Photoinduced double proton transfer in the glyoxal–methanol complex revisited: the role of the excited states.

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Streszczenie

Under irradiation in the visible range, the glyoxal–methanol complex in a cryogenic argon matrix undergoes a double proton transfer (DPT) reaction through which the glyoxal molecule isomerizes into hydroxyketene. In this work, we employ electronic structure simulations in order to shed more light on the underlying mechanism. Rewardingly, we find that the lowest singlet excited state (S_1) of the complex acts as a gateway to two previously unknown isomerization pathways, of which one takes place entirely in the singlet manifold and the other also involves the lowest triplet state (T_1). Both of these pathways are fully compatible with the available experimental data, implying that either or both are operative under experimental conditions. In either pathway, the methanol molecule acts as a proton shuttle between the proton-donating and proton-accepting sites of glyoxal, resulting in a dramatic lowering of the potential energy barrier to isomerization with respect to the case of isolated glyoxal. The occurrence of DPT in the singlet manifold is demonstrated directly with the use of nonadiabatic molecular dynamics simulations at the spin-flip time-dependent density functional theory level.

Słowa kluczowe

Chemical structure, Isomerization, Energy, Quantum mechanics, Potential energy

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