Electronic relaxation dynamics in $(\text{water})_n^-$ $(n=25-100)$ and $(\text{CH}_3\text{OH})_n^-$ $(n \sim 140-530)$ clusters via femtosecond photoelectron imaging

ASTER KAMMRATH, GRAHAM GRIFFIN, UC Berkeley, JAN VERLET, University of Durham, ART BRAGG, UC Los Angeles, DANIEL NEUMARK, UC Berkeley and Lawrence Berkeley National Laboratory — Large clusters of $(\text{H}_2\text{O})_n^-$ $(n=25-50)$, $(\text{D}_2\text{O})_n^-$ $(n=25-100)$ and $(\text{CH}_3\text{OH})_n^-$ $(n \sim 140-530)$ are studied with femtosecond time-resolved photoelectron imaging. For all three systems, the excess electron is promoted to an excited state with a pump laser pulse at 1.55 eV. Subsequent dynamics are monitored by observing photoelectrons detached after a variable delay with a probe pulse at 3.1 eV. For all three systems the excess electron is seen to decay via internal conversion back to the ground state with lifetimes of 190-130 fs for $(\text{H}_2\text{O})_n^-$, 360-150 fs for $(\text{D}_2\text{O})_n^-$ and 260-170 fs for $(\text{CH}_3\text{OH})_n^-$. For all three systems, lifetime of the excited state decreases with increasing cluster size and is found to vary linearly with $1/n$. Extrapolation to the bulk yields lifetimes of $54\pm30$ fs for H$_2$O, $72\pm22$ fs for D$_2$O and $\sim 150$ fs for CH$_3$OH.

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