Material science of the long-rage electron transfer in protein environment

Hirotaka Nishioka,[1] Kakitani Toshiaki[1]*
[1] Graduate School of Environmental and Human Sciences, Meijo University
Tempaku-ku, Nagoya 468-8502, Japan
*E-mail; kakitani@ccmfs.meijo-u.ac.jp

Electron transfer (ET) reactions in protein environment play an important role in biological functions such as photosynthesis and respiration. In these biological systems, the ET takes place by the long-range (ca. 5-30 Å) electron tunneling in which the super-exchange mechanism mediated by the protein environment works. Usually the rate of such an ET was expressed by the Marcus theory as equation (1) [1]

$$k_{DA} = \frac{2\pi}{\hbar}\left|T_{DA}\right|^2 \frac{1}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}} \exp\left[-\frac{\left(-\Delta G-\lambda\right)^2}{4\lambda k_{\mathrm{B}}T}\right] \qquad (1)$$

,where T_{DA} is the electronic tunneling matrix element, $-\Delta G$ is the free energy gap between the initial and final states in the equilibrium state, and λ is the standard reorganization energy. Here, T_{DA} was usually assumed to be independent of the nuclear dynamics (Condon approximation). However, our recent computational studies of the molecular dynamics simulations and the quantum chemical calculations have revealed that the very rapid (ca. 10-80 fs) and large amount (2-4 orders of magnitude) of fluctuations in T_{DA} take place due to the thermal fluctuation of the protein conformation.[2,3]

In this talk, we first present the influence of such a rapid and large fluctuation of T_{DA} on the ET rate. We produced a new non-Condon theory for the rate of ET in which very rapid fluctuation of T_{DA} due to thermally fluctuating protein media was taken into account.[4,5] We succeeded in decoupling the ET rate into contributions from elastic and inelastic tunneling mechanisms. [4,5] Dynamic character of the fluctuation of T_{DA} appears by means of the inelastic tunneling mechanism. We applied this theory to the ET from the bacteriopheophytin anion to the primary quinone in the bacterial photosynthetic reaction center. As a result, we found that the calculated energy gap dependence of the ET rate is nearly Marcus' parabola[1] in most of the normal region and around the maximum region, but it does not decay substantially in the inverted region due to the inelastic tunneling mechanism, which we call the anomalous inverted region.[4]

Next, we investigated the origin of the rapid and large fluctuation of T_{DA} in terms of the interatomic tunneling currents. The coherent interference between the initial and final wave-functions which have a long tail over the protein brings a sensitive effect of the whole protein conformation fluctuation to the tunneling currents. Therefore, we observed that the fluctuation of the interatomic tunneling current has little correlation with the fluctuation of the corresponding atom-atom distance. These aspects of the electron tunneling will open a new field of material science of the long-range ET.

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