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Electronic coupling matrix elements of U-shaped donor-bridge-acceptor molecules and influence of mediated benzene solvent

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Abstract

The electronic coupling in the electron transfer of the U-shaped anion model systems has been investigated in detail. Both the two-state model and Koopmans' theorem are employed to evaluate the electronic coupling. It is found that the total coupling is dominated by the through-space coupling, and the presence of a bridge partially cancels the through-space coupling. In order to investigate the solvent effect that facilitates the electronic coupling through the low-lying excited state of the aromatic solvent, a benzene molecule is adopted to mimic the solvent molecule and related discussions have been made.

1. Introduction

Electron transfer (ET) is a fundamental chemical process of immense scientific and technological importance [1] and has hence received great attention. Donor-bridge-acceptor (DBA) molecules have been used to successfully address the important issues in ET because they provide a systemic control over molecular properties such as bridge geometries [2–5], electronic state symmetries [6,7], reaction free energies [8], and so on. ET in DBA molecules can be viewed as a super-exchange mechanism that occurs through the orbitals of the intervening bridge along a path between the donor and acceptor groups [9,10]. The concept of super-exchange coupling in ET has its roots in the works of Halpern [11], McConnell [12], and Larsson [13]. Physically, it arises from weak interactions of the diabatic states of the donor and/or the acceptor with localized or delocalized states of the intervening bridge. The electronic coupling matrix element V_{rp} plays the essential role in both adiabatic and nonadiabatic ET processes. Henderson et al. [14] studied the orientation-, distance-, and energy-dependence of solvent effects on the electronic coupling elements for ET by using quantum chemical methods and the generalized Mulliken-Hush scheme.

The U-shaped DBA systems designed by Zimmt [15–17] and Paddon-Row [18,19] provide deep insights into the nature of nonadiabatic ET processes that involve electron tunneling through solvent molecules. These systems consist of the donor and acceptor groups that are held apart at a fixed distance and orientation by highly curved, rigid and covalent bridging units. An increase in the electron-transfer rate constant was observed in such systems when solvents with appropriate sizes and orbital energies are present. Such an effect was ascribed to the occupation of the interior cavity by a solvent molecule

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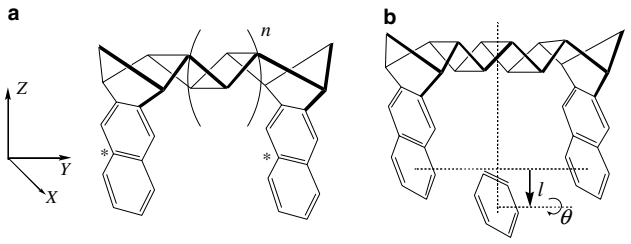

Fig. 1. Schematic description of U-shaped D-B-A without (a) and with (b) a benzene intervening between the donor and the acceptor. n is the number of bridge units.

(e.g., benzene or benzonitrile) that allows for an enhanced line-of-sight electron tunneling between the donor and acceptor. More recently, Head et al. [20] have constructed some super-molecular systems in which a pendant group, covalently attached to the intervening bridge, occupies the interior of the cleft. The ET rates for three different systems were measured as a function of the solvent polarity. Comparisons showed that when an aromatic moiety is positioned in the line-of-sight between the donor and acceptor pair, the observed rate constant is significantly higher than systems in which the aromatic moiety is not present or not in the line-of-sight.

The present note is primarily concerned with the influence of the intervening bridge units on the coupling. We design some U-shaped model systems (Fig. 1) in which the donor and acceptor are aligned face to face to enhance the overlap between the electron-localized diabatic states. Moreover, ET often takes place in solution, and hence the solvent molecule may enter between the donor and the acceptor, and acts as a 'bridge'. We take a single benzene molecule to investigate the influence of the orientation and position of the solvent upon the electronic coupling.

2. Theoretical method

To investigate the mechanism of an intra-molecular ET, quasi-diabatic (i.e., electronically localized) states should be constructed at first. There are several theoretical approaches for the evaluation of V_{rp}, such as the variational treatment based on the two-state model [21], the energy difference method in terms of Koopmans' theorem (KT) [22–24], and the energy difference method considering the nonadiabatic and adiabatic activation states [25]. In the two-state model, we first carry out Hartree-Fock (HF) calculations for both the reactant and product of the system to generate two sets of molecular orbitals (MO), $\{\phi_{\mathrm{r},j}\}$ and $\{\phi_{\mathrm{p},j}\}$, which correspond to different electron-localized states, namely, the reactant state (r) and the product state (p). If the sum and difference of two delocalized MOs, ϕ_a and ϕ_b which are usually the frontier MOs of a closed-shell HF calculation, localize, respectively, on the donor and acceptor, they can be used to induce the subsequent SCF calculations. The convergent determinantal wave functions η_{r} and η_{p} are then good approximations to the diabatic states. It should be noticed that η_{r} and η_{p} are degenerate in energy but have different electron localization characters at the transition state structure. By virtue of the variational principle, the electronic coupling matrix element can be expressed as [21,24]

$$V_{\mathrm{rp}} = (1 - S_{\mathrm{rp}}^2)^{-1} |H_{\mathrm{rp}} - S_{\mathrm{rp}}(H_{\mathrm{rr}} + H_{\mathrm{pp}})/2|, \tag{1}$$

where $H_{ij} = \langle \eta_i | \mathbf{H} | \eta_j \rangle$ $(i,j = \mathrm{r,p})$, $S_{\mathrm{rp}} = S_{\mathrm{pr}} = \langle \eta_{\mathrm{r}} | \eta_{\mathrm{p}} \rangle$, and $\mathbf{H}$ is the electronic Hamiltonian of the system. On the other hand, according to Koopmans' theorem, V_{rp} can simply be approximated as [24]

$$V_{\mathrm{rp}} = (\varepsilon_a - \varepsilon_b)/2. \tag{2}$$

Note that, Eq. (2) can be used only if the sum and difference of the MOs, ϕ_a and ϕ_b, are localized on the donor and acceptor, respectively. Otherwise, V_{rp} might be abnormally estimated [24].

The ET mechanisms may be classified as either through-space (TS) or through-bond (TB) [26]. Different models for defining TS were proposed in the literatures. Here, we prepare the system by deleting the bridge atoms. The carbon atoms that connect directly the donor and acceptor are replaced by hydrogen atom. We take the coupling of this artificial system as the through-space coupling. The coupling through-bond is obtained simply by subtracting the through-space term from the total coupling, i.e., $V_{\mathrm{rp}}^{\mathrm{TB}} = V_{\mathrm{rp}} - V_{\mathrm{rp}}^{\mathrm{TS}}$.

For a long-range ET, it is generally assumed that the electronic coupling V_{rp} depends exponentially (or nearly so) on the donor–acceptor distance, i.e.

$$V_{\mathrm{rp}} = V_{\mathrm{rp}}^0 \exp\left[\frac{-\beta(d - d_0)}{2}\right], \tag{3}$$

where d is donor–acceptor distance and d_0 is the van der Waals distance. V_{rp}^0 is the value of V_{rp} at $d = d_0$. β is the so-called decay coefficient.

All the calculations in this note are carried out with the HONDO99 package [27].

3. Results and discussion

3.1. Geometry optimization

The model systems studied here are shown in Fig. 1, which are similar to those investigated by Napper et al. [28]. The donor and acceptor in [28] are dimethoxynaphthalene (DMN) and dicyanicvinyl (DCV), respectively, but we take naphthalene as both the donor and acceptor in the present study. From Fig. 1 we know that the neutral systems have the C_{2v} symmetry, but the sym-