INFRARED ABSORPTION OF METHANOL-WATER CLUSTERS $M_n(H_2O)$, *n* = 1-4, RECORDED WITH THE VUV-IONIZATION/IR-DEPLETION TECHNIQUES

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We investigated IR spectra in the CH- and OH-stretching regions of size-selected methanol-water clusters, $M_n(H_2O)$ with M representing CH_3OH and *n* = 1-4, in a pulsed supersonic jet by using the VUV (vacuum-ultraviolet)-ionization/IR-depletion technique. The VUV light at 118 nm served as the source of ionization in a time-of-flight mass spectrometer. The tunable IR laser served as a source of dissociation for clusters before ionization. Spectra of methanol-water clusters in the OH region show significant variations as the number of methanol molecules increase, whereas spectra in the CH region are similar. For $M(H_2O)$, absorption of a structure with H_2O as a proton donor was observed at 3570, 3682, and 3722 cm^{-1}, whereas that of methanol as a proton donor was observed at 3611 and 3753 cm^{-1}. For $M_2(H_2O)$, the OH-stretching band of the dangling OH of H_2O was observed at 3721 cm^{-1}, whereas overlapped bands near 3425, 3472, and 3536 cm^{-1}correspond to the OH-stretching modes of three hydrogen-bonded OH in a cyclic structure. For $M_3(H_2O)$, the dangling OH shifts to 3715 cm^{-1}, and the hydrogen-bonded OH-stretching bands become much broader, with a band near 3179 cm^{-1}having the smallest wavenumber. Scaled harmonic vibrational wavenumbers and relative IR intensities predicted for the methanol-water clusters with the M06-2X/aug-cc-pVTZ method are consistent with our experimental results. For $M_4(H_2O)$, observed spectrum agree less with theoretical predictions, indicating the presence of isomers other than the most stable cyclic one. Spectra of $M_n(H_2O)$ and M_{n+1} are compared and the cooperative hydrogen-bonding is discussed.