VIBRATIONAL COUPLING PATHWAYS IN THE CH STRETCH REGION OF CH_3OH AND CH_3OD AS REVEALED BY IR AND FTMW-IR SPECTROSCOPIES

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Infrared spectra of jet-cooled CH_3OD and CH_3OH in the CH stretch region are observed by coherence-converted population transfer Fourier transform microwave-infrared (CCPT-FTMW-IR) spectroscopy (E torsional species only) and by slit-jet single resonance spectroscopy (both A and E torsional species, CH_3OH only). Previously, we reported[a] the analysis of ν_3 symmetric CH stretch region ($2750-2900$ cm^{-1}), and the present work extends the analysis to higher frequency ($2900-3020$ cm^{-1}). The overall observed spectra contain 17 interacting vibrational bands for CH_3OD and 28 for CH_3OH. The signs and magnitudes of the torsional tunneling splittings are deduced for three CH fundamentals (ν_3, ν_9, ν_2) of both molecules and are compared to a model calculation and to ab initio theory. The number and distribution of observed vibrational bands indicate that the CH stretch bright states couple first to doorway states that are binary combinations of bending modes. In the parts of the spectrum where doorway states are present, the observed density of coupled states is comparable to the total density of vibrational states in the molecule, but where there are no doorway states, only the CH stretch fundamentals are observed. A time-dependent interpretation of the present FTMW-IR spectra indicates a fast ($\sim$ 200 fs) initial decay of the bright state followed by second, slower redistribution ($\sim 1-3$ ps). The qualitative agreement of the present data with the time-dependent experiments of Iwaki and Dlott [b] provides further support for the similarity of the fastest vibrational relaxation processes in the liquid and gas phases.

[a] Twagirayezu, S.; Clasp, T. N.; Perry, D. S.; Neill, J. L.; Muckle, M. T.; Pate, B. H. *J. Phys. Chem. A* **2010**, 114, 6818

[b] Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, 104, 9101