

Water Homogeneous Nucleation: Importance of Clustering Thermodynamics

Hua Du, Fangqun Yu, and Alexey B. Nadykto

Abstract Quantum methods, which are developed to accurately predict the physical properties of small clusters, are applied to study the water nucleation phenomenon. The self-consistency corrected (SCC) theory of water homogeneous nucleation, which satisfies the law of mass action and avoids the mismatch in the cluster distribution for monomers, overpredicts the nucleation by several orders of magnitude. In this study, we show that the overprediction is likely due to the inadequate description of thermodynamic properties of small water cluster using capillarity approximation. The Density Functional Theory (DFT) methods – PBEPBE and PW91PW91, were used to calculate the thermodynamic properties of $(\text{H}_2\text{O})_n$ ($n = 1-10$). These data were then used in the kinetic water nucleation model to study the effect of thermochemistries of the first ten water clusters on the prediction of nucleation rate by SCC. A considerable difference between Gibbs free energy changes of the $(\text{H}_2\text{O})_n$ formation used in classical nucleation theory (CNT) and results obtained using quantum methods has been illustrated. We also found that predicted nucleation rates by the SCC model can be improved when the model is constrained by the stepwise Gibbs free energy changes obtained by DFT methods. This study highlights the importance of properly treating the thermochemistry of small cluster formation and demonstrates the feasibility of employing thermodynamic properties of small clusters obtained using quantum methods instead of those derived based on traditional capillarity approximation.

Keywords Water homogeneous nucleation, density functional theory, thermochemistry

Atmospheric Sciences Research Center, State University of New York at Albany, Albany, NY 12203, USA

167

C. D. O'Dowd and P. E. Wagner (eds.), *Nucleation and Atmospheric Aerosols*, 167–171.
doi: ; © Springer 2007

Comparisons of Stepwise Gibbs Free Energy Change of Formation of Small Water Clusters

A comparison of stepwise dG^0 in Figure 1 shows that dG^0 of formation of water dimer given by PBEPBE and PW91PW91 with aug-cc-pvtz are in good agreement with those predicted by high-accuracy model chemistry methods and MP2/6-311 + + G(2d,2p) with the anharmonic correction. They also fall within the experimental uncertainty range. The stepwise dG^0 for $(\text{H}_2\text{O})_n$ ($n = 1-10$) given by the PBEPBE and PW91PW91 is in agreement within ~ 0.5 kcal/mol per step. The difference between the DFT-calculated dG^0 and those given by the above three model chemistry methods ranges from 0.06 to 0.17 kcal/mol per step and 0.42–0.65 kcal/mol per step for PBEPBE/aug-cc-pvtz and PW91PW91/aug-cc-pvtz, respectively. Compared to PW91PW91/aug-cc-pvtz, PBEPBE/aug-cc-pvtz yields closer results to the model chemistry methods. In addition, the dG^0 curve given by CNT¹ is much lower than those given by the quantum methods. The Gibbs free energy of 2.77 kcal/mol is assigned by CNT to $n = 0@1$ transition, which is obviously unphysical. Since the nucleation rate is very sensitive to the dG^0 , the significant difference in dG^0 of formation of small water clusters between CNT and quantum methods is expected to lead to a large difference in the predicted nucleation rates.

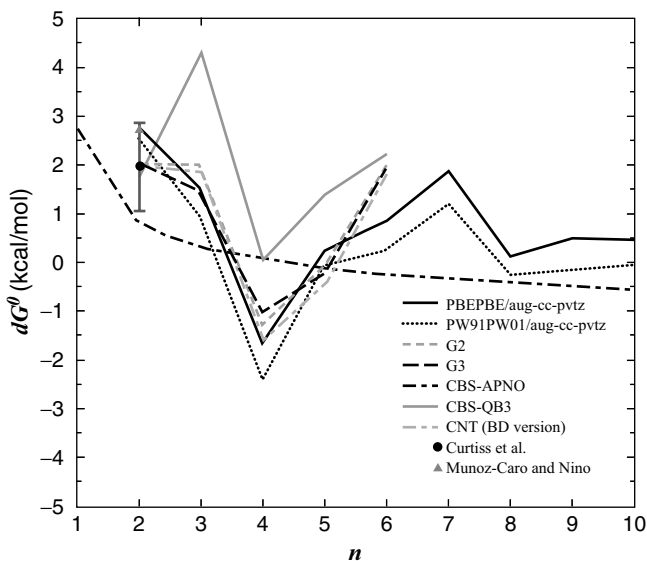


Figure 1 dG^0 for $(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_n$ reaction as a function of the number of molecules in the cluster at standard condition ($T = 298.15\text{K}$ and $P = 1\text{ atm}$). The square with the error bar and triangle refer to Curtiss et al.,² and Munoz-Caro and Nino,³ respectively

Comparisons of Nucleation Rates from Various Studies

Figure 2 shows the nucleation rates based on QM-based nucleation model, SCC theory,⁴ the Monte Carlo study,⁵ and experimental results as a function of supersaturation ratio at four different temperatures. For the QM-based model, the stepwise dG^0 for $(\text{H}_2\text{O})_n$ ($n = 1-10$) are derived from two DFT methods while those for $(\text{H}_2\text{O})_n$ ($n > 10$) are calculated in the same way as in SCC theory.⁴ Compared to PW91PW91/aug-cc-pvtz (the long-dashed curves), PBEPBE/aug-cc-pvtz (the dot-dashed curves) gives much better agreement with the experimental data due to the different prediction of stepwise dG^0 (Figure 1). Under all four temperatures studied here, the nucleation rates predicted by PBEPBE/aug-cc-pvtz are consistently lower than those predicted by both SCC theory and the Monte Carlo study. The only difference between PBEPBE/aug-cc-pvtz and SCC is the different dG^0 for the first ten water clusters, however, the deviations in the predicted nucleation rate range from

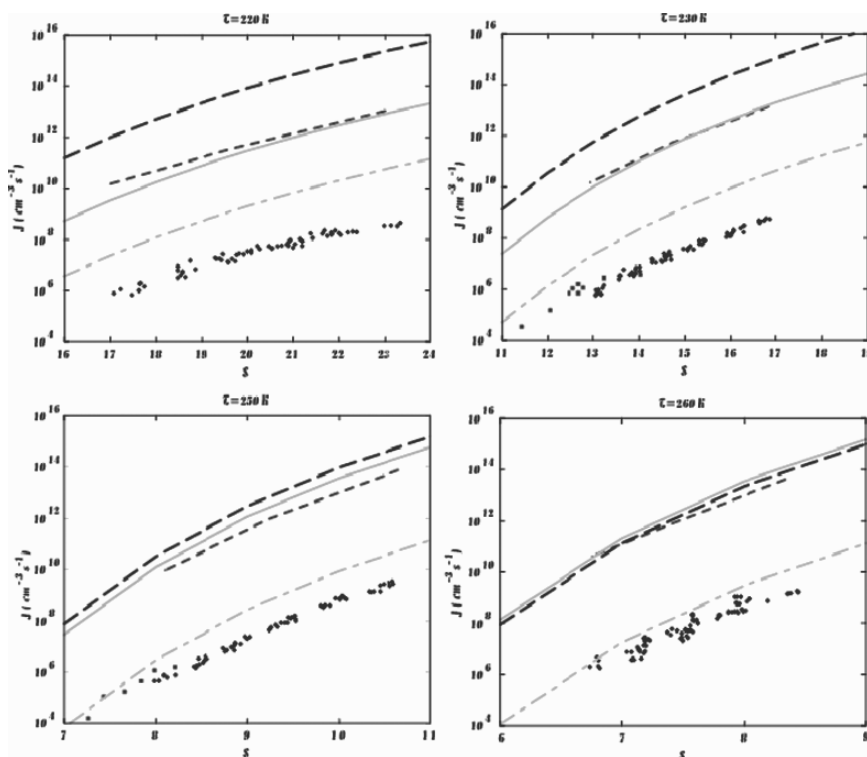


Figure 2 Supersaturation ratio dependence of the water nucleation rates at $T = 220, 230, 250,$ and 260K (as indicated): **Circles** – experimental data of Wolk and Strey⁶; **squares** – experimental data of Mikheev et al.⁷; **solid curves** – SCC prediction; **dashed curves** – Monte Carlo simulations⁵; **long-dashed curves** – PW91PW91/aug-cc-pvtz; **dot-dashed curves** – PBEPBE/aug-cc-pvtz

10^2 at $T = 220\text{K}$ to 10^4 at $T = 260\text{K}$. It clearly indicates that the more accurate description of dG^0 for the first ten clusters significantly improves the nucleation rate prediction of SCC nucleation theory. The overprediction of nucleation rate by SCC is likely due to the underestimation of dG^0 for the small clusters which suggests that the disagreement of SCC theory with experimental results may be associated with the error in the capillarity approximation for the small clusters.

Effects of Thermochemistry of $(\text{H}_2\text{O})_n$ ($n > 10$) on Predicted Nucleation Rates

The quantum-derived dG^0 significantly improve the prediction of nucleation rate by SCC theory in terms of magnitude, however, the temperature dependence of its prediction is not satisfying. We speculated this may be due to the use of dG^0 predicted using capillarity approximation for $(\text{H}_2\text{O})_n$ ($n > 10$). Due to the unavailability of quantum-calculated thermodynamic properties of water clusters larger than $(\text{H}_2\text{O})_{10}$, we extrapolated the dG^0 from $(\text{H}_2\text{O})_{10}$ to the $(\text{H}_2\text{O})_{20}$, as shown in Figure 3(a). It is done in such a way that the dG^0 rapidly decreases, and then gradually approaches the classical value of $(\text{H}_2\text{O})_{20}$. The choice of $(\text{H}_2\text{O})_{20}$ is arbitrary as the main purpose is to qualitatively show the importance of thermodynamic properties of larger water clusters on the temperature dependence of the predicted nucleation rate. Figure 3(b) shows the comparison of nucleation rates calculated based on the updated dG^0 as shown in Figure 3(a) with the experimental study. Clearly, the temperature dependence of nucleation rates has been significantly improved. The

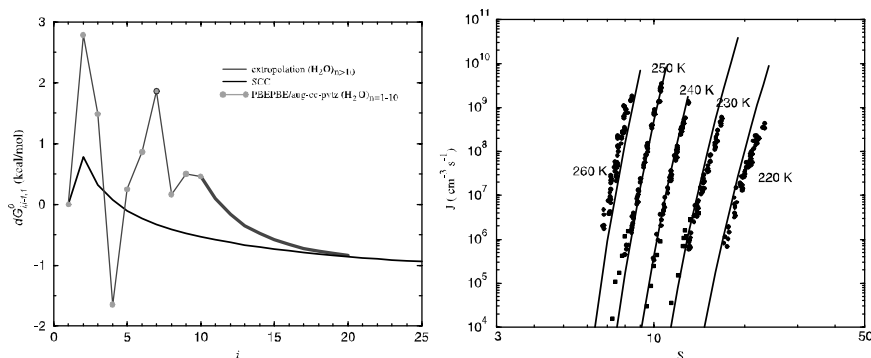


Figure 3 The stepwise Gibbs free energy changes from DFT using PBEPBE/aug-cc-pvtz method for water clusters from monomer to decamer (circles) at the standard condition. The dot-dashed curve is the extrapolation, so that the Gibbs free energy changes approach to that predicted by the SCC model. (b) Predicted nucleation rates at five different temperatures (as indicated), calculated with the DFT-based stepwise Gibbs free energy changes and extrapolations as shown in Figure 3(a)