Doorway State Enhanced Intramolecular Vibrational Energy Redistribution In The Asymmetric Ethylenic C-H Stretch Of *Cis* Methyl Vinyl Ether

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The microwave-infrared double-resonance capabilities of an electric-resonance optothermal spectrometer have been used to assign the high resolution (5MHz) infrared spectrum of the asymmetric $=CH_2$ stretch of the *cis* conformer of methyl vinyl ether (2-methoxy propene) near 3130cm^{-1}. This vibrational state is anharmonically coupled to a near-resonant bath state by a 0.69(2)cm^{-1} matrix element resulting in two vibrational bands separated by 1.44(1)cm^{-1}. The two mixed states resulting from this interaction are further coupled to other near-resonant bath states with an average matrix element of 0.006(2)cm^{-1}. The total state density increases with total angular momentum, J, however, the Intramolecular Vibrational Energy Redistribution (IVR) rate is approximately independent on the total angular momentum quantum number. Therefore, the rotationally mediated coupling mechanisms are weaker than the anharmonic terms in the redistribution process. A two-state analysis of the strong coupling, which includes a phenomenological IVR rate constant, suggests that the IVR rate in the two mixed states is dominated by the contribution from the strongly coupled dark state.