

INSIGHT INTO THE CHARGE TRANSFER MECHANISMS OF HEAVY ATOM SUBSTITUTED MALDI MATRICES

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The underlying mechanism of how MALDI matrices work is poorly understood. Experimental literature suggests that the triplet excited state (T_1) of the matrix plays a significant role in its ability to transfer charge to the analyte effectively. The heavy atom substitution effect predicts that the addition of a heavy atom to an otherwise "dead" matrix, such as 2,4-dihydroxybenzoic acid, would increase the rate of Intersystem Crossing (ISC) to the T_1 state via spin-orbit coupling. This effect was observed experimentally as there was a visible decay in singlet lifetime and an increase in triplet lifetime, as well as a better matrix performance when compared to its original, unsubstituted partner. To provide insight into the photophysical properties of 2,4-dihydroxybenzoic acid and its halogenated isomers, calculations were performed using *Gaussian09*. Geometry optimizations, frequencies, and IR spectra of all isomers were calculated using Density Functional Theory (DFT) with B3LYP functional and the 6-31G+(d,p) basis set. UV-Vis and fluorescence spectra were generated using Time-Dependent DFT (TDDFT). The following values for the singlet ground state (S_0), triplet excited state (T_1), and singlet excited state (S_1) were tabulated and compared: optimization energies, HOMO-LUMO energies and orbital contours, and bond distances. In addition, the energy values for Proton Affinity (PA) and Gas Phase Acidity (GPA) were determined.