Excited State Dynamics of Cytosine Using Ultraviolet Resonance Raman Spectroscopy

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Long-term exposure and overexposure to sunlight is linked to the occurrence of skin cancer. Absorption of UV rays from the sun causes adjacent pyrimidine (thymine, cytosine, uracil) base residues in the DNA molecule to dimerize, as well as other damage. The photoproducts of this process consequently lead to mutations in DNA. At present, although a reasonable amount of information is available regarding the excited state processes of thymine and uracil, little is known about the cytosine-cytosine photodimer formation and the extent of its contribution to DNA damage and repair. Interest persists in this area of research due to the fact that cytosine is also a photochemically active pyrimidine base found both in DNA and RNA.

The excited state dynamics of a molecule can be examined using resonance Raman spectroscopy. The ultraviolet resonance Raman spectra of cytosine have been acquired here throughout the lowest energy cytosine absorption bands centered at 220 nm and 268 nm, using the third harmonic of a continuously tunable Ti:sapphire laser. Na_2SO_4 is chosen as an internal standard for the purpose of quantitative resonance Raman cross-section determination. Analysis of the spectra involves the conversion of the resonance Raman intensities into resonance Raman cross-sections for all of the vibrational modes at each excitation wavelength. Following that, the resonance Raman excitation profiles are obtained and a time-dependent model is used to build the excited state geometry of cytosine.

Preliminary results show that the resonance Raman spectrum of cytosine changes as the excitation wavelength is tuned from 233 nm to 256 nm. Specifically, the 798 cm^{-1}, 1235 cm^{-1}, 1297 cm^{-1}, 1370 cm^{-1}, and 1650 cm^{-1} modes increase in intensity while the 1531 cm^{-1} mode intensity decreases with increasing wavelength, suggesting that the equilibrium geometries of the S_2 and S_1 $\pi \rightarrow \pi^*$ states are different. Using a previous vibrational assignment of cytosine, vibrational bands can be correlated with certain nuclear motions. For instance, the bands at 1531 cm^{-1} and 1650 cm^{-1} are attributed to the C-N and C_2=O stretches, respectively. The changes in intensity of each vibrational peak in the resonance Raman spectra are further confirmed by the trends observed in the excitation profiles. Data from this analysis are useful in understanding the structural changes in the excited state of cytosine, as well as the mechanism of the formation of cytosine-cytosine photodimers.