Laser Chemistry Moves Toward Smaller and Faster Probes

by Jack A. Syage

Molecular-level studies examine properties of materials at the most fundamental chemical component. Progress with lasers and molecular beams has allowed for single-quantum-state studies. Ultrafast lasers have reduced the time scale to bond breaking, ushering in an era of transition-state spectroscopy. Laser polarization techniques are achieving molecular alignment and making possible angular distribution measurements of photoproducts.

The effect of individual molecules on the properties of chemistry and materials is the target of experiments on molecular complexes or clusters formed in supersonic expansions. These aggregates can be studied by laser probes and their size dependence sorted out by mass spectrometry.

A fundamental question is: What happens when a diatomic molecule dissociates in a solvent cage? Key insights have been provided by a history of time-resolved studies of I_2 dissociation/recombination in condensed phases. However, only recently have the research groups of Zewail at the California Institute of Technology and Lineberger at the University of Colorado been able to conduct real-time measurements on I_2-M_n clusters where M_n is a solvent of n molecules of M, as a function of specific cluster size. These experiments have provided a critical new understanding of the precise interaction between each solvent molecule, leading to cage escape vs. recombination probabilities, and measurements of coherent motions in the solvent.

A prototypical cluster reaction with direct bearing on real-world chemistry is the acid-base reaction $ROH^*\text{-}B_n \rightarrow RO^{*-} H^+B_n$ (excited-state proton transfer) where R is an organic group and B a base molecule. Direct time-domain measurements by the groups of Zewail, Syage at the Aerospace Corp., Bernstein and Kelley at Colorado State University, and Castleman at Pennsylvania State University have shown that changing a single-solvent molecule can lead to distinct chemical changes, which sometimes affect reaction rates by over two orders of magnitude.

An exciting area

An exciting new area of laser chemistry is the study of details of bimolecular chemistry using alignments of molecules in van der Waals complexes. Recently, differential reactive cross sections in angle and velocity have been measured in photodissociation of van der Waals complexes with product quantum resolution in the Syage group and femtosecond time resolution in the Zewail group. Both groups conducted measurements on $(CH_3I)_2$. The quantum-resolved work revealed a bimodal angle-velocity distribution for the I- atom fragment, indicating an inequivalency of the two individual molecules and rapid spin-orbit relaxation in the I atom. The real-time measurements showed a 150-fs C-I bond scission and a build up of I_2 in less than 500 fs.

These experiments hold great promise for providing information needed to test quantum chemical dynamics codes. The van der Waals bond in a dimer complex helps to fix the geometry and limit the range of impact parameters under study. The Zewail group has shown that the full dimensionality of how molecules collide and break up into products can be followed in real-time using femtosecond excitation and angular probing of product velocities. In a landmark study, the researchers directly observed the time evolution of the transition state and products for the charge transfer reaction $Bz\text{-}I_2 \rightarrow [Bz^+ \ldots I^- \ldots I] \rightarrow Bz\text{-}I + I$, while monitoring the change in anisotropy and fragment translational energy.

Meet the author

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