Lon Knight’s Research Group

The laboratory operates three research grade ESR (electron spin resonance) spectrometers, each with its dedicated 4K liquid helium cryostat and custom-designed radical generation capabilities. High energy pulsed lasers, neon resonance lamps (16 eV), X-irradiation, electron bombardment and high temperature Knudsen ovens are employed in a variety of schemes to generate, trap and study new radicals – including both neutral and charged molecules.

Recently, high spin, open-shell radicals composed entirely of closed shell metal atoms (Mg, Ca, etc.) have been created in various rare gas matrices. For Mg (...3s²), the Mg₄ cluster has two unpaired electrons yielding a triplet electronic ground state; for Ca(...4s²), the Ca₄ cluster has four unpaired electrons yielding a quintet state that can be unambiguously assigned by its ESR spectrum. These specific cluster sizes seem to reflect a “magic number” stability considering all the cluster sizes that could form under the experimental conditions. In earlier work, the team reported experimental and theoretical studies of small metal cluster cations (i.e., Mg₂₋₆⁺), which have to be open-shell radicals. These surprising new results reveal the onset of metallic properties (near degeneracy of the band structure) at an unexpectedly small molecular size level. Other closed-shell metal atom systems will be investigated in future work, including Zn and Cd; in addition, theoretical studies with colleagues at other institutions are planned.

Major breakthroughs in recent ESR matrix work conducted in the Knight laboratory include the formation of various metal hydrides in solid para-hydrogen matrices at 2.5 K, the first trapping of the free electron in rare gas solids, and the first experimental arrangement for coupling mass-selection of cation radicals with the rare gas matrix ESR trapping technique. They have made the first ESR assignments for CH₂⁺, BH⁺, C₂H₆⁺, Kr₂⁺ and XeKr⁺ using this new approach. These newly developed experimental methods for studying noble gas – transition metal complexes (neutral and charged) have been reported recently in the literature.

Matrix experiments originally designed to trap the H₂⁺ radical during the 2009 program have yielded some most exciting and unexpected results. Preliminary spectra indicate that a series of polymeric hydrogen cluster ions are being generated in neon matrices by X-irradiation if the neon host is maintained below 3 K. A large number of isotopic experiments with deuterium and hydrogen-deuterium mixtures are planned in addition to utilizing pure HD(g) as a starting material. The H₄⁺ cation is proving to be an extremely exciting molecular radical, showing extreme fluxional behavior between 3 and 8 K. It is a major challenge to interpret, since the fluxional properties change with the substitution of various numbers of D atoms. Our matrix ESR experiments will also include the pulsed laser vaporization of metals in the presence of hydrogen. The intent will be to study strategically important metal hydrides that might be candidates for hydrogen storage applications.