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## Action spectroscopy of chlorophyll and other coordination complexes.

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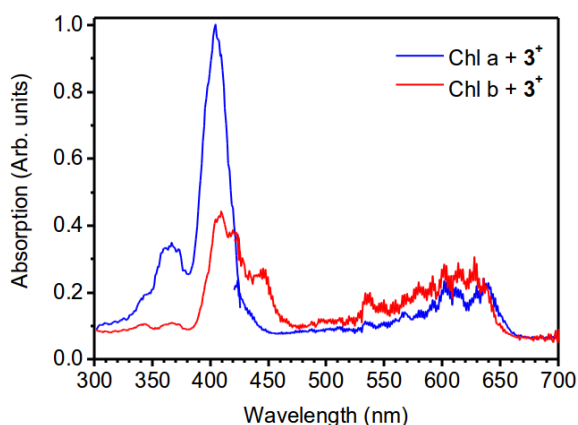
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**Synopsis** Action spectroscopy provides key insights into the nature of electronic transitions of coordination complexes such as porphyrin-containing biochromophores like chlorophyll or transition metal complexes such as tris(bipyridine)ruthenium.

Coordination complexes where a metallic ion core is surrounded by organic ligands are common to important biochromophores as well as synthetic transition metal complexes. These molecules are strong light absorbers but the nature of their electronic transitions, as well as the role of the protein or solvent micro-environment, is not always obvious. Studying these molecules in the gas phase or in nano-solvated complexes significantly reduces these complexities and allows more direct comparison with theoretical calculations. Here, we provide two recent examples of how gas-phase action spectroscopy can provide clarity to otherwise intractable problems.



**Figure 1.** Photodissociation action spectra of Chl *a* and *b* tagged with acetylcholine.

Chlorophyll (Chl) *a* and *b* are the light-absorbers of plants and are composed of a porphyrin macrocycle with a divalent magnesium ion in the center. It is nontrivial to predict the absorption spectra of these molecules or what effect the protein environment may have. As a starting point, we have measured the absorption spectra of *gas-phase* Chl *a* and *b* using photodissociation

action spectroscopy of Chl molecules tagged with quaternary ammonium ions. Chl *a* and *b* differ only on one peripheral substituent, but their absorption band maxima are shifted relative to each other by more than 30 nm. These shifts were reproduced in our gas-phase data, shown in Figure 1, meaning that they are intrinsic effects and not due to interactions with the micro-environment. On the other hand, the bands of both Chl *a* and *b* were significantly blue-shifted relative to plant-phase spectra. Interactions with the protein and solvent environments are thus crucial to understanding the absorption of chlorophylls.

Tris(bipyridine)ruthenium,  $\text{Ru}(\text{bipy})_3^{2+}$ , has become a textbook case for the chemistry of coordination complexes over several decades of extensive study. The lowest-energy electronic transition involves a metal-to-ligand charge transfer (MLCT) from the divalent ruthenium core to the bipyridine ligands. The character of the MLCT transition has been an important, long-standing question. The permanent dipole moment of  $\text{Ru}(\text{bipy})_3^{2+}$  is zero in the ground state, but in the excited state depends on whether the symmetry of the electronic structure is broken by localization of the photoexcited electron to just one of the bipyridine ligands, rather than delocalization over all three. We attempt to elucidate this unresolved debate by comparing the photodissociation action spectra of gas phase  $\text{Ru}(\text{bipy})_3^{2+}$  with that of the monosolvated  $[\text{Ru}(\text{bipy})_3+\text{CH}_3\text{CN}]^{2+}$  complex. We find that the addition of a single solvent molecule (in this case acetonitrile  $\text{CH}_3\text{CN}$ ) has no effect on the position of the band maximum. We conclude that, in the gas phase, the transition is delocalized and that a single solvent molecule is insufficient to break the symmetry of the transition.

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