

INFRARED PREDISSOCIATION SPECTRA OF $\text{Cl}^-(\text{CH}_3\text{OH})_n\text{Ar}$ CLUSTER IONS, $n=1-3$

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Infrared predissociation spectra of $\text{Cl}^-(\text{CH}_3\text{OH})_n\text{Ar}$ and $\text{Cl}^-(\text{CH}_3\text{OD})_n\text{Ar}$, $n=1-3$, will be presented and discussed in terms of isomer trapping and cooperative enhancement of hydrogen bonds. Due to the strong ionic hydrogen bonds between the chloride ion and methanol, spectra with d_1 -methanol were obtained to distinguish between CH stretches and hydrogen-bonded OH features. For $\text{Cl}^-(\text{CH}_3\text{OH})_1\text{Ar}$, the ionic hydrogen bond shifts the OH stretch -584 cm^{-1} from the gas-phase value of neutral methanol, which is slightly larger than the shift reported for the non-argonated, $\text{Cl}^-(\text{CH}_3\text{OH})_1$ cluster^a. A methanol...methanol hydrogen bond was observed as the dominant feature in the $n=2$ spectrum. For $n=3$, we observe three isomers, including a methanol trimer chain which is calculated to be approximately 9 kJ/mol above the minimum-energy isomer. The cooperative effects of hydrogen bonding are pronounced in the $n=2-3$ spectra. The largest effect comes in the methanol trimer chain where the ionic hydrogen bond results in a shift of the OH stretch of -364 cm^{-1} compared to the $n=1$ structure, or in comparison to neutral methanol, a remarkable -948 cm^{-1} shift. These results indicate that high-energy isomers which exhibit very strong hydrogen bonds can be readily formed by introducing Cl^- into cold, argonated methanol clusters.

^aO. M. Cabarcos, C. J. Weinheimer, T. J. Martinez and J. M. Lisy, *J. Chem. Phys.* **1999**, 110, 9516-9526.