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Ultrafast Dynamics of Ionized Biomolecules in Aqueous Solution Observed via Few-Femtosecond Transient Absorption Spectroscopy

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Abstract

Few-femtosecond optical transient absorption spectroscopy elucidates the ionization-induced vibrational coherences and ultrafast dynamics of small biomolecules in aqueous solution. Strong-field ionization of such biomolecules by intense, few-cycle (~ 5 fs) laser pulses yields the radical species and the accompanying hydrated electron *via* multiphoton ionization. The vibrational coherences observed are due to the structural reorganization of the biomolecule in aqueous solution upon photoionization. Previous study on the photodetachment of aqueous phenoxide ion leads to wave packet dynamics of the phenoxyl radical along 12 different vibrational modes.^[1] In our study, we studied the vibrational coherences of ionized tryptophan, tyrosine and phenol in aqueous solution that is accompanied by the structural reorganization of the molecule upon photoionization or photodetachment.

The absorption of the tryptophan radical at ~ 580 nm is concealed by the strong absorption of the hydrated electron in the visible region,^[2] while the tyrosyl radical appears in the near-ultraviolet region at ~ 410 nm. The vibrational wave packets lead to pronounced modulations of the differential absorption spectra as a function of time delay. Fourier transformation of the first-moment time traces yields the frequencies of the vibrations that are coupled to the structural reorganization. These frequencies are assigned with the aid of density functional theory calculations. In addition, the amplitude, dephasing time and oscillation phases of each of the observed vibrational frequencies are obtained.

Upon ionization of phenol, the absorption of the phenoxyl radical at 392 nm is observed instead of the expected absorption of the phenol radical cation at ~ 425 nm.^[3] This points to an ultrafast proton transfer process between the phenol radical cation and a neighboring water molecule, consistent with previous experimental observations.^[4] The short lifetime of the phenol radical cation is evident from the first-moment analysis, where the two unique vibrational modes involving $-\text{OH}$ (OH wag and OH bend) have a short dephasing time of < 0.18 ps. This is further supported by *ab initio* calculations, which reveal a nearly barrierless proton transfer pathway (Figure 1). These studies provide insight into the elementary dynamics of ionized biomolecules in aqueous solution.

Fig. 1: Potential energy surface contour plot to account for the ultrafast proton transfer of the micro-hydrated phenol radical cation to proton transferred product, phenoxyl radical *via* the low energy pathway.

Keywords: Femtosecond, photoionization, photodetachment, vibrational coherence, tryptophan, tyrosine, phenol, radical, proton-transfer

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