Ultrafast dynamics in sodium-doped water clusters

J.P. Müller, H.T. Liu, C.P. Schulz, N. Zhavoronkov, and I.V. Hertel[1]

Max-Born-Institut, Max-Born-Strasse 2a, 12489 Berlin, Germany
[1] also: Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Even after more than four decades of research the behaviour of loosely bound electrons in a polar environment is still a challenging topic. Gas phase clusters of polar solvent molecules doped with an alkali metal atom are a well suited model system, since the number of molecules interaction with the bound electron can be varied.
In the past years our group has investigated some spectroscopic properties of size-selected $(H_2O)_n\cdots Na$ and $(NH_3)_n\cdots Na$ clusters, such as ionization potential [1] and energy of the first electronically excited state [2,3]. In addition femtosecond-pump-probe experiments allow studying the dynamics of electronically excited states [4]. Previous work on $(NH_3)_n\cdots Na$ clusters has shown the lifetime of the lowest electronically excited states to decrease strongly with cluster size. For $n \geq 4$ it is on the order of picoseconds and lower. The situation resembles that of pure water cluster anions [5].
In the present work we are dealing with two colour femtosecond pump probe spectroscopy on $(H_2O)_n\cdots Na$ clusters. The clusters were created by expanding water vapour through a 50 µm nozzle into vacuum, creating a continuous beam of water clusters. The clusters traverse a pickup oven, where they are doped with a sodium atom. The cluster is excited using a 800 nm photon and the population of the excited state is probed with a 400 nm pulse, using laser pulses of 35 fs duration. Finally the ions created are detected in a linear time of flight mass spectrometer. Due to Franck-Condon principle only the excited state can be ionized, in contrast to a highly vibrationally excited ground state. Hence the decay of the ion signal is a measure for lifetime of the excited state.
The lifetime of clusters up to n = 40 has been measured. Since binding of the electron in $(H_2O)_n\cdots Na$ clusters is similar to water cluster anions, it is not astonishing to find their lifetimes to be in the same range. The measured values around 100 fs for $(H_2O)_n\cdots Na$ with $n \geq 14$ is even smaller than the lifetimes for $(H_2O)_n^-$ clusters.
A process explaining this fast decay of this state is a fast internal conversion to intra molecular vibrations [4]. To back up this assumption the lifetimes of $(D_2O)_n\cdots Na$ clusters have been measured, which exhibit larger lifetimes of the excited state.

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