

## 2,7-Diazaindole as a Photophysical Probe for Excited State Hydrogen/Proton Transfer

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**Abstract :** Photoinduced tautomerization reactions have been the centre of attention among the scientific community over the past several decades because of their significance in various biological systems. 7-azaindole (7AI) is considered a model system for DNA base pairing and to understand the role of such tautomerization reactions in mutations. To the best of our knowledge, extensive studies have been carried out on 7-azaindole and its solvent clusters exhibiting proton/ hydrogen transfer in both solution as well as gas phases. Derivatives of the above molecule, like 2,7- and 2,6-diazaindoles are proposed to have even better photophysical properties due to the presence of -aza group on the 2nd position. However, there are studies in the solution phase that suggest the relevance of these molecules, but there are no experimental studies reported in the gas phase yet. In our current investigation, we present the first gas phase spectroscopic data of 2,7-diazaindole (2,7-DAI) and its solvent cluster (2,7-DAI-H<sub>2</sub>O). In this, we have employed state-of-the-art laser spectroscopic methods such as fluorescence excitation (LIF), dispersed fluorescence (DF), resonant two-photon ionization-time of flight mass spectrometry (2C-R2PI), photoionization efficiency spectroscopy (PIE), IR-UV double resonance spectroscopy, i.e., fluorescence-dip infrared spectroscopy (FDIR) and resonant ion-dip infrared spectroscopy (IDIR) to understand the electronic structure of the molecule. The origin band corresponding to the S<sub>1</sub> ← S<sub>0</sub> transition of the bare 2,7-DAI is found to be positioned at 33910 cm<sup>-1</sup>, whereas the origin band corresponding to S<sub>1</sub> ← S<sub>0</sub> transition of the 2,7-DAI-H<sub>2</sub>O is positioned at 33074 cm<sup>-1</sup>. The red-shifted transition in the case of solvent cluster suggests the enhanced feasibility of excited state hydrogen/ proton transfer. The ionization potential for the 2,7-DAI molecule is found to be 8.92 eV which is significantly higher than the previously reported 7AI (8.11 eV) molecule, making it a comparatively complex molecule to study. The ionization potential is reduced by 0.14 eV in the case of 2,7-DAI-H<sub>2</sub>O (8.78 eV) cluster compared to that of 2,7-DAI. Moreover, on comparison with the available literature values of 7AI, we found the origin band of 2,7-DAI and 2,7-DAI-H<sub>2</sub>O to be red-shifted by -729 and -280 cm<sup>-1</sup> respectively. The ground and excited state N-H stretching frequencies of the 27DAI molecule were determined using fluorescence-dip infrared spectra (FDIR) and resonant ion dip infrared spectroscopy (IDIR), obtained at 3523 and 3467 cm<sup>-1</sup>, respectively. The lower value of ν<sub>NH</sub> in the electronically excited state of 27DAI implies the higher acidity of the group compared to the ground state. Moreover, we have done extensive computational analysis, which suggests that the energy barrier in the excited state reduces significantly as we increase the number of catalytic solvent molecules (S= H<sub>2</sub>O, NH<sub>3</sub>) as well as the polarity of solvent molecules. We found that the ammonia molecule is a better candidate for hydrogen transfer compared to water because of its higher gas-phase basicity. Further studies are underway to understand the excited state dynamics and photochemistry of such N-rich chromophores.

**Keywords :** excited state hydrogen transfer, supersonic expansion, gas phase spectroscopy, IR-UV double resonance spectroscopy, laser induced fluorescence, photoionization efficiency spectroscopy

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