

Photoionization and infrared excitation of clusters with radical sites: Probing size and structure of neutral, sodium doped water clusters

¹C. C. Pradzynski, ²U. Buck, ¹R. M. Forck, ¹F. Zurheide, and ¹T. Zeuch

¹Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Göttingen, 37077, Germany

²Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen 37077, Germany

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Presenting author email: cpradzy@gwdg.de

An interesting application of the sodium doping technique is the size selection of neutral clusters or aerosol particles (Bobbert et al. 2002, Yoder et al. 2011). The most general method to prepare size selected clusters is a crossed beam scattering experiment, where the mass dependency of cluster deflection by the second beam is exploited. However, this approach is experimentally demanding and restricted to cluster sizes up to around 12 molecules (Pradzynski et al., 2012). Tagging neutral clusters with a sodium atom has emerged in the last decade as a general and experimentally much less complicated method for neutral particle sizing in laboratory experiments.

A key idea of this technique is the formation of a solvated electron when the alkali metal (usually sodium, but lithium and caesium atoms work very similar) interacts with the cluster after pick-up. The site where the metal atom is attached features a single or multi radical type chemical environment, which is crucial for the photoionization of the cluster. This effect is quite general and works with many hydrogen bonded complexes (secondary organic aerosol are highly hydrogen bonded aggregates) and even rare gas clusters. This first stage of the method has the character of chemical pre-ionization. The sodium atom is ionized at the particle surface which decreases the binding energy of the Na 3s electron such that photoionization with tuneable, commercially available lasers becomes possible. When photoionized at the threshold only the

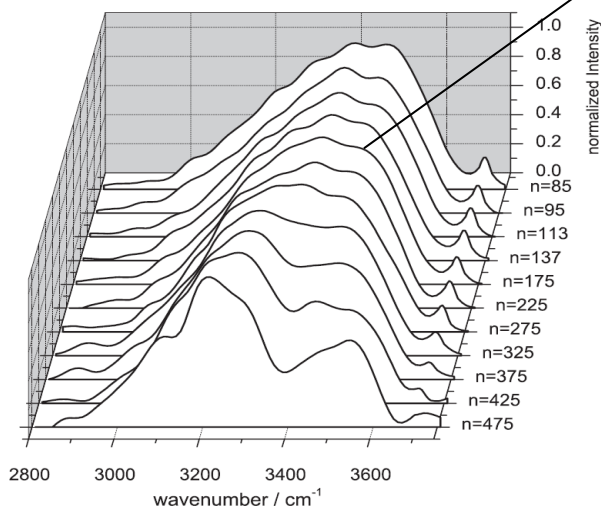


Figure 1. Evolution of crystalline core of water clusters with increasing cluster size (Pradzynski et al., 2012).

most sodium centered clusters become visible. In this case the zwitterionic type potential of the neutral and the cationic potential of the photoionized clusters are quite similar near the energy minimum. This property explains the formation of cold cations without fragmentation because in the cation only low energy modes are populated. The method has a hybrid character. It combines the softness of chemical ionization with the universal applicability of single photon ionization, which is also a rather soft method, even for clusters. The chemical pre-ionization component can be modulated by IR excitation, which provides an additional dimension – the generation of size resolved infrared spectra of the clusters (see Figures 1 and 2).

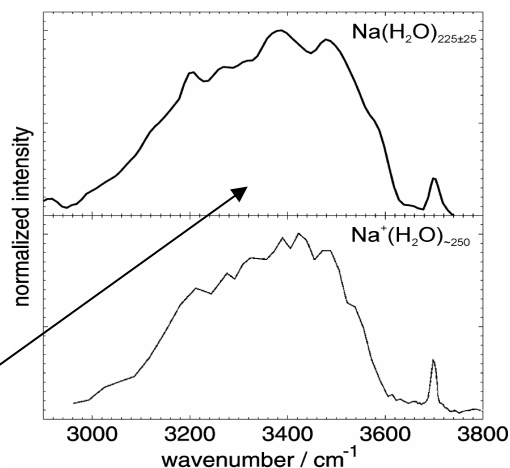


Figure 2. Comparison of infrared spectrum of $\text{Na}(\text{H}_2\text{O})_{225\pm 25}$ with $\text{Na}^+(\text{H}_2\text{O})_{-250}$ clusters (O'Brien and Williams, 2012).

In recent years we applied and refined the sodium doping technique and tested some new applications. In a recent work we could experimentally observe for the first time in the cluster size range between 250 to 500 molecules the transition between amorphous and crystalline ice on the basis of precisely size selectively determined infrared spectra in the OH stretching region, see Pradzynski et al., 2012.

Bobbert, C. et al. (2002) *Eur. J. Phys. D* **19**, 183-192.

Yoder, B. L., et al. (2011) *Phys. Chem. Lett.* **2**, 2623-2628.

Pradzynski, C. C. et al. (2012) *Science* **337**, 1529-1532.

O'Brien, J. T. and Williams, E. R. (2012) *J. Am. Chem. Soc.*, **134**, 10228-10236.