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Abstract

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Investigation of photoisomerization processes induced in molecules by excitations with monochromatic laser light

The investigations presented in current dissertation concern conformational equilibria and *near-IR*-induced conformational transformations observed for molecules of oxamic (**OA**), furoic (**FA**), thiazole-2-carboxylic (**TA**), glycolic (**GA**) and kojic (**KA**) acids as well as for 2-thiocytosine (**TC**). Matrix-isolation technique is used to trap monomeric molecules from the gas phase and infrared spectroscopy is applied for identification of the conformational structures.

As a result of the studies, carried out within the current work, the most stable conformers of the compounds listed above have been identified. This identification relies on the fact that for most of the molecules the gas-phase conformational ratio is preserved in a low-temperature environment. Special attention is devoted to the search of the lowest-energy conformational forms of heterocyclic compounds (**FA**, **TA**) containing an acid moiety in the alpha position with respect to the heteroatom of the ring. The dependence of *OH* group configuration and the strength of the intramolecular hydrogen-bond-like interaction on heteroatom (*O* or *N*) in the ring has been investigated. In particular, the interaction of the *N* atom of the heterocyclic ring with the *OH* moiety appeared to be stronger than the interaction of analogous *OH* group with the *O* heteroatom.

Current studies demonstrate that excitation of molecules with near-IR light often results in conformational transformations. In such *near-IR*-induced transformations, higher-energy conformational structures are generated. It was observed that many of these conformational conversions are *photoreversible* and can be repeatedly induced by selective excitation of each conformer with monochromatic *near-IR* light. In the studies on **GA** molecule, photogeneration of two higher-energy conformational structures has been observed. These studies revealed also a photoreversible conformational transformation involving exclusively two photogenerated structures.

In the studies presented in this dissertation, conformational conversions were induced by excitation of molecules with narrowband *near-IR* light emitted by a Nd:YAG laser equipped with OPO or by a tunable diode laser. The latter type of *near-IR* laser was used for this purpose for the first time. The same conformational transformations were observed independently of the kind of laser used as a source of monochromatic *near-IR* light. Hence, full applicability of tunable diode lasers for studies of conformational conversions has been successfully tested.

One of the main achievements of the studies, carried out in the current work, is the first observation of long-distance intramolecular transfer of vibrational excitation energy. Evidence of such an occurrence has been found by the studies on *near-IR*-induced conformational changes in molecules of **TC** and **KA**. In **TC** molecule, excitation of *NH₂* group with *near-IR* light leads to the conformational changes within the remote *SH* moiety. Similarly, it has been experimentally proven that conformational change within the *CH₂OH* fragment of the **KA** molecule occurs not only upon *near-IR* excitation of *OH* group belonging to this fragment, but also upon *near-IR* excitation of another, remote *OH* group.

Finally, for several investigated molecules spontaneous structural changes, occurring by tunneling of hydrogen atom, were observed. Since in these conformational conversions only one light hydrogen atom significantly changes its position, tunneling effects must play an important role. Investigations on these processes concerned their dependence on temperature, matrix environment and the configuration of moiety in which the rotating hydrogen is built in.

The results presented in this dissertation have been published in the form of articles in the *Journal of Physical Chemistry A*.

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