

## Monitoring the UV-photoinduced events in solvated nucleosides: first steps towards accurate time-resolved non-linear electronic spectroscopy

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Photoinduced events occurring in the genomic material upon UV-light irradiation are of paramount interest as they relate directly to the intrinsic photostability of the DNA/RNA,[1] as well as to the triggered photochemical pathways leading to photo-damage.[2] These deactivation channels are often coupled and cannot be directly resolved with standard pump-probe spectroscopic techniques.[3] In order to tackle the problem from a bottom-up approach, the photophysics and photochemistry of water-solvated nucleosides,[4] adenosine in particular, are here characterised within a CASSCF/CASPT2 QM/MM protocol.[5] The photoinduced events are described in terms of both static and dynamic approaches, featuring conical intersection characterisations and minimum energy path computations, together with semi-classical excited state trajectories yielding a time-resolved estimate. Novel bidimensional optical spectroscopic techniques, recently introduced by coupling the QM/MM scheme with non-linear response theory,[6-8] are then used on top of the static and dynamic pathways characterised. Monomeric species and their fingerprints are firstly tackled and their main fingerprints characterised yielding a robust approach to differentiate the monomer-localised processes. The model is then extended to deal with dimeric diribonucleotide systems,[9] comprising a range of  $\pi$ - and T-stacking interacting motifs enhancing a variety of intermolecular interactions with overlapping spectroscopic fingerprints requiring novel approaches for their accurate characterisation. Theoretical bidimensional electronic spectroscopy methods are then employed to provide state-specific fingerprints to unequivocally disentangle the diverse photo-excited decay channels populated upon UV-light absorption and their concrete contributions as well as their dependence on relative conformation.

### References

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