

## Modelling the sign preference in heterogeneous nucleation

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Nucleation on ions is an important process in the atmosphere. Ions of opposite sign were observed to exhibit different nucleation rates as early as 1897 (Wilson, 1897) but the reason for this sign preference remained a mystery for more than a century. In a recent paper by Nadykto *et al.* (2006) it was demonstrated that the sign effect can be predicted by carrying out relatively simple quantum chemical calculations. This means we can use quantum chemical methods to help us understand the role of ion-induced nucleation in atmospheric nucleation reactions. However, the computational methods in use today are generally iterative methods that employ a variety of approximations in order to keep the cost in computational resources reasonable. Because of this, we must compare the theoretical predictions with high quality experimental results in order to gain reliable insight on the initial steps of ion-induced nucleation.

We studied the binding energies of small charged and neutral n-propanol – tungsten oxide and n-propanol - silver clusters. The objective of our study was to replicate the experimental results obtained by Winkler *et al.* (2008), which indicated a negative sign preference for both cases. This was done to get quantitative results which could be used to explain the experimental data and to test the limits and reliability of the used quantum chemical methods.

Silver and tungsten atoms are relatively large, so out of computational considerations we began our studies by considering very small, neutral or singly charged seed molecules (WO<sub>3</sub>, W<sub>3</sub>O<sub>9</sub>, Ag<sub>2</sub> and Ag<sub>3</sub>) and a single n-propanol molecule. This choice was also supported by the fact that the experimentally observed sign effect was stronger for smaller seed particles. However, even in these simple cases we experienced computational difficulties and were unable to replicate the sign preference on a qualitative level. The absolute values of the electronic energies for the positively charged clusters were not only larger than for the negatively charged clusters in all cases (which would imply a positive sign preference), but the difference was also as much as one order of magnitude in the worst cases. We also noted that cations proved to be computationally more demanding than anions. Different programs, methods and levels of accuracy have been employed in the computations, but the qualitative results of the computations have so far stayed unchanged.

While the exact reasons for both the computational problems and the results remain at this time unknown, we suspect that the computational methods used are too approximate to model clusters and molecules where constituent atoms have such a large number of electrons accurately enough to provide qualitatively reliable results. Different methods and levels of accuracy are not equally suitable even for all the cases tested here, so further studies are still required. Another plausible explanation is the difference between the size of the seed molecules in our simulations and the size of the actual nucleating clusters observed in the experiment, which were approximated to contain around 20 to 25 molecules based on the heterogeneous nucleation theorem (Vehkamäki *et al.*, 2007). In addition to trying to solve the computational difficulties, we have started to model a case where the n-propanol molecule is adsorbed on a neutral or singly charged seed molecule consisting of 20 silver atoms (Ag<sub>20</sub>).

Our calculations have been performed using the Gaussian 03 (Frisch *et al.*, 2004), SIESTA (Soler *et al.*, 2002) and TURBOMOLE (Ahlrichs *et al.*, 1989; versions 5.9 & 5.10) quantum chemistry programs.

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- Wilson, C.T.R., *Phil. Trans. R. Soc. A* 189, 265 (1897).
- Nadykto, A.B., Natsheh, A.A., Yu, F., Mikkelsen, K.V. and Ruuskanen, J., *Phys. Rev. Lett.* 96, 125701 (2006).
- Ahlrichs, R., Bär, M., Häser, M., Horn, H. and Kölmel, C., *Chem. Phys. Lett.* 162, 165 (1989).
- Frisch, M.J. *et al.*, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT (2004).
- Soler, J.M., Artacho, E., Gale, J.D., García, A., Junquera, J., Ordejón, P. and Sánchez-Portal, D., *J. Phys. Condens. Matt.* 14, 2745 (2002).
- Winkler, P.M., Steiner, G., Vrtala, A., Vehkamäki, H., Noppel, M., Lehtinen, K.E.J., Reischl, G.P., Wagner, P.E. and Kulmala, M., *Science* 319, 1374 (2008).
- Vehkamäki, H., Määttänen, A., Lauri, A., Kulmala, M., Winkler, P., Vrtala, A. and Wagner, P.E., *J. Chem. Phys.* 126, 174707 (2007).