INTRAMOLECULAR HYDROGEN BONDING IN 1,8-DIHYDROXYANTHRAQUINONE, 1-AMINOANTHRAQUINONE AND 9-HYDROXYPHENALENONE STUDIED BY PICOSECOND TIME-RESOLVED FLUORESCENCE SPECTROSCOPY IN A SUPERSONIC JET

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Static and dynamic fluorescence properties of the $S_1 \leftarrow S_0$ transitions of three intramolecularly hydrogen-bonded molecules, 1,8-dihydroxyanthraquinone (1,8-DHAQ), 1-aminoanthraquinone (1-AAQ) and 9-hydroxyphenalenone (9-HPA), were investigated using Fluorescence Excitation Spectroscopy (FES) and Time-correlated Single Photon Counting in order to assess spectroscopic evidence indicating the occurrence of excited-state intramolecular proton transfer (ESIPT) and the types of potentials governing the intramolecular hydrogen bonding. Moreover, ab initio calculations were performed on one-dimensional hydrogen transfer potential energy curves for both S_0 and S_1 states at different levels of theory.

As to 1-AAQ, the uniform excess energy dependence of the comparatively long fluorescence lifetimes, which can quantitatively be accounted for according to Fermi's Golden Rule, suggests that the energy- and time-resolved fluorescence properties are associated with a single-minimum-type potential. The non-radiative relaxation mechanism is attributed to internal conversion to the S_0 state. These findings are also in line with calculations based on the quantum theory of atoms in molecules (QTAIM).

The FES of 1,8-DHAQ exhibits two distinct excess energy ranges which are characterized by different spectral congestions and relative intensities in the frequency-domain measurements and by different fluorescence lifetimes in the time-domain measurements. In agreement with previous findings, we suggest that the fluorescence bands below $\sim 600\,\mathrm{cm}^{-1}$ are due to transitions originating in the 9,10-quinone well, while the bands above $\sim 600\,\mathrm{cm}^{-1}$ are due to transitions originating in the proton-transferred 1,10-quinone well.

For 9-HPA, only the frequency-domain measurements give tentative evidence as to the presence of a pronounced double-minimum-type potential. The rapid non-radiative relaxation mechanism as revealed by fluorescence lifetime measurements is attributed to intersystem crossing to a triplet state.