

ULTRAFAST REACTION DYNAMICS OF NEUTRAL ALUMINUM OXIDE CLUSTERS USING TWO COLOR FEMTOSECOND SPECTROSCOPY

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Ultrafast relaxation dynamics of neutral aluminum oxide clusters (Al_nO_m , $n, m \leq 20$) in the gas phase were studied by combining two-color femtosecond spectroscopy and time-of-flight mass spectrometry. The clusters are pumped using the second harmonic of a Ti:Sapphire femtosecond (fs) laser system (400 nm = 3.1 eV) and subsequently ionized through strong field ionization of the fundamental beam (800 nm = 1.55 eV) with a time resolution of < 35 fs. The excited states explored here are high binding energy excited states, which are mainly of oxygen 2p character into the Al sp-type orbitals. Changes in the ultrafast dynamics are observed to be strongly influenced by the stoichiometry and size of these clusters. Neutral clusters are ideal mimics of the true active sites of condensed phase and surface chemistry. We have developed an approach that involves the calculation of several topological descriptors to interpret the influence of the structural differences between clusters on the excited state lifetimes. Time-dependent density functional theory (TDDFT) calculations reveal the energies and structures of the excited states at both ground and excited state structure. These studies on molecular scale clusters provide an ideal arena for probing chemical activities and mechanisms in an unperturbed environment that can assist in the analysis of condensed phase catalysis systems. Using the atomic precision of clusters, we identify preferred bonding arrangements, electronic structure, and oxidation states that lead to increased excited state lifetimes and therefore enhance photochemical transformation.