Sodium in Water Cluster - Part II: Reactivity of a Sodium Atom in Vibrationally Excited Water Clusters

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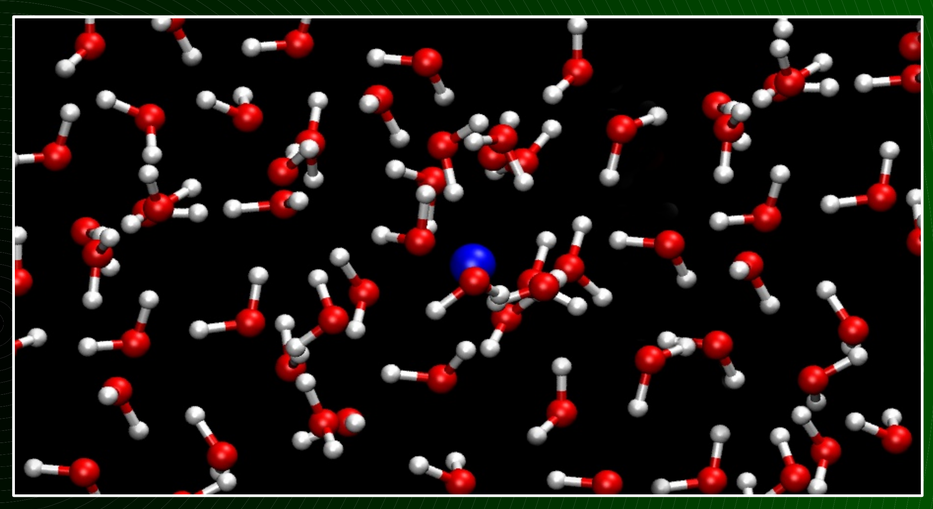
Big Issue

What is the mechanism of 'sodium-in-water' reaction?

- the reaction is extensively studied and its microscopic mechanism is still an open issue
- recently conducted DFT calculations resulted with proposal of a new one requiring the presence of only one sodium atom[1,2,3]
- DFT calculations furthermore suggested that the reaction path is connected with an elongation of the O-H bond in a water molecule from the first solvation shell therefore in this work such bonds were vibrationally excited

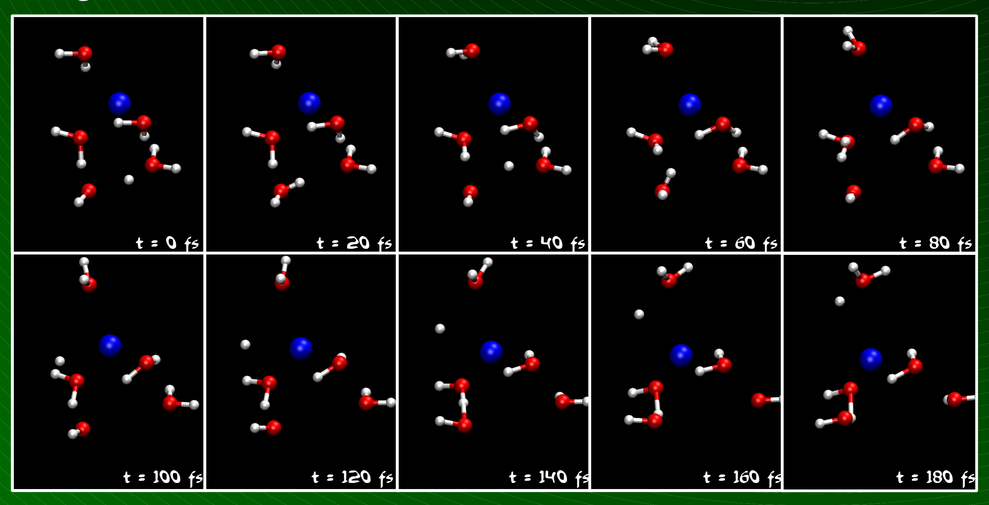


Computational details:

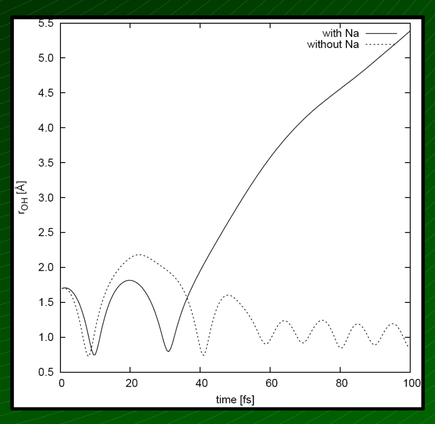
- Born-Oppenheimer Molecular Dynamics from CP2K/Quickstep software package
- Density Functional Theory with mixed Gaussian/PW approach
- BLYP functional with DVZP basis set

Small water clusters (n = 5)

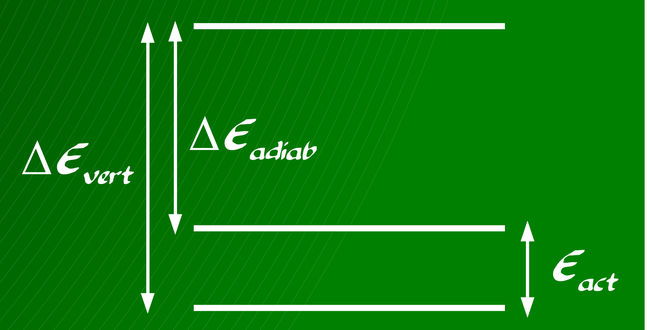
Trajectory



Time evolution of O-H distance (n = 5)



Estimation of activation energy



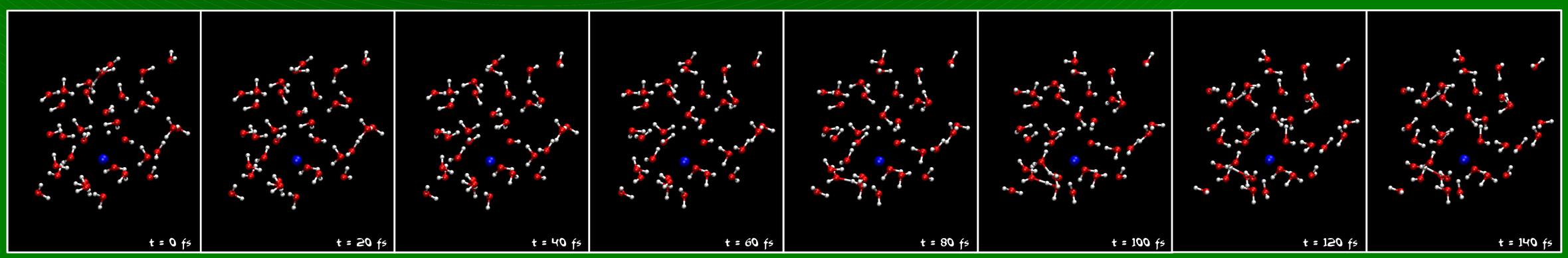
$\Delta\epsilon_{vert}$ = 83 kcal/mol

$\Delta\epsilon_{adiab}$ = 67 kcal/mol

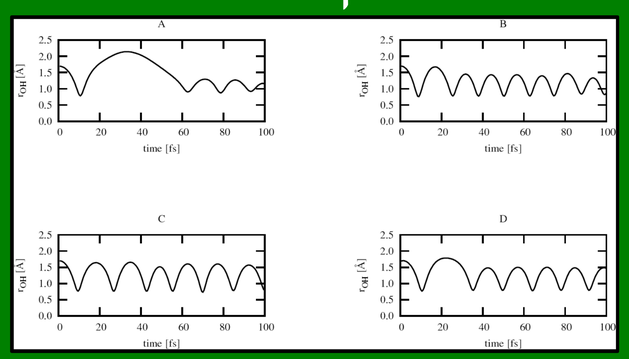
$\epsilon_{act} = \Delta\epsilon_{vert} - \Delta\epsilon_{adiab}$ = 16 kcal/mol

Medium-size water clusters (n = 34)

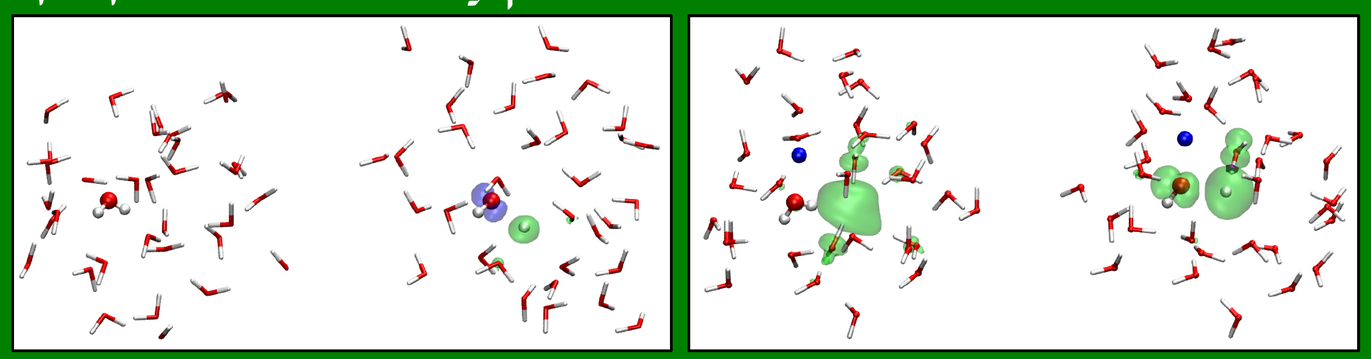
Trajectory



Time evolution of O-H distance



Spin polarization/density for cluster without/with sodium atom



Dissociation reaction

$H_2O + Na^{\bullet} \rightarrow Na^{+} + OH^{-} + H^{\bullet}$

$Na^{\bullet} \rightarrow Na^{+} + {}^{\bullet}$

$H_2O \rightarrow H^{+} + OH^{-}$

$H^{+} + {}^{\bullet} \rightarrow H^{\bullet}$

Activation energy is estimated to be less then 16 kcal/mol

Conclusions

- we confirmed the possibility of both water dissociation and NaOH formation in small vibrationally excited water clusters (n = 4, 5)
- vertical vibrational excitation energy of about 80 kcal/mol is needed in order to initiate the reaction
- if water molecules are allowed to relax a low-barrier reaction path is possible (16 kcal/mol)
- we observed water dissociation and a transient Na+OH- formation in a 34 water vibrationally excited cluster

References

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