SPECTROSCOPIC INVESTIGATION OF LIGNIN LINKAGES: UV AND IR SIGNATURES OF PRIMARY DILIGNOLS

JACOB C. DEAN, PATRICK S. WALSH, JOSEPH R. GORD, BIDYUT BISWAS, P. V. RAMACHANDRAN, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*.

Lignin is an abundant, aromatic biopolymer ubiquitous to all plant matter; its properties are vital to the structural rigidity of plants as well as protection of the cell wall from degradation. As the major structural framework for plants, the breakdown of lignin for harvestable biomass is a formidable challenge. At a fundamental level, the characterization of lignin sequences and structures lag far behind those of proteins. One of the unique aspects of lignin is that it is composed of only three monolignols which are themselves structurally similar, all of which are aromatic derivatives. The structural complexity of lignin is in large measure due to the unique variety of chemical linkages between these three sub-units. As a result, there is a need for spectroscopic characterization of individual lignin linkages, and for elucidating potential fragmentation pathways and the relative energetics associated with those linkages in the polymer network. In this light, spectroscopic interrogation of these dilignol bichromophores yield signatures characteristic of their specific linkages which can also be found in high-order lignin oligomers. The β-O-4 and β-β linkages have been studied and their UV and IR signatures have been uncovered on a single-conformation basis in a supersonic expansion by use of IR/UV-UV HB and RIDIR spectroscopy. Fragmentation following resonant two-photon ionization of the neutral species was also explored and evidence for linkage-specific fragmentation has been revealed.