

論文の内容の要旨

A study of chemical reactions in terms of dynamical electron theory

(動的電子論による化学反応の研究)

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1. Introduction

What I am going to hereby report is some fundamental results in my study on the nonadiabatic electron wavepacket dynamics in which electron wavepackets couples with nuclear motions kinematically; dynamical electron theory. The real-time dynamics of electron wavepackets are carried quantum mechanically along non-Born-Oppenheimer nuclear paths. The theory is readily extended so as to treat such dynamics in intense laser field. The method is tractable even for molecules of a medium size and gives a vivid and novel view in chemical reaction dynamics.

It would be quite interesting to investigate how electrons may flow within and/or in between molecules in real time as chemical reactions proceed. Also, new light can be shed on classic chemical concepts such as valence bond and Pauling resonance structure from the view point of electron dynamics. Also a study of the possible synchronous electronic and nuclear motions in highly excited states is quite interesting, since densely degenerate electronic states may bring about unknown properties of molecules. As such, so many things inspire our imagination on what would happen if the chemical theory is released from the traditional Born-Oppenheimer framework.

I have analyzed the quantum mechanical mechanism of these dynamics, in which simultaneous transfers of proton and electron are involved. Dynamical electron theory has been found extremely useful in scrutinizing the real time dynamics of coupled electron-nucleus motion.

Theory

I first apply the semiclassical Ehrenfest theory (SET), which provides electron wavepacket dynamics coupled with nuclear motion. The wavepacket dynamics is given by time dependent electronic Schrödinger equation including nuclear kinematic interaction.

$$i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}; \mathbf{R}(t)) = \mathcal{H}^{el}(\mathbf{r}; \mathbf{R}(t)) \Phi(\mathbf{r}; \mathbf{R}(t))$$

At the same time, the nuclei are treated as classical particles driven by Hellmann-Feynman force generated by the electron wavepacket.

$$M\ddot{\mathbf{R}}_k(t) = - \left\langle \Phi(\mathbf{r}; \mathbf{R}(t)) \left| \frac{\partial \mathcal{H}^{el}(\mathbf{r}; \mathbf{R}(t))}{\partial R_k} \right| \Phi(\mathbf{r}; \mathbf{R}(t)) \right\rangle$$

This equation gives non-Born-Oppenheimer paths driven by the electron wavepacket. Thus these two equations are to be solved simultaneously.

2. Keto-Enol Tautomerization for Proton Transfer in Formamide

The electron wavepacket dynamics is tracked in the proton transfer reaction from enol to keto form. Electron currents in the opposite direction to proton motions have been observed.

These dynamical electron currents are caused by electrons tightly bound with shifting protons. In general, the protons are always covered by a tight electron cloud during their shift of positions. In this case the population is as much as about 0.6 on each proton. Therefore the backward electron-flow should be always followed through a different pathway to compensate the amount of the tightly bound electrons. To clarify the pathway of electron motion, I calculated the electron flow associated with the proton transfer by using Schiff's current of probability density (simply referred to as electron flux).

$$\mathbf{j}(\mathbf{r}_1) = N \int \frac{\hbar}{2im} \left(\Phi^*(\mathbf{r}, t) \nabla_N \Phi(\mathbf{r}, t) - \Phi(\mathbf{r}, t) \nabla_N \Phi^*(\mathbf{r}, t) \right) d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

As readily understood from the above equation, the electron flux gives simply zero to a real valued wavefunction such as the eigenfunctions in stationary quantum chemistry. On the other hand, the wavepackets obtained by SET are inherently complex valued and include the time variable, thereby giving a finite value of the space-time distribution of the electron flux.

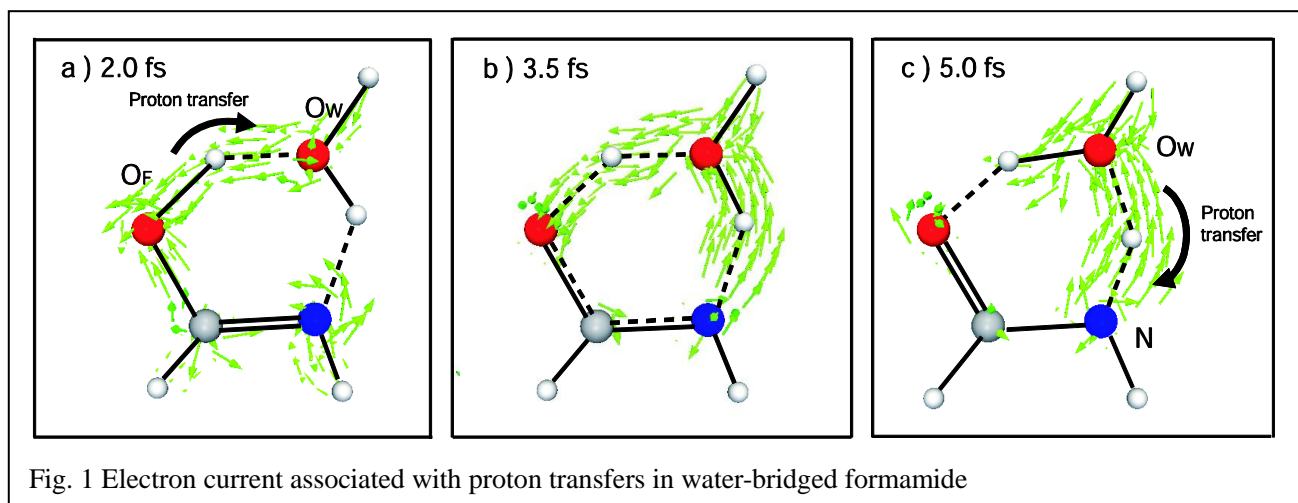
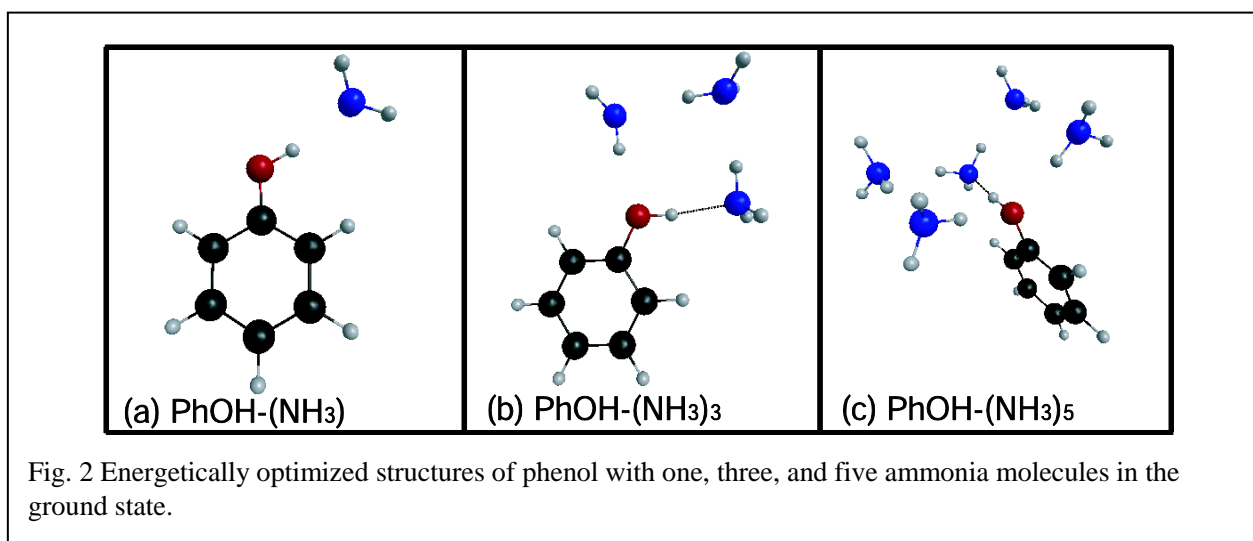


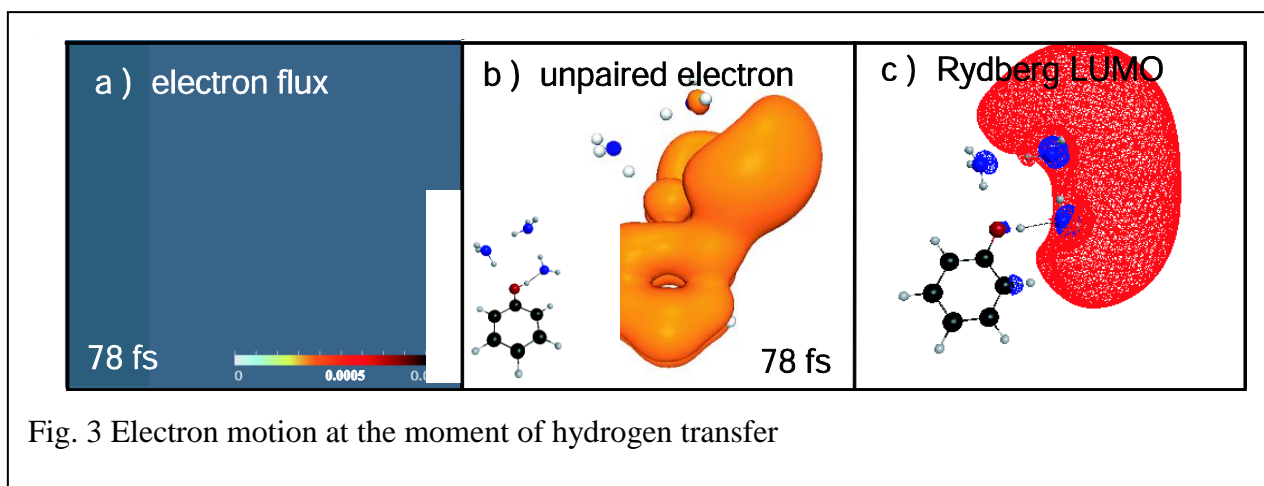
Figure 1 show the σ -electron flux (flux arising from the so-called σ -electrons) on the molecular plane in the water-bridged system. It is clearly observed that electron flux is indeed induced by the nuclear dynamics in the direction opposite to the proton motions, as though they are compensating the electrons carried tightly by the proton nuclei.

3. Coupled Proton-Electron Transfer of Phenol to Solvent Ammonia Cluster

Finally I treat the large scale semiclassical Ehrenfest dynamics in terms of many configuration state functions in densely quasi-degenerate excited electronic states in the photochemical reaction of phenol with small ammonia clusters $\text{PhO}^*\text{H}-(\text{NH}_3)_n$ ($n < 6$).



It turns out that the mechanism is more complicated than that referred to as excited-state hydrogen-atom transfer, which was widely accepted. The pathways of jumping electron and shifting proton nucleus are identified to be mutually different, which necessarily results in charge separation in ammonia clusters after the transitions. The global feature of the present transfer dynamics is fully analyzed and found to be one of the general prototypes of coupled electro-proton transfer in excited states.



4. Conclusions

I have carried out nonadiabatic electron-wavepacket studies on proton transfer reactions in formamide and coupled electron and proton transfers in excited state in phenol-ammonia cluster system, clarifying the qualitative mechanism of electron flow in molecules associated with proton transfers. These mechanisms are general and valid in other systems and set a theoretical foundation, on which further investigation should stand.