



Theoretical calculation of the photo-induced electron transfer rate between a gold atom and a gold cation solvated in CCl₄

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ABSTRACT

A theoretical calculation was performed to evaluate the photo-induced electron transfer (PIET) rate between a gold atom and a gold ion solvated in carbon tetrachloride (CCl₄) in the framework of Marcus electron transfer (ET) theory, including both solvent reorganization effects and electronic wavefunction coupling between the ET diabatic states. A novel component of this work involves calculation of the electronic coupling strength using a recently developed constrained real-time time-dependent density-functional-theory (CRT-TDDFT) method. It is found that the PIET rate reaches its maximum value at the electronic resonance wavelength regardless of the inter-particle separation, suggesting a strong correlation between PIET and light absorption. In comparison with thermally activated electron transfer (TAET) at room temperature, light irradiation is demonstrated to be much more efficient than thermal fluctuations in promoting long-range ET, at least for the most common situations, when the light travelling substantially exceeds thermal energy. This work is the first step towards a quantum theory of plasmon enhanced electron transfer, and the theory can also be used to calculate electron transfer rates quite generally for condensed phase problems.

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1. Introduction

Many chemical reactions can be associated with electron transfer [1], in which an electron moves from a donor chemical species to an acceptor chemical species either through thermal fluctuation [2] or under light irradiation [3]. The wide-ranging importance of electron transfer phenomena was highlighted by the Nobel Prize in chemistry awarded to Rudolph A. Marcus, who first realized that the electron transfer (ET) rate, k_{ET} , is governed by three important factors, namely the driving force ΔG_0 , the reorganization energy λ_0 , and the electronic coupling strength J_0 , as shown below in the Marcus formula in the high temperature limit [4]:

$$k_{ET} = \frac{2\pi}{\hbar} |J_0|^2 \frac{1}{\sqrt{4\pi\lambda_0 k_b T}} e^{-(\Delta G_0 + \lambda_0)^2 / 4\lambda_0 k_b T} \quad (1)$$

Assuming the Born–Oppenheimer approximation, a system's total wavefunction, $\Psi(R, r)$, can be decomposed into a vibrational part, $\varphi_N(R)$, and an electronic part, $\psi_e(r)$,

$$\Psi(R, r) = \varphi_N(R)\psi_e(r) \quad (2)$$

Therefore, in Eq. (1), the density-weighted Franck–Condon factor (DWFC) of $(1/\sqrt{4\pi\lambda_0 k_b T})e^{-(\Delta G_0 + \lambda_0)^2 / 4\lambda_0 k_b T}$ reflects the vibrational

wavefunction overlap, $\langle \varphi_N(A) | \varphi_N(D) \rangle$, between the donor (D) and the acceptor (A), whereas J_0 is related to the electronic Hamiltonian coupling:

$$J_0 = \langle \psi_e(A) | \hat{H}_0 | \psi_e(D) \rangle \quad (3)$$

Following its original application to the so-called “outer sphere” ET, which is primarily driven by thermal fluctuations in the solvation medium [5], Marcus theory has been successfully expanded to describe the so-called “inner sphere” ET in which structural change in the redox centers and their coordinated solvents, such as in the Creutz–Taube ion with mixed valence, play a dominant role [6].

A widely used manner to probe ET mechanism is to connect a donor and an acceptor by a typically conjugated molecular bridge to comprise the so-called D–B–A system [7–9], which ET rate heavily depends on the donor–acceptor separation primarily because of sensitivity of the bridge-mediated electronic wavefunction overlap with distance [10–12]. From a theoretical perspective, there has been a long-standing issue of the accuracy of the calculated electronic coupling strength until the recent development of constrained density functional theory (C–DFT) [13]. By applying a systematically determined position-dependent Hartree potential to impose charge localization on the reacting centers, C–DFT achieves a rather reliable description of ET diabatic states that is critical for evaluating ΔG_0 , λ_0 and J_0 . Once all of the three key parameters are known, we are in a good position to evaluate the ET rate according to the Marcus formalism.

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