UNIMOLECULAR PROCESSES IN $CH_2OH$ BELOW THE DISSOCIATION BARRIER STUDIED BY O-H STRETCH OVERTONE EXCITATION

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Infrared spectra in the fundamental, the first, and the second OH-stretch overtone transitions ($\nu_1$, $2\nu_1$, $3\nu_1$) were obtained by using double resonant ionization via the $3p_z$ Rydberg state. The rotationally well-resolved spectra show that intramolecular vibrational redistribution (IVR) is restricted even in the $3\nu_1$ energy region around 10 490 $cm^{-1}$, which is 960 $cm^{-1}$ above the thermochemical threshold for dissociation to H + $CH_2O$.

The spectrum in the third overtone region ($4\nu_1$) at 13 600 $cm^{-1}$, which is 3 950 $cm^{-1}$ higher than the dissociation threshold, was obtained by monitoring atomic hydrogen photofragments. The overtone spectrum is partially rotationally resolved with a line width of 1.1 $cm^{-1}$. The long dissociation lifetime ($>$ 6 ps) and the similar O-H stretch anharmonicities (obtained from the Birge-Sponer plot) for $CH_2OH$ (91 $cm^{-1}$) and other molecules with much higher O-H dissociation energies indicate that the examined energy region is below the barrier to direct O-H bond fission.

The lack of signal from deuterium fragments in $CD_2OH$ excitation shows that tunneling through the barrier followed by direct O-H bond fission is the dominant pathway following $4\nu_1$ excitation. Theoretical calculations predicted that dissociation via isomerization to the methoxy radical, $CH_3O$, has a barrier lower by 1 000 $cm^{-1}$ - 2 000 $cm^{-1}$ than that for direct O-H bond fission, but this channel appears to be unimportant in the $4\nu_1$ region.

Ongoing work involves accessing higher energy regions that may exceed the reaction barriers.

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