SPECTROSCOPIC SIGNATURES AND STRUCTURAL MOTIFS OF DOPAMINE: A COMPUTATIONAL STUDY

SANTOSH KUMAR SRIVASTAVA, VIPIN BAHADUR SINGH, *Department of Physics, Udai Pratap Autonomous College, Varanasi, India*.

Dopamine (DA) is an essential neurotransmitter in the central nervous system and it plays integral role in numerous brain functions including behaviour, cognition, emotion, working memory and associated learning.[ab] In the present work the conformational landscapes of neutral and protonated dopamine have been investigated in the gas phase and in aqueous solution by MP2 and DFT (M06-2X, ωB97X-D, B3LYP and B3LYP-D3) methods. Twenty lowest energy structures of neutral DA were subjected to geometry optimization and the gauche conformer, GIa, was found to be the lowest gas phase structure at the each level of theory in agreement with the experimental rotational spectroscopy.[c] All folded gauche conformers (GI) where lone electron pair of the NH2 group is directed towards the π system of the aromatic ring ('non up') are found more stable in the gas phase. While in aqueous solution, all those gauche conformers (GII) where lone electron pair of the NH2 group is directed opposite from the π system of the aromatic ring ('up' structures) are stabilized significantly.Nine lowest energy structures, protonated at the amino group, are optimized at the same MP2/aug-cc-pVDZ level of theory. In the most stable gauche structures, g-1 and g+1, mainly electrostatic cation - π interaction is further stabilized by significant dispersion forces as predicted by the substantial differences between the DFT and dispersion corrected DFT-D3 calculations. In aqueous environment the intra-molecular cation- π distance in g-1 and g+1 isomers, slightly increases compared to the gas phase and the magnitude of the cation- π interaction is reduced relative to the gas phase, because solvation of the cation decreases its interaction energy with the π face of aromatic system. The IR intensity of the bound N-H+ stretching mode provides characteristic 'IR spectroscopic signatures' which can reflect the strength of cation- π interaction energy. The CC2 lowest lying S1 ($1\pi\pi^*$) excited state of neutral dopamine is significantly red shifted upon protonation at amino site.

[a] E. Dragicevic, J. Schiemann and B. Liss, Neuroscience, 2015, 284, 798.

[b] Y. T. Chien et al. Science, 2010, 330, 1091.

[c] Cabezas etal., J. Phys. Chem. Lett. 2013, 4, 486.