Universality of two gigahertz-ranged cluster lifetimes in hydrogen bonding liquids and mixtures

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Hydrogen bonding liquids are know to form various patterns of short lived hydrogen bonded clusters. A typical example is that of short mono-ols such as methanol and ethanol, which form chain-like clusters of various shapes[1]. By studying the lifetime distribution of various Hbonded liquids and mixtures through Molecular Dynamics simulations, we put in evidence two universal lifetimes in the gigahertz frequency domain[2]. The first frequency, of 50Ghz, corresponds to a mean cluster vibrational mode, while the lower frequency of 20Ghz would correspond to the internal topology of the cluster (linear, chain, etc...) [2,3]. In addition to these two modes, an additional mode is found, which however depends strongly on the Hbonding distance criteria, and spans a lifetime range from 0 to 0.15ps with increasing distances from bonding oxygen atom contact ($r_c \approx 2.8\,\mathring{A}$) to approximatively $r_c \approx 3.5\,\mathring{A}$. In contrast to these universal very short time features, we find that the long time kinetics of the lifetimes are very strongly dependent the bonding distance r_c for a given density or concentration in case of a mixture[2], in line with this third cluster lifetime. These 2 findings, namely universality of atom-level lifetimes and microscopic details depending kinetics, are surprisingly in variance with the intuitive view of the kinetics of molecular association.

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