based on microscopic description of solubility can be used to reliably predict thermodynamic properties of the system beyond experimentally determined PVTx space, provided they based on a correct force field. Typical classic molecular dynamics and Monte-Carlo simulations utilize force field that is parametrized at the ambient conditions and hence are not generally applicable at extreme conditions. To overcome this limitation, one can treat solute-solvent interactions quantum mechanically from the first-principles and use them as a perturbation to the classical Hamiltonian model. Classical simulations were performed with the 4-site fluctuating charge TIP4P-FQ model for water and flexible 3-site Buckingham exp-6 model for carbon dioxide. Solvent-solute interaction energy was calculated ab initio and was used to correct classical force field parameters for carbon dioxide. The resulted model for carbon dioxide adequately describes the solvation energy of carbon dioxide in water at 573K and 1 kbar.