

11:30 – 12:15

Gas-phase spectroscopy of donor-acceptor chromophore ions

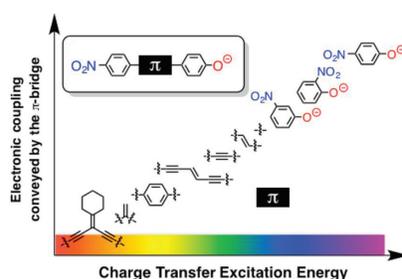
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In this talk, I review our results over the last 5 years from mass spectroscopy experiments using specially designed apparatus on several charged donor-acceptor ions that are based on the nitrophenolate moiety and π -extended derivatives. These are textbook examples of donor-acceptor chromophores.

The phenolate oxygen is the donor, and the nitro group is the acceptor. The choice of this system is also based on the fact that phenolate is a common structural motif of biochromophores and luminophores; for example, it is a constituent of the oxyluciferin anion responsible for light emission from fireflies. A presentation of the setups used for gas-phase ion spectroscopy in Aarhus is given, and I will address issues of whether double bonds or triple bonds best convey electronic coupling between the phenolate oxygen and the nitro group, the significance of separating the donor and acceptor spatially, the influence of cross-conjugation *versus* linear conjugation, and along this line *ortho versus meta versus para* configuration, and not least the effect of a single solvent molecule (water, methanol, or acetonitrile). From systematic studies, a clear picture has emerged that has been supported by high-level calculations of electronically excited states. Our work shows that CC2 coupled-cluster calculations of vertical excitation energies are within 0.2 eV of experimental band maxima, and importantly, that the theoretical method is excellent in predicting the relative order of excitation energies of a series of nitrophenolates. The molecular ions that have been studied are shown on the figure below in the order of increasing charge-transfer excitation energy. The results were recently reviewed in *Accounts of Chemical Research* [1]. Finally, I will discuss future challenges such as



following the change in absorption as a function of the number of solvent molecules and when gradually approaching the bulk limit.

Reference

- [1] S. Brøndsted Nielsen, M. Brøndsted Nielsen, A. Rubio, *Acc. Chem. Res.* **47**, 1417–1425 (2014).