MULTI-TIER VIBRATIONAL COUPLINGS IN THE ν_3 CH STRETCH FUNDAMENTAL REGION OF METHANOL AS REVEALED BY COHERENCE-DETECTED FOURIER TRANSFORM MICROWAVE (FTMW) - INFRARED SPECTROSCOPY

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Rotational state-selection on the methanol E species transitions $2_0 \leftarrow 3_{-1}$ and $2_1 \leftarrow 3_0$ is used to record the infrared (IR) spectra of the connected rotational levels. Population transfer induced by the pulsed IR laser is detected by FTMW spectroscopy using a two-pulse sequence. The first pulse converts the thermal population difference to a coherence using an approximate "$\pi/2$" pulse. The pulsed IR laser interacts with the polarized sample. A second microwave pulse with 180° phase shift interacts with the sample after a 100 ns delay to perform a "-$\pi/2$" excitation. If the laser pulse does not induce population transfer, this second pulse cancels the microwave signal. For resonant IR excitation from either rotational level, the second pulse converts the laser-induced population transfer to a coherence which is detected by the FTMW spectrometer. The phase of this FTMW signal determines which rotational level was excited by the laser. Before this work, the only band in the region 2750-2900 cm^{-1} region with torsion-rotation assignments was the ν_3 fundamental at 2844 cm^{-1}. Ten additional vibrational band origins are reported in the interval 2755-2855 cm^{-1} along with their approximate relative intensities. A direct state count in this interval gives a total of 14 vibrations arranged into 6 tiers of coupled states. Each tier is related to the ν_3 bright state by a successively higher coupling order. A discussion of the possible coupling pathways through these tiers of states is presented.