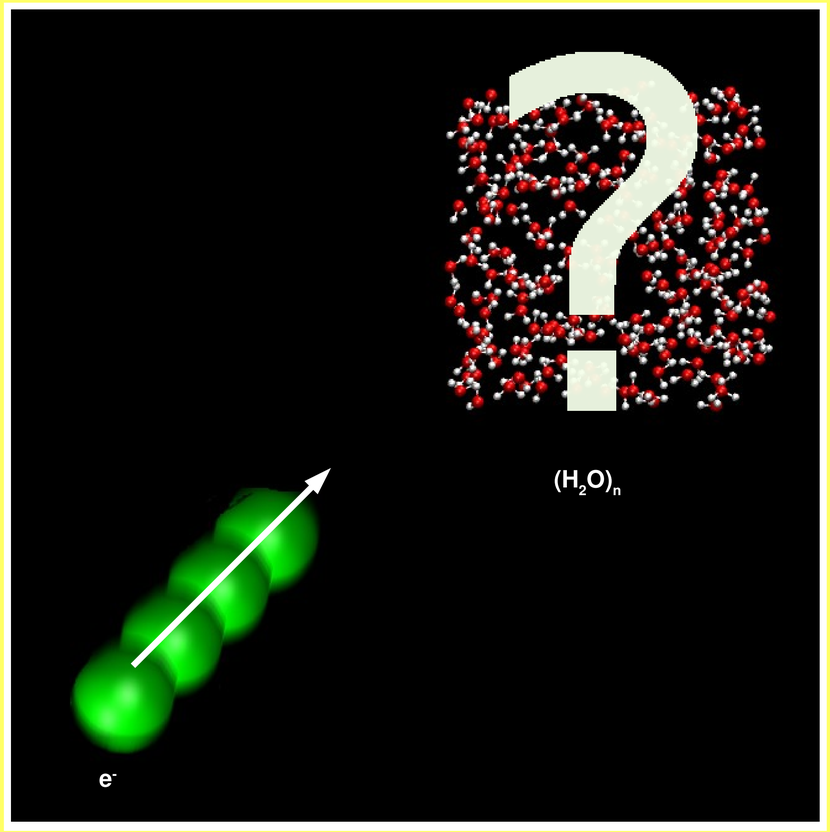
Sodium in water cluster – Part I: IR spectrum and formation of the solvated electron

Waldemar Kulig and Piotr Kubisiak

K. Gumiński Department of Theoretical Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

Question: What happens with excess electron in alkali doped large water clusters?



GOAL

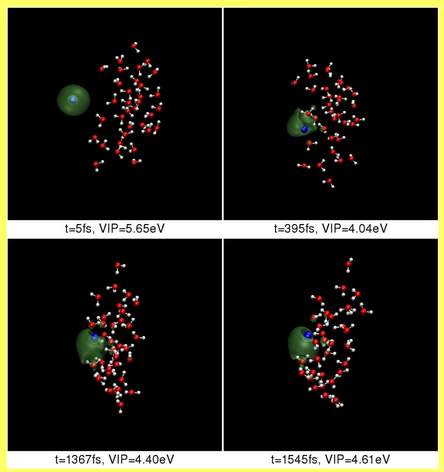
- MD simulations modeling collisions of a sodium atom with a cluster with 34 water molecules.
- dynamics of the hydrated-electron formation
- calculations of the IR spectrum in O-H stretch region.

COMPUTATIONAL DETAILS

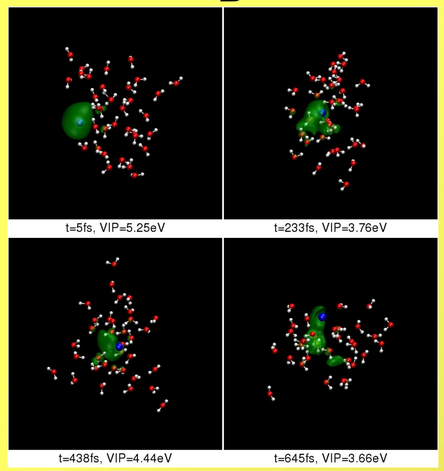
- *ab initio* BOMD (CP2K/Quickstep)
- DFT (BLYP/DZVP, GTH pseudo potential)
- timestep 0.5fs
- energy cutoff - 400Ry

TRAJECTORIES

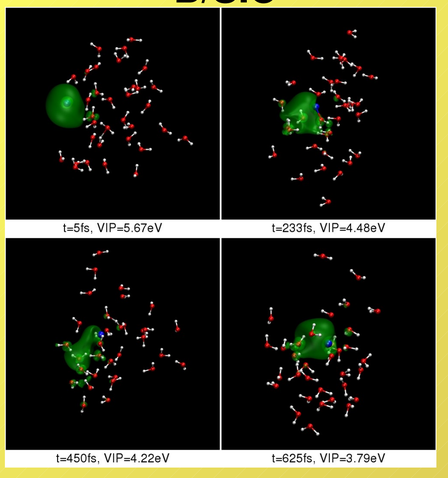
A

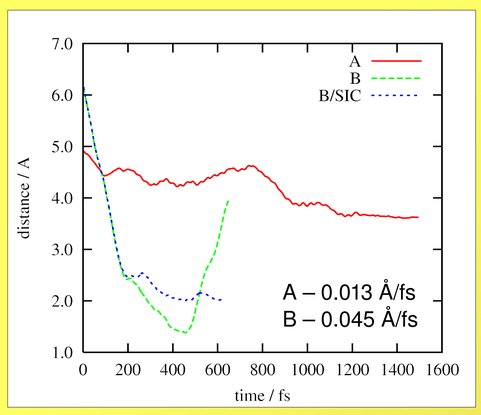


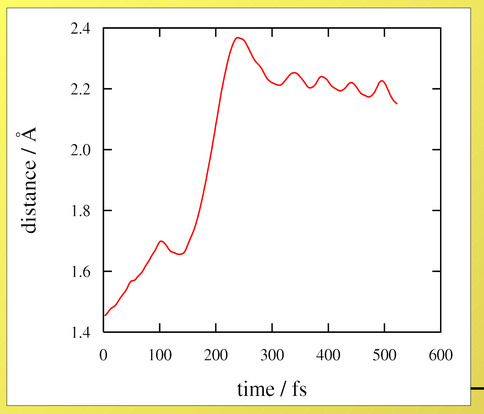
B



B/SIC



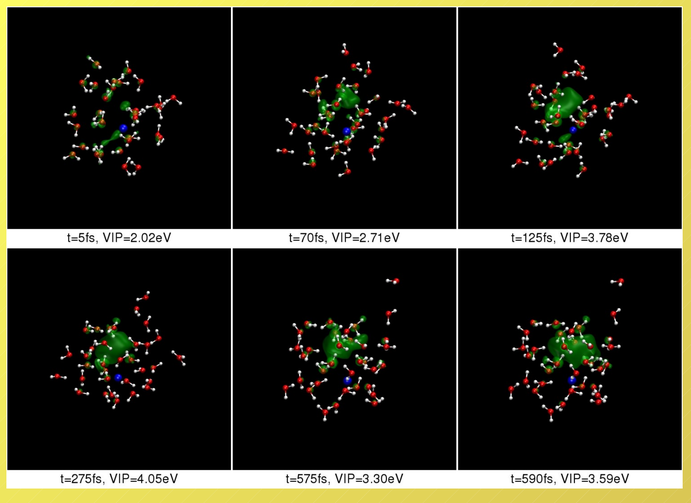




B		B/SIC	
time [fs]	VIP [eV]	time [fs]	VIP [eV]
5	5.25	5	5.67
233	3.76	233	4.48
438	4.44	450	4.22
645	3.66	625	3.79

a) spin density volume $\langle \Psi | (\vec{r} - \vec{r}_{center})^2 | \Psi \rangle$
b) spin density shift

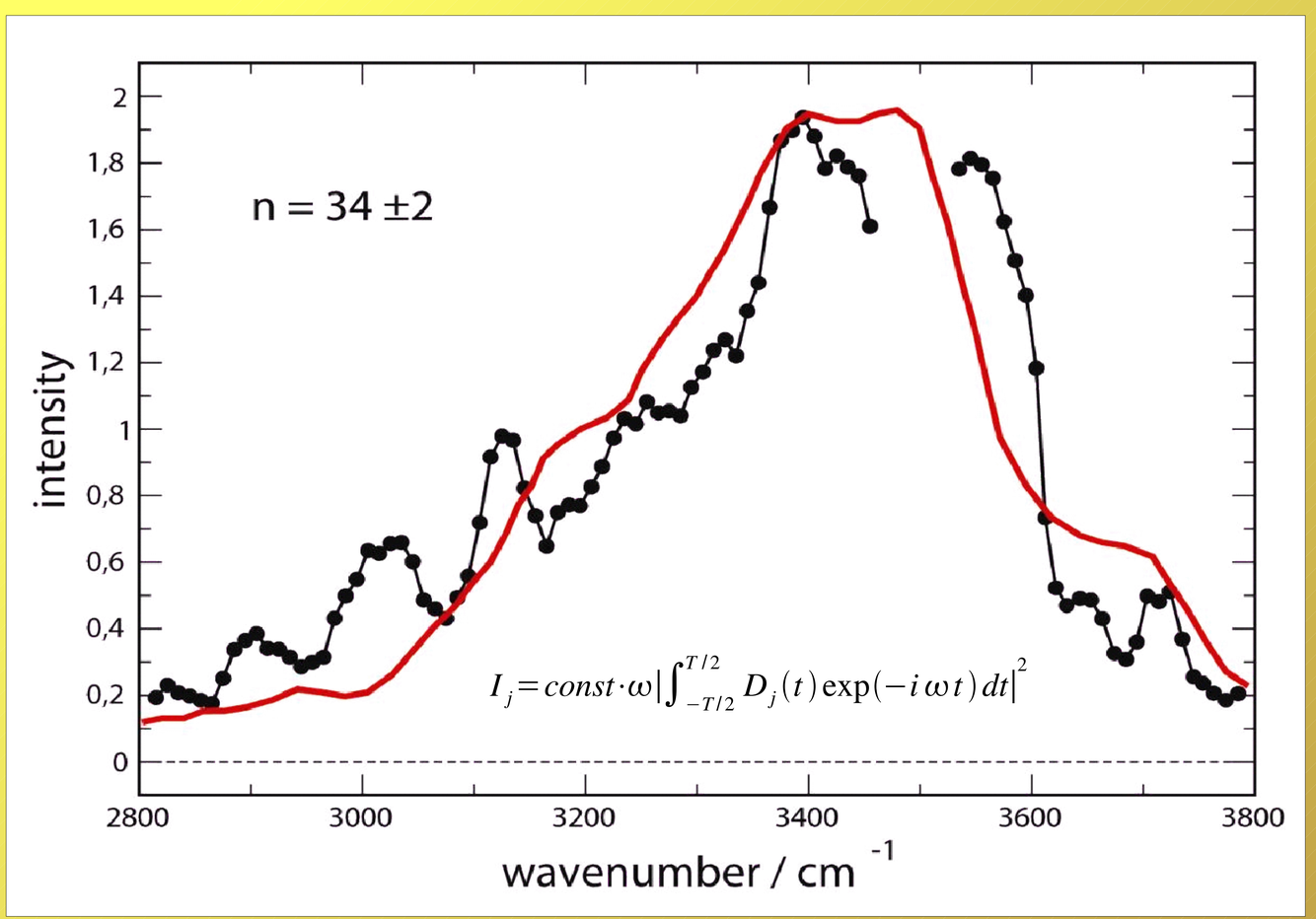
C



B/SIC			
time [fs]	VIP [eV]	V[a] [Å^{-3}]	S[b] [Å]
5	5.67	318	0.5
233	4.48	258	1.6
450	4.22	197	2.5
625	3.79	235	1.3

C			
time [fs]	VIP [eV]	V [Å^{-3}]	S [Å]
0	2.07	56	1.9
50	3.32	151	2.6
100	5.04	171	3.2
200	4.38	204	2.6
300	4.94	186	2.8
400	4.54	213	2.4

IR SPECTRUM



CONCLUSIONS

- the results suggests delocalization of the excess electron between the alkali atom and water molecules

- time scale of the relaxation of electron density is in the range of hundreds of femtoseconds

- location of the excess density depends on the initial velocity of a sodium atom, nevertheless, it tends to be located mostly in the bulk of the cluster

- the values of vertical IP correlate well with previous data [1] and indicate that the experimental IP is adiabatic

- good agreement was obtained between the calculated (based on the Fourier transform of the dipole-dipole auto-correlation function [2]) and experimental IR spectrum (black dots).

ACKNOWLEDGEMENTS

The authors express their gratitude to Prof. Pavel Jungwirth (Czech Academy of Science) and Dr. Łukasz Ćwiklik (Hebrew University) for inspiration to this work and for valuable discussions.

[1] B. Gao, Z.F. Liu, J. Chem. Phys. 126 (2007) 084501.
[2] V. Buch, F. Mohamed, M. Parrinello, and J. P. Devlin, J. Chem. Phys. 126, 074503 2007.
[3] L. Cwiklik, P. Kubisiak, W. Kulig, P. Jungwirth, Chem. Phys. Lett. (2008), doi:10.1016/j.cplett.2008.05.075.
[4] L. Cwiklik, U. Buck, W. Kulig, P. Kubisiak, P. Jungwirth, J. Chem. Phys. 128 (2008) 154306.