FEMTOSECOND MID-INFRARED SPECTROSCOPY OF PYRIMIDINE DNA BASES: INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION, VIBRATIONAL COOLING AND EXCITED STATE PHOTOPHYSICS

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The photophysics of pyrimidine bases following excitation at 267 nm were studied using femtosecond IR and UV/Vis spectroscopy. A majority of excited molecules rapidly undergo internal conversion to the electronic ground state, which is formed with $\approx$ 37 000 cm^{-1} of excess vibrational energy. Vibrational cooling of this hot ground state was followed via recovery of the thermalized ground state spectrum. Vibrational cooling times obtained from the recovery of electronic vs. vibrational bands differ and are sensitive to the isotopic composition of the solvent. These results suggest that intramolecular vibrational redistribution is 10-100 times slower than expected in these molecules. A fraction of molecules in the initially excited $\pi\pi^*$ state decay to other electronic excited states. Vibrational bands of these states are observed at $\sim$1600 cm^{-1} and $\sim$1750 cm^{-1} and are assigned to triplet and singlet nπ^* states, respectively. While the electronic absorption bands of these states have been observed previously, the greater resolution provided by their vibrational spectra provides new insights into excited state photophysics of pyrimidine bases.