Action spectroscopy of chlorophyll and other coordination complexes.
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, Ru(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 Ru(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 Ru(bipy)$_3^{2+}$ with that of the monosolvated [Ru(bipy)$_3$+CH$_3$CN]$_{32+}$ complex. We find that the addition of a single solvent molecule (in this case acetonitrile CH$_3$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.