PROBING THE DEGREE OF NITROGEN ACTIVATION BY TRIDENTATE COPPER(I) COMPLEXES USING CIVP SPECTROSCOPY

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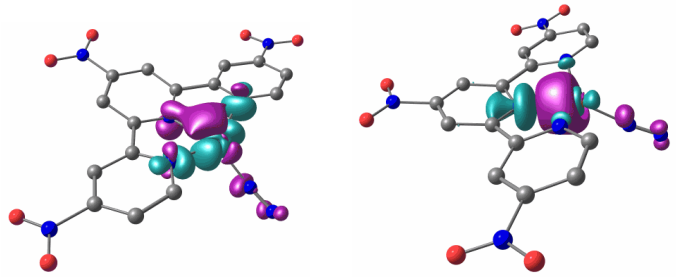
The activation and utilization of N_2 have become attractive areas of research, with the ultimate goals of dinitrogen fixation and reduction. A deep understanding of the interaction and electronic influences between transition metal atoms and the inert N2 molecule would allow facilitating the transformation of inert molecular nitrogen to useful nitrogen-containing chemicals. In this work, we used cryogenic ion vibrational predissociation (CIVP) spectroscopy to experimentally probe the activation of the molecular nitrogen by copper complexes bearing terpyridine and pyridine-2,6-bis(oxazoline) ligands. We used the N_2 stretching vibration as a reporter chromophore to estimate how electronic and steric effects affect the activation of the molecular nitrogen by these copper complexes. In contrast to the previous studies on nitrogen activation that probe "late activation" of the nitrogen molecule, our cryogenic studies give access to the "early activation" states that otherwise difficult to access. Our data show that the electronic character, as well as position and number of substituents, can affect the N-N vibrational frequency, leading either to a bigger or to a lesser degree of N_2 activation.



$\Delta E^{I}_{orb} = -24.36$ kcal mol^{-1} $\Delta E^{II}_{orb} = -21.15$ kcal mol^{-1}