

# Excited State Dynamics of Thymine Using Ultraviolet Resonance Raman Spectroscopy

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The strong correlation between sunlight and skin cancer is well known and is believed to arise from the formation of *cis-syn* thymine-thymine cyclobutane dimers induced by the absorption of ultraviolet (UV) wavelengths present in sunlight. These photodimers are considered the most important class of UV induced mutations in DNA molecules and have recently become the subject of renewed interest. This has been due primarily to concerns about the depletion of stratospheric ozone leading to a greater flux of UV radiation at the earth surface.

Detailed information can be obtained on a very fast timescale about the excited state structure and dynamics of a molecule using Resonance Raman (RR) intensities. The UVRR spectra were measured at five wavelengths, using the third and fourth harmonics of a continuously tunable Ti:sapphire picosecond laser, throughout the lowest-energy thymine absorption band centered at 264 nm. Using a previous vibrational assignment of thymine, the resonantly-enhanced vibrational modes were assigned to vibrations localized around the C=C bond, confirming the identity of this transition as a ( $\pi\pi^*$ ) transition. The excited state geometry and reorganization energy of the molecule was obtained from a quantitative measurement of the resonance Raman cross-sections and analysis using a time-dependent model. This information will be used to propose a possible reaction pathway for the formation of the thymine-thymine cyclobutane photoproduct.