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O–H vibrational motions promote sub-50 fs nonadiabatic dynamics in 3-hydroxypyran-4-one: interplay between internal conversion and ESIPT†

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A theoretical study is used to explore the involvement of O–H vibrational motions in the $S_0 \rightarrow S_2$ photo-induced dynamics of 3-hydroxypyran-4-one (3-HOX). Two transitions, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, are attributed to the experimentally observed electronic absorption spectral features in the range of 3.5–5.5 eV. We compute model potential energy surfaces of vibronically coupled S_1 ($n\pi^*$) and S_2 ($\pi\pi^*$) states with the aid of extensive electronic structure calculations. The S_1–S_2 conical intersection is characterized in the O–H bend and O–H stretch vibrational coordinate space. Quantum wavepacket dynamics simulations reveal an ultrafast $S_2 \rightarrow S_1$ internal conversion decay, where about 90% of the S_2 population disappears within the first 50 fs of the propagation time. The participation of O–H vibrational motions in the early events of nonadiabatic dynamics is analyzed based on the time evolution of nuclear densities on S_2. We discuss the implications of these observations to provide fundamental insights into the nonadiabatic excited-state intramolecular proton transfer in 3-HOX and its derivatives.

The molecular photoinduced proton transfer (either inter- or intra-molecular) reaction represents one of the most fundamental processes in chemical and biological sciences. The intermolecular proton transfer reaction plays an important role in the photo-stability of nucleic acids,[1–3] catalysis,[4,5] proton exchange membrane fuel cells[6,7] and so forth. Molecules that exhibit excited-state intramolecular proton transfer (ESIPT) have drawn much attention recently due to their unusual optical properties. The dual fluorescence emission phenomenon originating from the enol–keto tautomerism was exploited in various fields ranging from molecular probes[8–16] to proton transfer lasers.[17,18]

Conventionally, mechanistic details associated with the ESIPT process are interpreted based on the computed one-dimensional potential energy profile of the first singlet excited state (S_1) along the reaction coordinate of the ESIPT molecule. The computed potential barrier height was often directly correlated to the observed experimental proton transfer rate.[19–31] Recent advances in experimental frequency- and time-domain spectroscopy measurements revealed deeper insights into the sub-picosecond structural dynamics of ESIPT.[32–47] For instance, multidimensional dynamics involving several degrees of freedom were found to evolve simultaneously on a timescale of about ~50 fs.[39,42,48–50] In such scenarios, identification of the role of each vibrational degree of freedom in the dynamical event taking place upon photoexcitation is of fundamental importance to understand and interpret different time-constants obtained from the experimental time-resolved spectroscopy measurements.

In this study, we investigate the multidimensional dynamics of the ESIPT process of 3-hydroxypyran-4-one (3-HOX) (*cf.*, Fig. 1) based on the combined analysis of experimental and theoretical findings. Two electronic transitions, "dipole-forbidden" $S_0 \rightarrow S_1$ and "dipole-allowed" $S_0 \rightarrow S_2$, are assigned for the observed experimental structureless broad absorption band in the range of 3.5–5.5 eV. The S_1–S_2 vertical energy gap is found to be very small (<0.5 eV), and hence the formally forbidden $S_0 \rightarrow S_1$ transition might appear in the experimental band due to the mixing of states facilitated by the vibronic coupling mechanism. The contribution of such a transition to the spectral intensity is usually meager and often the intensity of this transition is masked by the fully allowed dipole transition.[51] To reveal the vibronic coupling effects, a model Hamiltonian in the diabatic basis is constructed with the aid of symmetry selection rules and dimensionless normal coordinates.[52] We observe the S_1–S_2 potential energy curve crossing along both the O–H bend and O–H stretch vibrational coordinates. Both the energetic and spatial locations of the minimum energy conical intersection are evaluated. Subsequently, quantum nuclear wavepacket dynamics

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