Ultrafast processes for photostability and photochemical reactions of nucleobases and “hot electron”-induced decomposition of chlorofluorocarbons in stratospheric cloud

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In order to address the “photostability” issue of nucleobases that has recently been hypothesized, we generated a molecular beam of nucleobases and measured their excited state lifetime by femtosecond transient ionization. The lifetime of the first electronically excited state of all nucleobases was of the order of 1 ps in the gas phase, which means that such a short lifetime is indeed an intrinsic molecular property that would allow living organisms to avoid mutagenesis resulting from photochemical reactions of nucleobases occurring in their excited state. The mechanism for the ultrafast energy relaxation of nucleobases was studied in the case of adenine. Facile internal conversion possibly through conical crossing between the potential energy surfaces of the ππ* and S0 states was found to be more consistent with the experimental findings in the energy range where the molecule most strongly absorbs the light than the recently proposed relaxation mechanism through conical crossing involving the πσ* state. Decay dynamics of the excited DNA base pairs of adenine-thymine (A-T), adenine-adenine (A-A) and thymine-thymine (T-T) were also investigated. All transients exhibited a bi-exponential decay with two distinct time constants. The fast component of A-T and A-A (530 and 390 fs, respectively) was attributed to the relaxation of a locally excited adenine moiety in the base pair from the initially prepared ππ* state to the electronic ground state through internal conversion, while the slow component (3.9 and 3.1 ps, respectively) was associated with the formation of a hydrogen-atom-transferred complex and its decay to the ground state. The transient of T-T showed a temporal behavior very similar to that of the thymine monomer (T1), indicating that its relaxation occurs through the same pathway as in T1. However, we also found evidence in the transient of T1H+ that there may be another relaxation pathway for hydrogen-atom transfer in T-T. We suggest that hydrogen bonding in DNA base pairs plays an important role in decay dynamics, not only by facilitating fast relaxation of the locally excited adenine or thymine moiety in A-T, A-A and T-T, but also by opening a new relaxation pathway via hydrogen-atom transfer. As an exploratory experiment to study photochemical reactions involving nucleobases, we studied the photodimerization reaction of thymine in solution by our newly developed pump-probe technique of transient stimulated Raman spectroscopy, which allows one to observe molecular vibrations in real time at the Uncertainty Principle limit. For a single-strand DNA of (dT)30 in solution, we found that the photodimerization reaction takes place in the time scale of 1 ps.

Dynamics of photo-excited hot electrons in thin ice film coadsorbed with CFCl3 on silver surface has been studied by femtosecond time-resolved two-photon photoemission
spectroscopy, as a model system for a newly proposed decomposition mechanism of chlorofluorocarbons on the ice surface of polar stratospheric clouds by quasi-free electrons produced by cosmic rays. Water molecules were found to solvate the photo-injected electron almost instantaneously within 1 ps. The lifetime of the solvated electron was markedly decreased upon adsorption of CFCl₃ on the ice film owing to the facile transfer of the solvated electron to CFCl₃. The photodissociation cross section of CFCl₃ adsorbed directly on Ag(111) was significantly increased when overlaid with an ice film, which extends the lifetime of the photo-excited electron. The observed dynamics of solvation and transfer of electron, and the water-induced enhancement of the photoreaction, demonstrate the active role of water as an electron solvent.

References


