INSIGHTS INTO PROTON TRANSFER MECHANISMS IN HALOGEN-SUBSTITUTED MALDI MATRICES

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In MALDI mass spectrometry, the role of a matrix is to transfer charge to the analyte so that it can be detected and quantified. The fundamental process of how this charge transfer actually occurs, however, is still largely unknown. Experimental evidence suggests that InterSystem Crossing (ISC) to the triplet excited state (T1) of the matrix is a crucial step in effective charge transfer to the analyte. To encourage ISC via spin-orbit coupling, we have utilized the heavy atom substitution effect, which suggests that the addition of a heavy atom to an otherwise "dead" matrix should increase the rate of ISC to the T1 state. With the addition of a halogen atom, experiments showed a visible decay in singlet lifetime and an increase in triplet lifetime, as well as improved matrix performance. Our system of interest in this study is 2,4–dihydroxybenzoic acid, which will be compared with two of its heavily substituted, halogenated (F,Cl, Br, and I) partners. Using *Gaussian09* software and Density Functional Theory (DFT), all structural isomers were identified and ranked by stability using the functional B3LYP and basis set 6-31g+(d,p). Zero-Point Energies (ZPE) and IR spectra were compared for S0, S1, and T1 states of both the substituted and unsubstituted isomers. Additionally, Time Dependent (TD)-DFT calculations generated UV-Vis and fluorescence spectra. Results showed that Proton Affinity (PA) and Gas Phase Acidity (GPA) values improved with heavy atom substitution in both the 5th and 6th ring positions of 2,4-dihydroxybenzoic acid. Comparison of the S0, S1, and T1 vibrational spectra of the heavily substituted isomers revealed the weakening of bonds between the molecule and its protons, which may be partially responsible for more effective charge transfer to the analyte.