

## **Excited State Dynamics of Pyrimidine Nucleobases using Ultraviolet Resonance Raman Spectroscopy**

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In this age, where the continuous depletion of the atmospheric ozone layer is a proven scientific fact, skin cancer has become a major medical concern. Due to the depleting ozone levels, UV radiation is ever-decreasingly shielded from us, causing photo-dependent mutations in our DNA. The most common type of UV light induced mutation in DNA is the formation of photodimers between adjacent pyrimidine base residues. The incidence of photodimer formation is strongly correlated to the incidence of skin cancer, and, thus, research on this topic has become important. Because thymine is thought to be the most photoactive pyrimidine, and most readily forms photodimers, this study will concentrate on it. However, data on the other pyrimidines, uracil and cytosine, has also been obtained and is included in the study for two reasons. First, the molecular structure of uracil differs from that of thymine only by the absence of the C<sub>5</sub> methyl group, and thus should exhibit a comparable excited state to that of thymine. Also, cytosine-cytosine and cytosine-thymine dimers have been known to form in our DNA in addition to thymine-thymine dimers, just to a lesser extent.

Information regarding the excited state dynamics and structure of a molecule on the femtosecond timescale can be obtained by using resonance Raman spectroscopy. In this study, the resonance Raman spectra of the 3 pyrimidine bases with a sulfate standard were obtained at 4 different excitation wavelengths using the third harmonic of a Ti:sapphire laser, all of which fell within the lowest energy absorption band of the pyrimidines. The spectra obtained were of good quality.

The resonance Raman cross-sections of all vibrational modes at each wavelength for the three pyrimidines were obtained from the resonance Raman intensities. Using a time-dependent formalism, the resonance Raman excitation profile of thymine was subsequently analyzed in order to obtain a model for the excited-state geometry of the molecule. It was found that the greatest molecular distortion in the excited state occurs along the C=C bond, which is what one would expect in photodimer formation. The molecular parameters obtained by modeling the cross-section data will be discussed in the context of the excited-state processes important in thymine, and, perhaps, in all of the pyrimidine bases. Time-dependent calculations of uracil and cytosine are ongoing.