Ultrafast Dynamics in Na-doped water Clusters

Claus Peter Schulz, Hongtao Liu, Christian Schröter, Nick Zhavoronkov, and Ingolf V. Hertel[1]
Max Born Institute, Berlin, Germany
[1]*also: Department of Physics, Free University, Berlin, Germany*

Abstract. *The lifetimes of the first electronically excited state of $(H_2O)_n\cdots Na$ clusters (n up to 40) are measured using two colour pump-probe spectroscopy. The measured lifetimes are compared to those of water cluster anions.*

Gas phase clusters of polar solvent molecules doped with an alkali metal atom are model systems for studying the behaviour of loosely bound metal valence electrons in a polar environment. In the past years, our group has investigated spectroscopic properties of size-selected $(H_2O)_n\cdots Na$ and $(NH_3)_n\cdots Na$ clusters, such as the ionization potentials[1] and the energy of the first electronic excited state[2,3]. It has been shown that pump-probe experiments provide a suitable tool to study the dynamics of the electronically excited state.[4] Previous work on $(NH_3)_n\cdots Na$ clusters has shown that the lifetimes of first electronically excited states strongly decreases for larger n. For $n \geq 4$ they are on the order of picoseconds and lower. Similar results have been obtained for the anions of pure water clusters.[5,6] These short lifetimes are presumably provoked by a fast internal conversion, which is strongly correlated to the DOS of the intra molecular vibrations. In the present work we focus on the water system. The lifetimes of the first electronically excited state of $(H_2O)_n\cdots Na$ clusters (corresponding to the 3p ← 3s transition in free sodium atoms) with n up to 40 are measured by two colour pump-probe spectroscopy (800/400 nm) with 30 fs pulses. The observed lifetimes are compared to those of water cluster anions, which are expected to have a similar electronic structure. It turns out that the lifetimes of $(H_2O)_n^-$ reported in the literature [5,6] are significantly larger.

From the curve of Figure 1 we learn that the lifetime trends of $(H_2O)_n\cdots Na$ clusters are somewhat different compared to water cluster anions. Bragg et al. [8] have concluded that their isomer I of $(H_2O)_n^-$ clusters (considered to be internal states) extrapolate linearly with 1/n toward to the known conversion lifetime of 50 fs in bulk water. The isomer II of $(H_2O)_n^-$ clusters (considered surface-bound) have larger sizes (n = 60−100), and their decay time is more or less independent of the cluster size. For our measurements of $(H_2O)_n\cdots Na$ clusters, the first excited states are shorter living than water cluster anions. The decay time of $(H_2O)_n\cdots Na$ clusters decreases massively with n up to 8 (to about 140 fs), however, the lifetime of $(H_2O)_9\cdots Na$ is distinctly longer than $(H_2O)_8\cdots Na$. For $n \geq 9$ the lifetimes change much slower but still constantly drop as the cluster size increases. For clusters with $n \geq 24$ the experimental results may indicate a somewhat more rapid decrease with size. Whether this trend continues and might be rationalized by evoking a significant influence of the solvation shells of water around the Na^+ ion will have to be discussed in the light of further measurements. The similarities of the lifetime behaviour of sodium-water and sodium-ammonia clusters give evidence that the short lifetimes of lowest excited state are caused by internal conversion. Extension of the experiments and further in depth theoretical simulations are still needed.

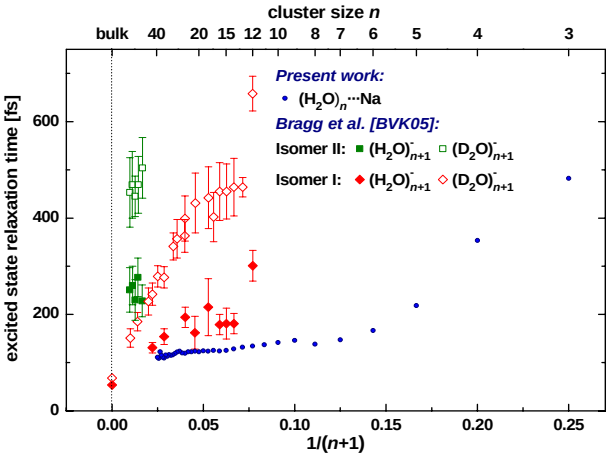

Fig. 1. *Size dependent lifetime trends of the lowest electronically excited state of $(H_2O)_n\cdots Na$ clusters.*

References

1 I. V. Hertel, C. Hüglin, C. Nitsch, and C. P. Schulz, Phys. Rev. Lett. **67**, 1767 (1991).
2 P. Brockhaus, I. V. Hertel, and C. P. Schulz, J. Chem. Phys. **110**, 393 (1999).
3 C. P. Schulz, C. Bobbert, T. Shimosato, K. Daigoku, N. Miura, and K. Hashimoto, J. Chem. Phys. **119**, 11620 (2003).
4 C. P. Schulz, A. Scholz, and I. V. Hertel, Isr. J. Chem. **44**, 19 (2004).
5 J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, Science **307**, 93 (2005).
6 A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, J. Am. Chem. Soc. **127**, 15283 (2005).