Light-induced tautomerization of 7-azaindole in doubly hydrogen-bonded dimeric complexes is one of the extensively investigated photoisomerization processes in recent years. The reaction, in the case of homodimer, takes place with equal ease in non-polar liquids at room temperature as well as in a cold supersonic jet expansion. A lot of studies were devoted arguing whether the double proton transfer occurs sequentially or in a concerted manner. Over the past three decades it has been assumed, on the basis of the observations of some low-temperature photophysical measurements, the double proton exchange barrier of the dimer is $\sim 2\text{ kcal/mol}$. However, we notice that such measurements are flawed by artifact; the apparent barrier depends on sample concentration in the solutions. The tautomerization of the isolated dimer is found stopped at 10 K in an argon matrix, and we propose that the double proton exchange is coupled with the large amplitude hydrogen bond vibrations. Furthermore, the process in several 1:1 complexes of the molecule with pyrazole and amides displays remarkable contrasts with that of the homodimer. While the tautomerization in the former cases occurs extremely efficiently in hydrocarbon solutions, is hindered fully in supersonic jet expansion condition. The observations also imply that the effective barrier of phototautomerization in the 1:1 complexes is intimately correlated with the details of double proton transfer mechanism. The details of our findings along with the predictions of some electronic structure calculations will be presented in the talk.

References: