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Reaction Dynamics by Time-Resolved Wave Packet Spectroscopies & Molecular Dynamics Simulation

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Abstract

Recent advances in short pulse lasers and time domain spectroscopies enabled investigation of molecular dynamics in a few femtosecond and even attosecond regime. For a coherent photochemical reaction occurring in an electronic excited state, molecular reaction dynamics can be studied by recording the nuclear wave packet motions in the reactant and product potential energy surfaces (PES) following photoexcitation to a Franck-Condon state. [1-4] Wave packets in the product state may also be formed by an impulsive chemical reaction. Evolution of the wave packets may contain extensive information on the PES and reaction coordinates. Time-domain experiments such as pump-probe transient absorption (TA) and time-resolved fluorescence (TF) with high enough time resolution can record nuclear wave packet motions spanning a full vibrational spectrum up to 3000 cm^{-1} . We have developed experimental methods to record the wave packets and a theoretical method based on a molecular dynamics simulation to analyze the wave packet motion of each vibrational mode following photoexcitation.

In this presentation, we show the method and application examples. The structural trajectories as a function of time acquired by quantum mechanical molecular dynamics (QM/MD) simulation can be projected onto the vibrational normal modes to determine the origin of the wave packet motions in the excited state, which provides a glimpse of the complicated multi-dimensional PES along the reaction coordinate and nuclear coordinates of interest. The method was applied to the excited-state intramolecular proton transfer of 10-hydroxybenzo[h]quinoline (HBQ). [1, 5-7] For an ultrafast chemical reaction ($<100\text{ fs}$), e.g., excited-state intramolecular proton transfer, it is known that low-frequency skeletal vibrations may deeply contribute to the reaction coordinates. The role of the low-frequency skeletal modes of HBQ was investigated by the method, and the results are consistent with the wave packet motions observed by TA and TF including both amplitudes and phases. It was concluded that the reaction barrier is not significantly affected by the low-frequency skeletal motions observed at $248, 403, 565, 638\text{ cm}^{-1}$. In particular, the 248 and 565 cm^{-1} modes are initially excited by the photoexcitation, whereas 403 and 638 cm^{-1} modes are created impulsively by chemical reaction. Several other examples will also be given in this presentation.

Keywords: Nuclear wave packets, Molecular dynamics simulation, ESIPT

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