Invited Lectures B

August 30, Tuesday, 11:00 – 12:30

Exploring Chemical Physics in Transient Plasma by Broadband Rotational Spectroscopy

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Rotational spectroscopy provides unrivalled precision for the determination of molecular structure in isolated, gas phase species. Electronics capable of digitising waveforms at gigahertz frequencies now allows chirped-pulse Fourier transform microwave spectroscopy[1] to be performed at high resolution, high bandwidth and with minimal or no cost to sensitivity. Two approaches are possible. Specific molecules or complexes can be targeted and selectively generated for study through a careful choice of appropriate precursors. Alternatively, a survey of chemical products generated under selected environmental conditions can be performed in an approach termed "broadband reaction screening".[2] Each of these approaches will be described during this presentation.

One focus will be recent experiments that have applied broadband rotational spectroscopy to probe interactions between isolated, metal-containing molecules and simple hydrocarbons such as ethene, ethyne and cyclopropane.[3] The complexes are generated through laser vaporisation of a metal target in the presence of an expanding gas sample containing the hydrocarbon precursor. Precise changes in the geometry of the hydrocarbons on their attachment to copper, silver and gold atoms will be described. The products of chemical reactions between platinum, palladium and hydrocarbons following laser vaporisation of the metal in the presence of a hydrocarbon precursor have also been characterised. It will be shown that many choices of hydrocarbon allow the efficient generation[4] of linear PtC_3 or PdC_3 units within the transient plasma. The fragmentation of halogenated hydrocarbon precursors has allowed the screening and characterisation of other chemical products, such as FPtCF, by broadband rotational spectroscopy. It will be shown that the method provides a new and powerful approach through which to explore the gas phase chemistry between platinum, palladium and hydrocarbons.

References

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Creating and Observing Coherently Rotating/Vibrating Molecular Ensembles

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Needless to say, high-resolution spectroscopy of molecules is based on the precise determination of energy levels and the detailed knowledge on the transition probability between these eigenstates. On the other hand, broadband excitation with ultrashort laser pulses inherently results in the creation of coherent superposition of several (and some cases *many*) eigenstates, commonly termed quantum wave packet (WP). One of the ultimate goals of ultrafast-laser experiments is to establish the way to create WPs as designed, and the main issue is to figure out the correlation between the way of excitation and the nature of the resultant WP. In this respect, how to characterize the WP is also essential. In this presentation, I will describe our recent endeavor on the creation and observation of rotational and vibrational WPs of several molecular systems.

We adopt nonadiabatic excitation of adiabatically cooled gaseous samples by intense nonresonant ultrashort laser pulses, where impulsive force to induce coherent motion is exert onto molecules via the interaction with the molecular polarizability. Initially, we have focused on the rotational excitation with a linearly polarized laser field, and have developed a method to detail the excitation processes by a quantum-state resolved manner.[1] In particular, it has been shown that implementation of a pair of excitation pulses enables us to reconstruct experimentally a rotational WP thus created.[2] As an attempt for advanced WP manipulation, sense of rotation around the laser propagation direction in the resultant rotational WP was controlled by adjusting the mutual polarization direction and the time delay between the two pulses.[3]

Quite recently, we have succeeded in recording the direct image pertinent to the unidirectionally rotating WP of simple molecules.[4] Here, time-dependent spatial distribution of the molecular-axis direction was probed as an ion image of fragments generated via Coulomb explosion. Our ion-imaging setup is based on a conventional MCP/phosphor-screen/camera combination, but in contrast to ordinary 2D imaging setups so far implemented, it is able to record images of the fragment-ion clouds sliced perpendicularly to the laser propagation direction. This new configuration enables us to take a "movie" of unidirectionally rotating molecules as a series of records for successive delays between the pump and probe pulses.

Nonadiabatic interaction with a nonresonant intense ultrashort laser field can also coherently excite vibration of molecules through the structural dependence of the molecular polarizability. We also have recently succeeded in creating and observing WPs pertinent to intermolecular vibrations of several molecular clusters in their electronic ground states.

References

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