

EXCITED-STATE DYNAMICS OF SINGLE DNA AND RNA BASES IN SOLUTION

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The Ohio State group recently reported the first direct measurements of the lifetimes of the lowest singlet excited states of DNA and RNA nucleosides in aqueous solution.^a Using the femtosecond pump-probe technique, excited state absorption was detected at visible wavelengths, which decayed in hundreds of femtoseconds by ultrafast internal conversion. Strong signals were also observed at near-UV probe wavelengths on the red edge of the ground-state absorption bands. These signals were assigned to absorption by vibrationally highly excited ground-state molecules, which have an estimated temperature of ≈ 1200 K immediately after internal conversion. Whereas internal conversion occurs on a subpicosecond time scale, hot ground-state absorption decays in a few picoseconds due to the slower rate of intermolecular vibrational energy transfer to the bath.

An open question is the role of the solvent in ultrafast electronic energy relaxation by the bases. Recently, ab initio study of cytosine has suggested that ultrafast decay channels exist even for the isolated molecule. Comparison of these theoretical results with experimental measurements in different solvent environments will be presented.

^aJ.-M. L. Pecourt, J. Peon, and B. Kohler, *J. Am. Chem. Soc.* **123**, 10370-10378 (2001).