

UNIMOLECULAR PROCESSES IN CH₂OH 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 (ν_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 $10\,490\text{ cm}^{-1}$, which is 960 cm^{-1} above the thermochemical threshold for dissociation to H + CH₂O.

The spectrum in the third overtone region ($4\nu_1$) at $13\,600\text{ cm}^{-1}$, which is $3\,950\text{ cm}^{-1}$ 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 ($> 6\text{ ps}$) and the similar O-H stretch anharmonicities (obtained from the Birge-Sponer plot) for CH₂OH (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 CD₂OH 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, CH₃O, has a barrier lower by $1\,000\text{ cm}^{-1}$ - $2\,000\text{ cm}^{-1}$ 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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