1-5-4. Infrared Laser Chemistry

Overview

Infrared laser chemistry is a technique that promotes desired chemical reactions by exciting vibrational modes that are directly or indirectly involved in the reaction coordinate, thereby enabling molecules to overcome the activation barrier (Fig. 1). It is also referred to as mode-selective chemistry. The field traces its origins to studies around 1960 in which thermal IR sources were used to accelerate the cis–trans isomerization of nitrous acid. Since then, it has advanced alongside the development of infrared lasers and pulse-shaping technologies. Today, its applications span from unimolecular reactions to bimolecular association processes.

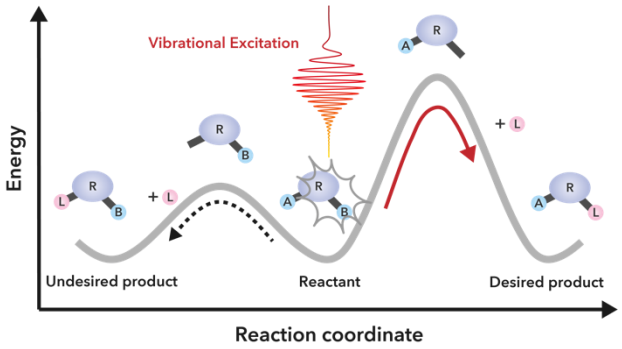

Figure 1. Reaction control via vibrational excitation.

Current Status and Frontiers

In the 1970s, infrared multiphoton excitation using nanosecond IR pulses was shown to induce dissociation of gas-phase molecules. At the same time, it became clear that mode selectivity is lost in polyatomic molecules because the density of quantum states increases at higher energies, leading to rapid intramolecular vibrational energy redistribution (IVR). In the 1990s, however, Crim and co-workers showed that clear mode selectivity can appear in the association reactions of small molecules such as water. Subsequent molecular-beam studies have elucidated in detail how vibrational excitation and conformational structures influence association reactions. From the late 1990s, multistep excitation and dissociation of gas-phase molecules using femtosecond IR pulses were reported, and theoretical efforts, including the search for optimal electric-field waveforms by Fujimura and co-workers, also advanced. More recently, multistep vibrational–rotational excitation using pulse shaping (Tsusaka, Ashihara et al.) and reaction control in the condensed phase have further expanded the field.

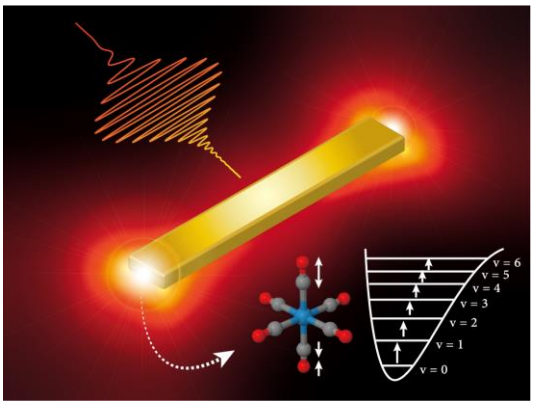

Figure 2. Multistep vibrational excitation and bond dissociation of metal–carbonyl molecules using plasmon-enhanced fields of infrared chirped pulses.

Because most practical chemical reactions proceed in liquids, achieving high vibrational excitation and reaction control in the condensed phase is of significant importance. Although high vibrational excitation had been attempted for molecules in solution, rapid vibrational relaxation limited the accessible quantum levels, preventing bond dissociation. Recently, by combining waveform-shaped femtosecond IR pulses with plasmonic field enhancement, high vibrational excitation and reaction control of metal–carbonyl complexes in solution have been achieved (Fig. 2). Due to the anharmonicity of vibrational potentials, transition energies decrease at higher vibrational levels; thus, down-chirped waveforms are effective. Time-resolved IR spectroscopy confirmed excitation up to the sixth vibrational level and the presence of dissociation products adsorbed on a gold surface (Morichika, Ashihara et al.).

Vibrationally accelerated association reactions have also been demonstrated in the condensed phase. Heyne and co-workers showed that selectively exciting a specific vibrational mode of reactants in a liquid mixture with femtosecond IR pulses accelerates urethane formation. Quantum chemical calculations revealed that the observed acceleration originates from structural changes in the reactants and the transition state. This work is important in demonstrating that reaction promotion is possible in liquids, where solvent interactions and conformational heterogeneity influence the pathway.

Weinstein and colleagues have also reported a significant advance toward controlling electron transfer. By exciting a specific vibrational mode of a molecule in solution with an IR pulse, they succeeded in shutting down one of its electron-transfer pathways. In a donor–bridge–acceptor system, picosecond IR excitation of a C≡C bridge vibration was shown to alter the dynamics and quantum yields of competing electron-transfer channels.

References

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Future Perspectives and Directions

Challenges to be addressed or achieved within the next decade: Precise control of vibrational and rotational quantum states of gas-phase molecules using infrared lasers; analysis of reaction coordinates through quantum chemical calculations; and expansion of controllable association reactions in the liquid phase.

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