Chirped-Pulse Millimeter-Wave (CPmmW) rotational spectroscopy provides a new class of information that is a step toward Transition State spectroscopy. Our CPmmW studies of the vinyl cyanide (acrylonitrile) photolysis reaction at 193 nm provide information about the vibrational state population distribution of the HCN, HNC products. These populations encode information about the structure of the transition state(s) traversed by the parent molecule as it dissociates. Two of the expected products of the reaction, vinylidene and local-bender levels of acetylene, have, however, escaped detection. The feasibility of CPmmW schemes for characterizing vinylidene-acetylene isomerization is discussed. The authors thank the Department of Energy for support.