PHOTODAMAGE TO ISOLATED MONONUCLEOTIDES: PHOTODISSOCIATION SPECTRA AND FRAGMENT CHANNELS

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We have obtained photodepletion and photofragment action spectra on the UV-photodissociation of deprotonated 2'-deoxyribonucleobase-5'-monophosphates with adenine, cytosine, guanine and thymine as nucleobases. We observe the same anionic fragments as in earlier experiments on collision-induced dissociation, although their relative intensities are quite different, especially with respect to the abundance of the deprotonated base anions. This behavior suggests a different sampling of phase-space prior to dissociation compared to collision-induced dissociation, where every energetically accessible part of phase space can be visited. The fragment channels correspond to loss of genetic information by cleavage of the CN glycosidic bond and to strand breaking by severing the phosphatesugar link. Comparison of the photodissociation spectra with UV absorption spectra of aqueous solutions of the same species reveals small solvatochromic shifts.