Chemical reactions induced by ultrashort pulsed laser ablation in organic liquids

Katharine Moore Tibbetts*, Ella Kaplan, Samuel Harris

Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284 US
*Corresponding author email: kmtibbetts@vcu.edu

Laser synthesis and processing of colloidal nanoparticles is often performed in organic liquid media to prevent metal oxidation, grow protective carbon shells around metal nanoparticles, and produce metal carbides and carbon nanomaterials [1]. Ablation in organic liquids induces a plethora of chemical reactions that form diverse molecular and material products, beyond the H_2, O_2, and H_2O_2 products that are observed from laser ablation in water. This presentation will highlight recent progress in my group towards elucidating reaction pathways of laser ablation in organic liquids using mass spectrometry to characterize molecular products of laser ablation and optical spectroscopy to measure laser-induced reaction kinetics.

Figure 1a shows mass spectra obtained after ablation of *n*-hexane with 800 nm laser pulses of widths 30 fs and 4 ps. Significantly enhanced yields of gases are observed for ablation with ps pulses. The increased gas yield is associated with formation of phenylacetylene derivatives and photoluminescent carbon dots (Figure 1a, inset). Enhancement of both avalanche ionization and cavitation bubble collapse energy for picosecond ablation contributes to the different reaction pathways observed [2]. Figure 1b shows gas chromatograms of four hexane isomers (*n*-hexane, cyclohexane, 2-methylpentane, 3-methylpentane) after ablation with 800 nm, 4 ps pulses. Each isomer produces a distinct distribution of alkane products that can be rationalized by laser-induced formation of statistical distributions of radical species and their combination to form specific C_9, C_{10}, and C_{12} products.

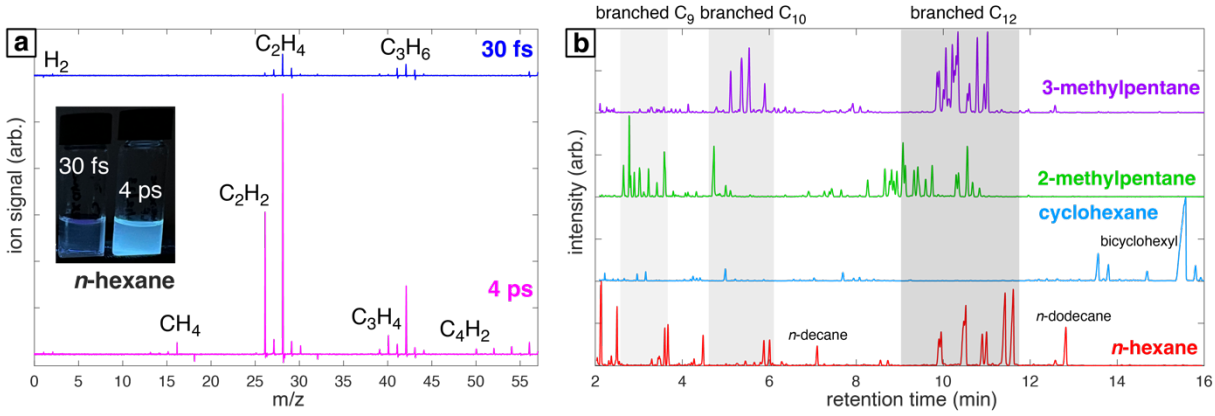

Figure 1: (a) Mass spectra of gaseous hydrocarbons produced from *n*-hexane by ablation with 30 fs and 4 ps pulses; inset depicts ablated solutions under 365 nm illumination. (b) Gas chromatograms of *n*-hexane, cyclohexane, 2-methylpentane, and 3-methylpentane after ablation with 4 ps pulses showing different distributions of alkane products.

References:

[1] L. M. Frias Batista, A. Nag, V. K. Meader, and K. M. Tibbetts, "Generation of Nanomaterials by Reactive Laser Synthesis in Liquid", *Sci. China Phys. Mech. Astron.* **65** 1-45 (2022)
[2] L. M. Frias Batista, E. Kaplan, C. Weththasingha, B. Cook, S. Harris, A. Nag, and K. M. Tibbetts "How Pulse Width Affects Laser Ablation of Organic Liquids", *J. Phys. Chem. B*, **127** 6551-6561 (2023)