

# Theoretical studies on the self-exchange electron-transfer reaction between 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) and its radical anion DDQ<sup>•-</sup>

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Received 2 August 2000; received in revised form 11 December 2000; accepted 24 December 2000

## Abstract

The structure of 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) and its radical anion was optimized by semi-empirical AM1, PM3, ab initio HF/3-21G, 6-31G, 6-31G(d), 6-31+G(d), and density functional B3LYP/6-31G(d), 6-31+G(d) methods. Nelsen's model was used to calculate the internal reorganization energy  $\lambda_i$ . The results of  $\lambda_i$  from the AM1, PM3 and B3LYP methods are reasonable, while those from the HF method are too large because of not considering the effect of electron correlation. The linear reaction coordinate  $R$  was used to construct the double-well potential surface for the donor and acceptor, and then the transition state was determined at the point of  $R = 0.50$ . Then Marcus's two-sphere model was applied to estimate the solvent reorganization energy  $\lambda_o$  in different solvents CH<sub>3</sub>CN, benzonitrile, acetone, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. The electron transfer (ET) matrix element  $V_{\text{TP}}$  was calculated using two-state model. The self-exchange ET reaction rate constants  $k_{\text{ET}}$  in different solvents were calculated and the results were consistent with the experimental values. The reason why the behavior of self-exchange ET reaction between DDQ and DDQ<sup>•-</sup> does not correlate with Marcus's theory was discussed as well. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** DDQ; Self-exchange electron transfer; AM1 and PM3; Ab initio; DFT-B3LYP

## 1. Introduction

The electron transfer (ET) reaction can take place when the electron donor has a weak interaction with the acceptor, in which case the ET reaction is called an outer-sphere one. On the other hand, when the donor and acceptor can interact more strongly in the sense of forming a partial bond between the reactive centers, the ET reaction is within the area of inner-sphere ET reaction [1]. There are two limits of ET reaction processes depending on the strength of the coupling of electronic states, non-adiabatic and adiabatic. It is widely believed that in the case of non-adiabatic, the ET coupling  $V_{\text{TP}}$  is in the lowest order, i.e.  $V_{\text{TP}} \ll RT$ , and the case of  $V_{\text{TP}} > RT$  corresponds to the adiabatic ET process [2]. The solvent dynamics is determined by the finite response time of the orientational polarization of the solvent. Under certain conditions, this dielectric response time can become

the rate-determining factor of the reaction. The relaxation time  $\tau_L$  depends on the electronic coupling  $V_{\text{TP}}$ . Related to the problem of strong electron coupling is the problem of solvent dynamic effects. The slow relaxation of the solvent makes the electronic time scale relatively faster, which in some sense is equivalent to strong electronic coupling.

Marcus's theory is one of the most important approach as to deal with the ET systems. According to the theory, for the outer-sphere bimolecular ET reaction, the rate constant  $k_{\text{ET}}$  is given by [3]

$$k_{\text{ET}} = \kappa A \sigma^2 \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (1)$$

where  $\kappa$  is the transmission coefficient for ET,  $A\sigma^2$  has the dimension of collision frequency,  $\sigma$  the average center-to-center distance in the reaction pair during the ET. The activation energy  $\Delta G^*$  for ET process is expressed as Eq. (2). For the self-exchange ET reaction,  $\Delta G^0 = 0$ , the activation energy  $\Delta G^*$  is approximately given by Eq. (2a)

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (2)$$

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$$\Delta G^* = \frac{1}{4}\lambda \quad (2a)$$

The total reorganization energy  $\lambda$  is expressed as

$$\lambda = \lambda_i + \lambda_o \quad (3)$$

$\lambda_i$  denotes the internal reorganization energy. The solvent reorganization energy  $\lambda_o$  shown in Eq. (4) is described by Born based continuum equation [3–5].

$$\lambda_o = \frac{e^2 N_L}{4\pi\epsilon_0} \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (4)$$

in which  $r_1$  and  $r_2$  refer to the radii of the reactants,  $r_{12}$  the contact distance in the transition state. It is normally approximated by  $r_1 = r_2 = r$ , and  $r_{12} = 2r$  for the self-exchange ET reactions,  $\epsilon_{op}$  denotes the optical dielectric constant of the solvent and usually characterized by  $\epsilon_{op} = n^2$  ( $n$  is refractive index),  $\epsilon_s$  is the static dielectric constant,  $e$  the electronic charge,  $\epsilon_0$  the dielectric constant in vacuum. This model will be described in detail later.

If we assume that  $\kappa$ ,  $A$ ,  $\sigma$  and  $\lambda_i$  are independent of solvent, then from Eqs. (1)–(4) we can get  $\ln k_{ET} = s + t\gamma$  ( $\gamma = 1/\epsilon_{op} - 1/\epsilon_s$ ,  $s$  and  $t$  refer to the slope and intercept respectively), i.e. a linear dependence of  $\ln k_{ET}$  on the solvent parameter  $\gamma$  is predicted for outer-sphere ET reactions.

Self-exchange ET reactions are simple examples for testing the Marcus's theory of ET in solution and have been actively pursued both experimentally and theoretically [6–12]. Recent experimental results of Grampp et al. [9] showed that the self-exchange ET behavior of 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) and its radical anion  $DDQ^{\bullet-}$  did not correlate with Marcus's theory, i.e.  $\ln k_{ET}$  does not depend linearly on the solvent parameter  $\gamma$ , while  $\ln(k_{ET}\tau_L\gamma^{-1/2})$  is linear to  $\gamma$ , so the longitudinal relaxation time  $\tau_L$  of the solvent will affect the solvent dynamical effect.

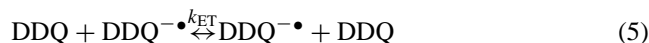
DDQ is a very important oxidant, but there are only a few works on it [9,13]. In this work, the self-exchange ET reaction rate constant of  $DDQ/DDQ^{\bullet-}$  in different solvents have been calculated, and we managed to seek the theoretical interpretation for its behavior of not being correlated with Marcus's theory.

## 2. Models and calculation methods

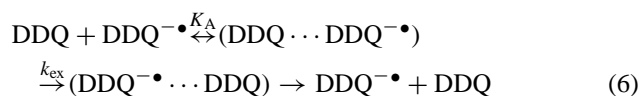
The structure of DDQ and  $DDQ^{\bullet-}$  is shown in Fig. 1.

The AM1 and PM3 semi-empirical methods in MOPAC (version 6.0) program package [14,15] and Gaussian 98 [16]/ab initio methods (HF/3-21G, 6-31G, 6-31G(d), 6-31+G(d)) and DFT methods (B3LYP/6-31G(d), 6-31+G(d)) were used in the calculation. The geometry was optimized by AM1, PM3, ab initio and DFT methods. The Baker's eigenvector following (EF) geometry optimization was used in AM1 and PM3, and the gradient norm was less than 0.01 kcal/Å. The Beryny method was used for the ab initio and DFT calculation. The RHF, RB3LYP were used for the closed-shell system, and the UHF, UB3LYP were used for the open-shell system. The solvent environment was modeled using a self-consistent reaction field (SCRf) approach [17,18], and the structure of DDQ and its radical anion  $DDQ^{\bullet-}$  was also optimized using B3LYP/6-31G(d) SCRf method in different solvents. All the optimized structures were verified by vibration frequency analysis. HONDO 99 package [19,20] was used to calculate the ET matrix element  $V_{fp}$ .

Self-exchange ET reaction between DDQ and  $DDQ^{\bullet-}$  can be represented as



According to Sutin's reaction scheme [21], reaction (5) can be divided into the following steps



Therefore, the overall ET reaction rate constant  $k_{ET}$  is expressed as

$$k_{ET} = K_A k_{ex} \quad (7)$$

where  $K_A$  is the association constant forming the precursor complex, and it can be calculated from Eq. (8) [21].

$$K_A = 4\pi N_L d^2 \Delta d \quad (8)$$

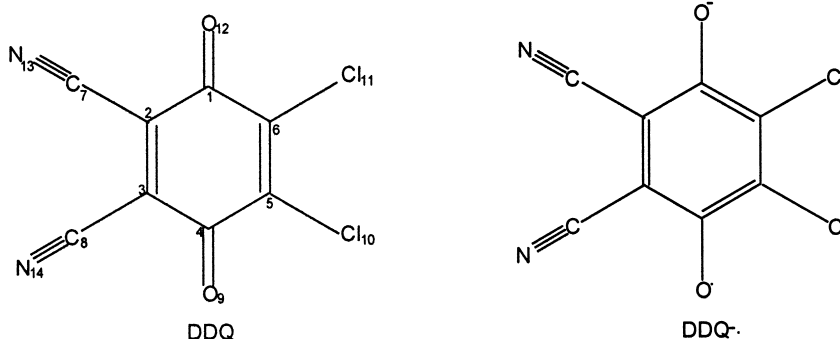


Fig. 1. The structure of DDQ and  $DDQ^{\bullet-}$ .

where  $d$  is the center-to-center distance between the reactants in the precursor complex, and  $\Delta d$  the thickness of the reaction zone, usually  $\Delta d = 0.8 \text{ \AA}$  is chosen.  $N_L$  is the Avogadro constant.

In the adiabatic limiting case, the relaxation overdamped rate constant  $k_{\text{ex}}$  for the self-exchange ET reactions is given by [7] Eq. (9a) according to Marcus and Sumi [22,23]

$$k_{\text{ex}} = \frac{\mu}{\tau_L} \exp\left(-\frac{\lambda_i + \lambda_o}{4RT}\right) \quad (9a)$$

where  $\mu$  is defined as

$$\mu = \left(\frac{\Delta G^*}{\pi RT}\right)^{1/2} \frac{2\lambda_o}{\lambda_i + 2\lambda_o} \frac{1}{\text{erfc}[\lambda_i \Delta G^*/(\lambda_i + 2\lambda_o)RT]^{1/2}}$$

and Eq. (9b) according to Jortner and Bixon [24]

$$k_{\text{ex}} = \frac{1}{\tau_L} \left(\frac{\lambda_o}{16\pi RT}\right)^{1/2} \exp\left(-\frac{\lambda_o}{4RT}\right) \quad (9b)$$

in which  $k_{\text{ex}}$  is independent of the internal reorganization energy.

So  $k_{\text{ET}}$  can be calculated from Eqs. (10a) and (10b), respectively

$$k_{\text{ET}} = K_A \frac{\mu}{\tau_L} \exp\left(-\frac{\lambda_i + \lambda_o}{4RT}\right) \quad (10a)$$

$$k_{\text{ET}} = K_A \frac{1}{\tau_L} \left(\frac{\lambda_o}{16\pi RT}\right)^{1/2} \exp\left(-\frac{\lambda_o}{4RT}\right) \quad (10b)$$

The internal reorganization energy  $\lambda_i$  is mainly caused by the change of vibrational energy due to the change of bond lengths and bond angles in the ET processes. For a self-exchange ET reaction  $A^- + A \rightarrow A + A^-$ , according to Nelsen's method [12,25,26], there is

$$\lambda_i = \lambda_i(A^-) + \lambda_i(A) \quad (11)$$

If the changes of entropy is negligible, we can obtain  $\lambda_i$  as

$$\lambda_i(A^-) = \Delta H_f^0(A_n^-) - \Delta H_f^0(A_a^-) \quad (12a)$$

$$\lambda_i(A) = \Delta H_f^0(A_a^0) - \Delta H_f^0(A_n^0) \quad (12b)$$

or

$$\lambda_i(A^-) = E(A_n^-) - E(A_a^-) \quad (13a)$$

$$\lambda_i(A) = E(A_a^0) - E(A_n^0) \quad (13b)$$

where  $\lambda_i(A^-)$  and  $\lambda_i(A)$  denote the internal reorganization energy of donor and acceptor, respectively and  $\Delta H_f^0$  is the heat of formation,  $E$  the total energy of molecule.  $A_n^-$  and  $A_a^-$  denote the molecules with optimized neutral structure and anion structure but with one negative charge, respectively and  $A_a^0$  and  $A_n^0$  correspond to the optimized anion structure and neutral structure without charge, respectively.

Marcus developed a continuum medium model for the calculation of solvent reorganization energy  $\lambda_o$  [3–5] as in

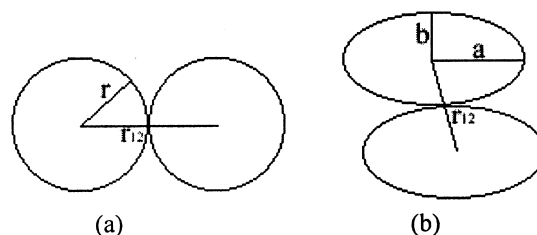


Fig. 2. Marcus's two-sphere model.

Fig. 2(a). In this model the two redox sites are assumed to be centrally located in two non-interpenetrating spheres, and image effects are neglected. The expression is shown as Eq. (4). In this work, we approximated DDQ and DDQ $^{\bullet}$  as two ellipsoids, so Fig. 2(a) was evolved as Fig. 2(b) [7]. Eq. (4) and Fig. 2(b) will be used to evaluate the solvent reorganization energy  $\lambda_o$  of DDQ/DDQ $^{\bullet}$  self-exchange ET reaction.

In addition, it is quite important to determine the transition state (TS) in order to calculate the solvent reorganization energy  $\lambda_o$ . The linear reaction coordinate  $R$  is employed to determine the nuclear configuration of the system [27–29], i.e.

$$Q_i = Q_i^r + R(Q_i^p - Q_i^r) \quad (14)$$

where  $Q_i$  is the  $i$ th internal coordinate including bond lengths, bond angles and dihedral angles. Superscript r and p denote the reactant and product, respectively. For a self-exchange ET reaction, the transition state will be at  $R = 0.50$ , i.e.

$$Q_i = \frac{1}{2}(Q_i^r + Q_i^p) \quad (14a)$$

In this work, we calculated the rate constant  $k_{\text{ET}}$  using Eqs. (10a) and (10b) in different solvents CH<sub>3</sub>CN, benzonitrile, acetone, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub> at 293 K.

### 3. Results and discussion

#### 3.1. The conformations of molecules

Table 1 shows some calculated geometrical parameters of both DDQ and DDQ $^{\bullet}$ . It can be seen that all the dihedral angles are close to 0 or  $\pm 180^\circ$ , i.e. both DDQ and DDQ $^{\bullet}$  are planar molecules. Besides, we also optimized DDQ with C<sub>2v</sub> and DDQ $^{\bullet}$  with C<sub>s</sub> symmetry using B3LYP/6-31G(d) and HF/6-31G(d) methods. The results were listed in column 6 of Table 1, and the vibrational frequency analysis verified the local minima for both DDQ and DDQ $^{\bullet}$ . In Table 1, it also shows that the differences of bond lengths and bond angles between DDQ and DDQ $^{\bullet}$  obtained from AM1, PM3 and B3LYP/6-31G(d), 6-31+G(d) are close to each other but less than those from HF/3-21G, 6-31G, 6-31G(d) and 6-31+G(d). These differences will lead to the differences

Table 1

The geometric parameters of DDQ and DDQ<sup>-•</sup> (in brackets) (length, Å; angle, °)

	AM1	PM3	B3LYP/6-31G(d)	B3LYP/6-31+G(d)	B3LYP/6-31G(d) <sup>a</sup>
C <sub>1</sub> C <sub>2</sub>	1.4900 (1.4453)	1.4991 (1.4501)	1.5036 (1.4576)	1.5047 (1.4578)	1.5035 (1.4576)
C <sub>2</sub> C <sub>3</sub>	1.3528 (1.3916)	1.3525 (1.3960)	1.3591 (1.4015)	1.3600 (1.4027)	1.3592 (1.4015)
C <sub>3</sub> C <sub>4</sub>	1.4900 (1.4454)	1.4992 (1.4501)	1.5036 (1.4576)	1.5047 (1.4578)	(1.4578)
C <sub>4</sub> C <sub>5</sub>	1.4851 (1.4760)	1.4869 (1.4763)	1.4959 (1.4775)	1.4957 (1.4767)	(1.4777)
C <sub>5</sub> C <sub>6</sub>	1.3540 (1.3580)	1.3489 (1.3505)	1.3554 (1.3648)	1.3570 (1.3666)	1.3554 (1.3647)
C <sub>6</sub> C <sub>1</sub>	1.4851 (1.4759)	1.4869 (1.4762)	1.4959 (1.4775)	1.4957 (1.4767)	1.4958 (1.4775)
C <sub>2</sub> C <sub>7</sub>	1.4222 (1.4173)	1.4237 (1.4175)	1.4269 (1.4260)	1.4276 (1.4267)	1.4269 (1.4260)
C <sub>3</sub> C <sub>8</sub>	1.4222 (1.4173)	1.4238 (1.4176)	1.4270 (1.4260)	1.4276 (1.4267)	(1.4260)
C <sub>1</sub> O <sub>12</sub>	1.2308 (1.2529)	1.2124 (1.2368)	1.2136 (1.2428)	1.2147 (1.2459)	1.2136 (1.2427)
C <sub>4</sub> O <sub>9</sub>	1.2308 (1.2529)	1.2124 (1.2368)	1.2136 (1.2428)	1.2147 (1.2459)	(1.2427)
C <sub>5</sub> Cl <sub>10</sub>	1.6881 (1.7064)	1.6652 (1.6840)	1.7184 (1.7466)	1.7172 (1.7439)	(1.7467)
C <sub>6</sub> Cl <sub>11</sub>	1.6881 (1.7064)	1.6652 (1.6839)	1.7184 (1.7466)	1.7172 (1.7439)	1.7182 (1.7467)
C <sub>7</sub> N <sub>13</sub>	1.1630 (1.1652)	1.1594 (1.1633)	1.1626 (1.1655)	1.1628 (1.1660)	1.1626 (1.1655)
C <sub>8</sub> N <sub>14</sub>	1.1630 (1.1652)	1.1594 (1.1633)	1.1626 (1.1655)	1.1628 (1.1660)	(1.1656)
C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	122.15 (122.41)	121.78 (122.02)	121.15 (122.44)	121.25 (122.28)	121.23 (122.45)
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	122.15 (122.41)	121.78 (122.02)	121.25 (122.44)	121.15 (122.28)	(122.43)
C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	115.61 (115.16)	116.06 (115.55)	117.23 (114.77)	117.42 (115.08)	(114.76)
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	122.24 (122.43)	122.16 (122.43)	121.51 (122.79)	121.43 (122.64)	(122.80)
C <sub>5</sub> C <sub>6</sub> C <sub>1</sub>	122.24 (122.43)	122.16 (122.43)	121.43 (122.79)	121.51 (122.64)	121.50 (122.80)
C <sub>6</sub> C <sub>1</sub> C <sub>2</sub>	115.61 (115.16)	116.06 (115.55)	117.42 (114.77)	117.23 (115.08)	117.27 (114.76)
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	0.0039 (0.0066)	0.0005 (0.0088)	0.0281 (0.0378)	0.0114 (0.0477)	
C <sub>3</sub> C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	0.0018 (0.0038)	0.0013 (0.0061)	0.0280 (0.0382)	0.0108 (0.0481)	
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub> C <sub>1</sub>	0.0006 (0.0007)	0.0002 (0.0028)	0.0036 (0.0024)	0.0109 (0.0022)	
HF					
	3-21G	6-31G	6-31G(d)	6-31+G(d)	6-31G(d) <sup>a</sup>
C <sub>1</sub> C <sub>2</sub>	1.4937 (1.4281)	1.4909 (1.4296)	1.5017 (1.4335)	1.5028 (1.4340)	1.5018 (1.4336)
C <sub>2</sub> C <sub>3</sub>	1.3263 (1.3756)	1.3359 (1.384)	1.3296 (1.3902)	1.3303 (1.3915)	1.3296 (1.3900)
C <sub>3</sub> C <sub>4</sub>	1.4937 (1.4281)	1.4909 (1.4296)	1.5017 (1.4335)	1.5028 (1.434)	(1.4334)
C <sub>4</sub> C <sub>5</sub>	1.4807 (1.4505)	1.4818 (1.4527)	1.4988 (1.4818)	1.4991 (1.4818)	(1.4817)
C <sub>5</sub> C <sub>6</sub>	1.3113 (1.3277)	1.3243 (1.3401)	1.3286 (1.3382)	1.3295 (1.3393)	1.3286 (1.3381)
C <sub>6</sub> C <sub>1</sub>	1.4807 (1.4505)	1.4818 (1.4527)	1.4988 (1.4818)	1.4991 (1.4818)	1.4988 (1.4814)
C <sub>2</sub> C <sub>7</sub>	1.4192 (1.4213)	1.4268 (1.4285)	1.4397 (1.4364)	1.4403 (1.4371)	1.4397 (1.4366)
C <sub>3</sub> C <sub>8</sub>	1.4192 (1.4213)	1.4268 (1.4285)	1.4397 (1.4364)	1.4403 (1.4371)	(1.4367)
C <sub>1</sub> O <sub>12</sub>	1.2037 (1.2573)	1.2092 (1.2623)	1.1823 (1.2215)	1.1827 (1.2227)	1.1823 (1.2214)
C <sub>4</sub> O <sub>9</sub>	1.2037 (1.2572)	1.2092 (1.2623)	1.1823 (1.2215)	1.1827 (1.2227)	(1.2213)
C <sub>5</sub> Cl <sub>10</sub>	1.7741 (1.8008)	1.7673 (1.7923)	1.7084 (1.7303)	1.7082 (1.7292)	(1.7305)
C <sub>6</sub> Cl <sub>11</sub>	1.7741 (1.8008)	1.7673 (1.7923)	1.7084 (1.7303)	1.7082 (1.7292)	1.7083 (1.7305)
C <sub>7</sub> N <sub>13</sub>	1.1383 (1.1420)	1.1446 (1.1495)	1.1339 (1.1387)	1.1342 (1.1392)	1.1339 (1.1387)
C <sub>8</sub> N <sub>14</sub>	1.1383 (1.1420)	1.1446 (1.1495)	1.1339 (1.1387)	1.1342 (1.1392)	(1.1386)
C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	121.65 (122.65)	120.94 (121.97)	121.27 (122.44)	121.23 (122.35)	121.28 (122.46)
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	121.65 (122.66)	120.94 (121.97)	121.27 (122.45)	121.23 (122.35)	(122.48)
C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	116.05 (114.13)	117.64 (115.60)	117.36 (115.10)	117.43 (115.27)	(115.04)
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	122.30 (123.21)	121.42 (122.42)	121.36 (122.45)	121.33 (122.38)	(122.50)
C <sub>5</sub> C <sub>6</sub> C <sub>1</sub>	122.30 (123.21)	121.42 (122.42)	121.36 (122.45)	121.33 (122.38)	121.37 (122.46)
C <sub>6</sub> C <sub>1</sub> C <sub>2</sub>	116.05 (114.14)	117.64 (115.60)	117.36 (115.10)	117.43 (115.27)	117.35 (115.06)
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub> C <sub>5</sub>	0.0549 (0.0092)	0.0260 (0.0220)	0.0038 (0.0034)	0.0033 (0.0071)	
C <sub>3</sub> C <sub>4</sub> C <sub>5</sub> C <sub>6</sub>	0.0540 (0.0084)	0.0262 (0.0221)	0.0039 (0.0037)	0.0033 (0.0067)	
C <sub>4</sub> C <sub>5</sub> C <sub>6</sub> C <sub>1</sub>	0.0303 (0.0127)	0.0184 (0.0065)	0.0027 (0.0027)	0.0072 (0.0001)	

<sup>a</sup> Optimized by C<sub>2v</sub> for DDQ and C<sub>s</sub> for DDQ<sup>-•</sup>.

Table 2

The internal reorganization energy  $\lambda_i$  of DDQ/DDQ<sup>-•</sup> ET system (kJ/mol)

	AM1	PM3	B3LYP		HF			
			6-31G(d)	6-31+G(d)	3-21G	6-31G	6-31G(d)	6-31+G(d)
$\lambda_i(A^-)$	17.16	18.89	20.56	21.03	44.92	43.58	42.49	42.48
$\lambda_i(A)$	17.49	19.18	20.37	20.89	47.82	46.54	44.46	44.69
$\lambda_i$	34.65	38.07	40.93	41.92	92.74	90.12	86.95	87.17

of internal reorganization energy from different methods as discussed later.

### 3.2. The internal reorganization energy $\lambda_i$

The results of internal reorganization energy calculated from different methods are listed in Table 2.

It can be seen that the results of  $\lambda_i$  calculated from AM1 and PM3 methods consist with those from B3LYP/6-31G(d) and 6-31+G(d) methods. This group of  $\lambda_i$  values are reasonable according to Nelsen's model [12,25,26] and they are consistent with reported result of  $\lambda_i$  (45.3 kJ/mol) [9], while those of  $\lambda_i$  from HF/3-21G, 6-31G, 6-31G(d), 6-31+G(d) are too large because of not considering the effect of electron correlation. It is thought that the DFT methods achieve significantly greater accuracy than Hartree–Fock theory because they include some of the effects of electron correlation [30]. In our previous paper [31], we also found that the electron correlation is important in the calculation of  $\lambda_i$  in ET reaction  $\text{O}_2^- + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2^{\bullet-}$ .

### 3.3. The solvent reorganization energy $\lambda_o$

According to Eq. (14), we constructed the double-well potential surface for DDQ/DDQ<sup>•-</sup> couple using the optimized geometries from B3LYP/6-31G(d) SCRF method as shown in Fig. 3. It shows that the nuclear configuration at  $R = 0.50$  corresponds to the transition state.

In this work, Eq. (4) and Fig. 2(b) have been used to evaluate the solvent reorganization energy  $\lambda_o$ , i.e. we approximated DDQ (and DDQ<sup>•-</sup>) as an ellipsoid, and assumed that both the donor and the acceptor are surrounded by solvent molecules. We adopted the distance from the mass center of the molecule to the nitrogen atom at  $R = 0.50$ , plus the covalent radius 1.50 Å of nitrogen, as the length of long semi-axis  $a$  of the ellipsoid, and the distance between the mass center

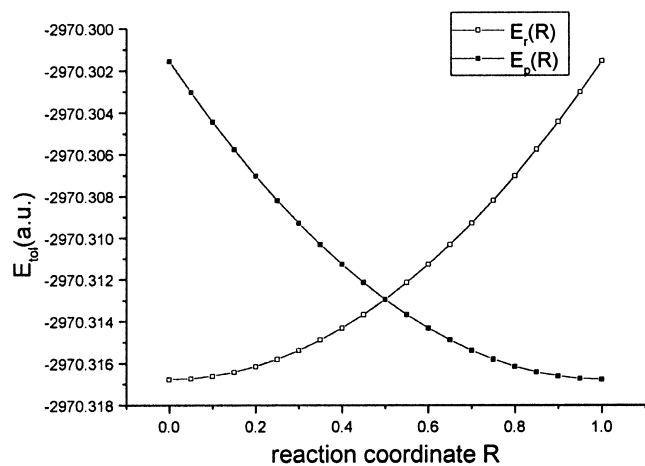


Fig. 3. The double-well potential for DDQ/DDQ<sup>•-</sup> self-exchange ET couple in CH<sub>3</sub>CN (the step  $\Delta R = 0.05$ ),  $r$  and  $p$  denote reactant and product, respectively.

Table 3

The values of  $a$ ,  $b$ ,  $c$ ,  $r$  and  $r_{12}$  (Å) (transition state geometry from B3LYP/6-31G(d) SCRF method)

	$a$	$b$	$c$	$r$	$r_{12}$
CH <sub>3</sub> CN	5.7296	4.1090	3.9930	4.6105	9.2210
Benzonitrile	5.7297	4.1090	3.9932	4.6106	9.2212
Acetone	5.7297	4.1090	3.9932	4.6106	9.2212
CHCl <sub>3</sub>	5.7301	4.1093	3.9934	4.6110	9.2220
CH <sub>2</sub> Cl <sub>2</sub>	5.7298	4.1092	3.9931	4.6107	9.2214

and the oxygen atom (at  $R = 0.50$ ) plus the covalent radius 1.40 Å of oxygen as the length of short semi-axis  $b$ , then the focal distance,  $c$  is calculated from  $a$  and  $b$  by the relationship  $c^2 = a^2 - b^2$ . So in the transition state, the radius of the reactant  $r$  is  $r = (a + b + c)/3$  [7] and the contact distance  $r_{12}$  ( $=2r$ ) in Eq. (4) is obtained as shown in Table 3. It can be seen that the solvents have little effect on the radius of reactants. After that, the solvent reorganization energy  $\lambda_o$  in different solvents CH<sub>3</sub>CN, benzonitrile, acetone, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub> were calculated. The results of  $\lambda_o$  have been listed in Table 4.

### 3.4. Electron transfer matrix element $V_{rp}$

The Hartree–Fock theory is reasonably good at computing the structures of stable molecules and some transition states in spite of its neglect of electron correlation [30]. So we optimized the geometry of the precursor complex using UHF/6-31G(d) method as shown in Fig. 4(a).

It can be seen that the relative orientation between the two reactants is of T-shape in the precursor complex, and the calculated distance between mass centers of DDQ and DDQ<sup>•-</sup> is 5.4581 Å, the corresponding closest distance between DDQ and DDQ<sup>•-</sup> (mass center of DDQ and O<sub>12</sub> of DDQ<sup>•-</sup>) is 2.7692 Å. There will be some strong intermolecular interaction between the reactant molecules within this small distance. It is thought that in bimolecular reactions, the separation distance where the ET reaction is adiabatic is frequently assumed to correspond to close contact of the two reactants [3], for the outer-sphere ET reaction, the reaction distance should be greater or equal to the sum of the radii of donor and acceptor. So the self-exchange ET reaction between DDQ and DDQ<sup>•-</sup> with this short distance may contain to some extent inner-sphere contributions, which lead to the ET behavior of this couple does not correlate with Marcus's theory.

Table 4

The calculated solvent reorganization energy  $\lambda_o$  in different solvents (kJ/mol)

	$\epsilon_{op}$ [32] = $n^2$	$\epsilon_s$ [32]	$\lambda_o$
CH <sub>3</sub> CN	1.80663	37.5	79.41
Benzonitrile	2.33549	25.20	58.56
Acetone	1.84688	20.7	74.33
CHCl <sub>3</sub>	2.09294	4.806	40.65
CH <sub>2</sub> Cl <sub>2</sub>	2.02892	9.08	57.69

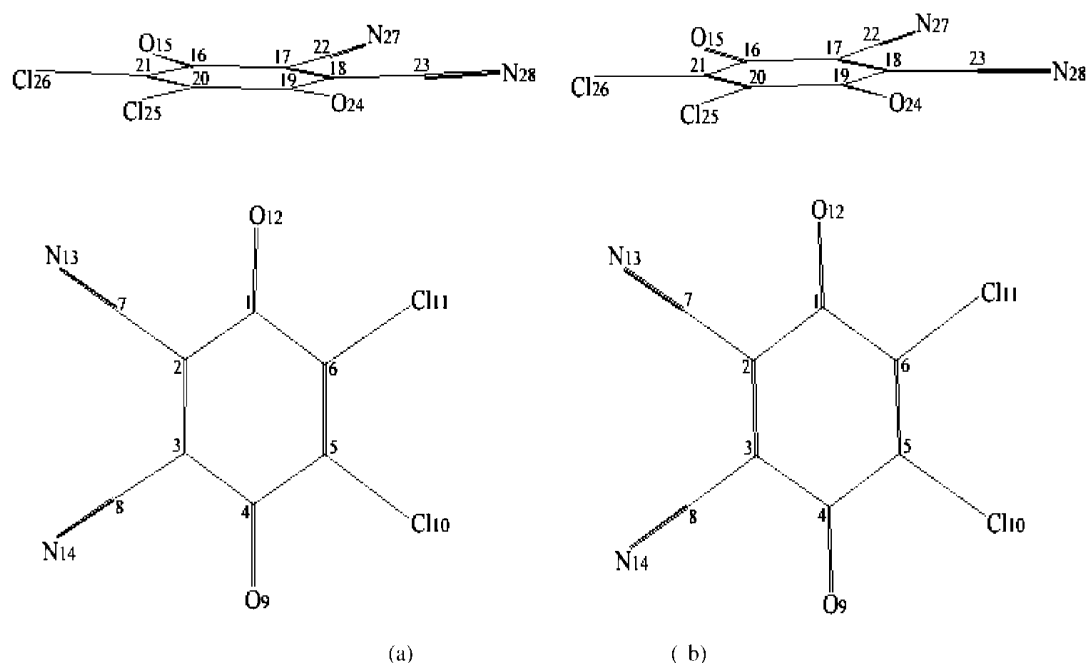


Fig. 4. The relative orientation between DDQ (the upper) and DDQ<sup>•-</sup> (the lower) in both: (a) precursor complex ( $d = 5.4581 \text{ \AA}$ ); and (b) transition state complex ( $d = 5.3581 \text{ \AA}$ ).

Rauhut and Clark have optimized the structures of the precursor and the transition state complexes of *p*-diaminobenzenes and their corresponding radical cations using AM1 molecular orbital theory [33,34], and their results show that the center-to-center distance in the TS complexes is about  $0.1 \text{ \AA}$  shorter than that in the precursor complexes, but the relative orientation between the two rings is identical in both the precursor and the TS complexes. Based on this fact, after the precursor complex was optimized using UHF/6-31G(d) method and the corresponding geometry of transition state was determined by the method used in Section 3.3, we got the TS complex (as Fig. 4(b)) by keeping the same relative orientation between DDQ and DDQ<sup>•-</sup> as in the precursor complex and decreasing their center-to-center distance by  $0.1 \text{ \AA}$ . There will be stronger interaction between DDQ and DDQ<sup>•-</sup> in the TS complex.

The ET matrix element  $V_{\text{rp}}$  is of importance in both theory and experiment. It is widely believed that the relationship between  $V_{\text{rp}}$  and reaction distance  $L$  can be described by Eq. (15) [35,36]

$$V_{\text{rp}} = V_{\text{rp}}^0 \exp[-\beta(L - L_0)] \quad (15)$$

where  $V_{\text{rp}}^0$  is the ET matrix element at the van der Waals contact distance  $L_0$  and  $\beta$  the distance decay factor.

In the framework of the two-state model, the ET matrix element  $V_{\text{rp}}$  can be directly calculated by solving the secular equation at the crossing point [37,38], i.e.

$$V_{\text{rp}}(1 - S_{\text{rp}}^2)^{-1} \left| H_{\text{rp}} - \frac{S_{\text{rp}}(H_{\text{rr}} + H_{\text{pp}})}{2} \right| \quad (16)$$

where  $H_{\text{rp}} = \langle \Phi_{\text{r}} | H | \Phi_{\text{p}} \rangle$ ,  $H$  is the electronic Hamiltonian of the system and  $S_{\text{rp}} = \langle \Phi_{\text{r}} | \Phi_{\text{p}} \rangle$  the overlap integral between  $\Phi_{\text{r}}$  and  $\Phi_{\text{p}}$ , the quantity  $H_{\text{rp}}$  can be divided into two parts, the one-electron contribution  $\Omega(1)$  and the two-electron contribution  $\Omega(2)$ , i.e.  $H_{\text{rp}} = \Omega(1) + \Omega(2)$ .

Both experimental and theoretical results show that  $V_{\text{rp}}$  is solvent independent [8]. In this work, we calculated  $V_{\text{rp}}$  of the TS complex as mentioned above using the two-state model. The calculated results are collected in Table 5.

It shows that the calculated ET matrix element  $V_{\text{rp}}$  from UHF/3-21G is  $0.219 \text{ eV}$ , which is greater than  $RT$  ( $0.025 \text{ eV}$ ,  $T = 293 \text{ K}$ ), this is the evidence that the self-exchange ET behavior between DDQ and DDQ<sup>•-</sup> is an adiabatic one.

### 3.5. The self-exchange ET rate constants $k_{\text{ET}}$

The association constant  $K_{\text{A}}$  forming the precursor complex can be calculated from Eq. (8). The corresponding

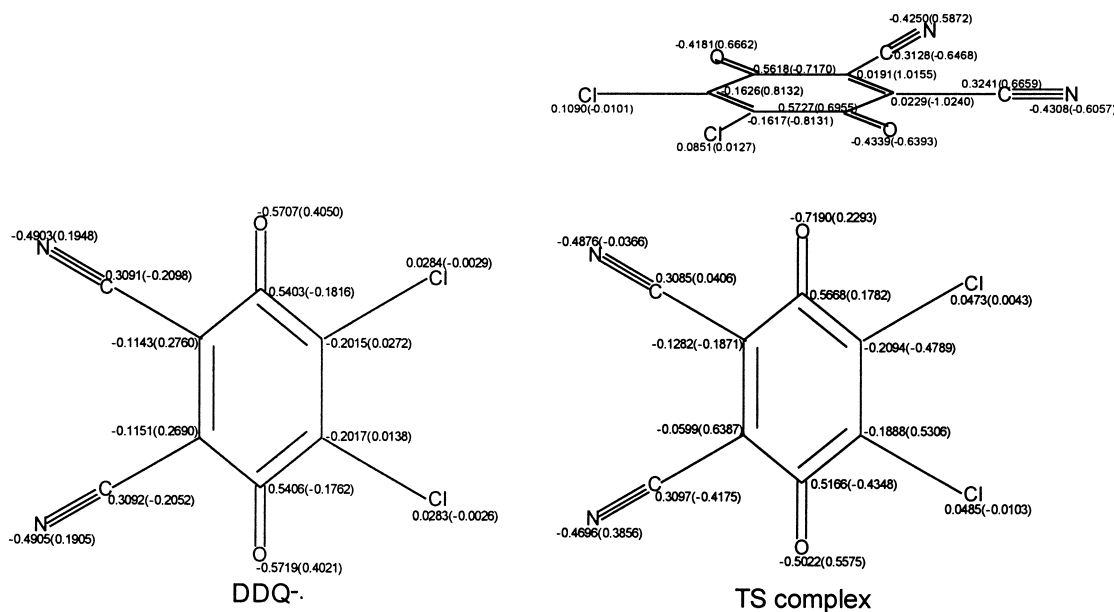
Table 5  
The calculated result of ET matrix element  $V_{\text{rp}}$  (eV) (UHF/3-21G)

$\Omega(1)$ (a.u.)	$\Omega(2)$ (a.u.)	$H_{\text{rp}}$ (a.u.)	$H_{\text{rr}}$ (a.u.)	$H_{\text{pp}}$ (a.u.)	$S_{\text{rp}}$	$V_{\text{rp}}$
-1213.2526	497.2014	-716.0512	-6026.0996	-6026.1177	0.11882	0.219

Table 6

The self-exchange ET rate constants  $k_{ET}$  for DDQ/DDQ $^{\bullet-}$  system in different solvents at  $T = 293$  K,  $K_A = 0.1804$  dm $^3$ /mol,  $\lambda_i = 40.93$  kJ/mol

	$\tau_L$ (ps) [7]	$\mu$	$k_{ET}/10^8/\text{MS}$ (Eq. (10a))	$k_{ET}/10^8/\text{MS}$ (Eq. (10b))	$k_{ET}(\text{exp}) [9]/10^8/\text{MS}$
CH $_3$ CN	0.20	63.84	2.49	2.10	29.2 $\pm$ 0.3
Benzonitrile	6.90	61.30	0.59	0.44	1.1 $\pm$ 0.05
Acetone	0.30	63.28	2.77	2.28	15.5 $\pm$ 0.6
CHCl $_3$	2.90	58.71	8.44	5.53	33.7 $\pm$ 1.5
CH $_2$ Cl $_2$	0.33	61.16	13.45	10.07	48.5 $\pm$ 0.2

Fig. 5. The charge and spin density (in brackets) distributions on both DDQ $^{\bullet-}$  and TS complex.

results at  $T = 293$  K are:  $d = 5.4581$  Å;  $\Delta d = 0.8$  Å;  $K_A = 0.1804$  dm $^3$ /mol.

The values of  $k_{ET}$  calculated from Eqs. (10a) and (10b) are summarized in Table 6, column 4 and 5, respectively.

It shows that our calculated results of  $k_{ET}$  for DDQ/DDQ $^{\bullet-}$  system from the two methods are in good agreement with each other, and they are consistent with the experimental values [9].

### 3.6. Discussions on the electron transfer path

Fig. 5 depicted the charge and spin density distributions on both the ground state DDQ $^{\bullet-}$  and the TS complex. It shows that whether in DDQ $^{\bullet-}$  or TS complex, the negative charges are mainly distributed on oxygen atoms and nitrogen atoms. It also indicated that from ground state to transition state, the negative charges on O $_{12}$  increases and those on O $_9$  decreases, while the change of spin densities is in the opposite direction, and more negative charges are distributed on N $_{13}$  than on N $_{14}$  in the TS complex, i.e. the negative charges of DDQ $^{\bullet-}$  are transferred from the lower side to the upper side of the molecule. And it can be seen from the charges and spin densities on DDQ in the TS complex that

the number of negative charges on O $_{24}$  and N $_{28}$  is greater than that on O $_{15}$  and N $_{27}$ , respectively; while the magnitude of spin densities on O $_{24}$  and N $_{28}$  is less than that on O $_{15}$  and N $_{27}$ , respectively. Therefore, in the self-exchange ET process between DDQ and DDQ $^{\bullet-}$ , the electron may be transferred from O $_{12}$  and N $_{13}$  of DDQ $^{\bullet-}$  to O $_{24}$  and N $_{28}$  of DDQ.

## 4. Conclusions

1. The results of internal reorganization energy  $\lambda_i$  from AM1, PM3 and B3LYP/6-31G(d), 6-31+G(d) methods are 34.65, 38.07, 40.93 and 41.92 kJ/mol, respectively, which are reasonable according to Nelsen's model and they are consistent with reported result of  $\lambda_i$  (45.3 kJ/mol). While those from HF(3-21G, 6-31G, 6-31G(d), 6-31+G(d)) are too large (about 90 kJ/mol) because of not considering the effect of electron correlation. Therefore, it is very important to include the effects of electron correlation when  $\lambda_i$  is to be calculated.
2. The center-to-center distance is 5.4581 Å for DDQ/DDQ $^{\bullet-}$  ET couple in the precursor complex, and the corresponding closest distance between DDQ and DDQ $^{\bullet-}$

(mass center of DDQ and O<sub>12</sub> of DDQ<sup>-•</sup>) is 2.7692 Å. There should be some strong intermolecular interactions between the reactant molecules within so small distance, which is the reason why the ET behavior between DDQ and DDQ<sup>-•</sup> does not correlate with Marcus's theory. Furthermore, the ET matrix element  $V_{ip}$ , 0.219 eV, is greater than  $RT$  ( $RT = 0.025$  eV,  $T = 293$  K). This indicates an adiabatic ET reaction, and large  $V_{ip}$  will lead to the solvent dynamic effect.

- The calculated results of self-exchange ET rate constant  $k_{ET}$  for DDQ/DDQ<sup>-•</sup> couple from the two methods in different solvents CH<sub>3</sub>CN, benzonitrile, acetone, CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> at  $T = 293$  K are in good agreement with each other, and they are consistent with the experimental ones.
- In the self-exchange ET process between DDQ and DDQ<sup>-•</sup>, the electron may be transferred from O<sub>12</sub> and N<sub>13</sub> of DDQ<sup>-•</sup> to O<sub>24</sub> and N<sub>28</sub> of DDQ.

### Acknowledgements

The project was supported by the National Natural Science Foundation of China (29733100,39890390) and the State Key Basic Research and Development Plan (G1998010100). The authors would like to thank Prof. G. Grampp for helpful discussion on the DDQ/DDQ<sup>-•</sup> couple. We thank Dr. Dupuis and Prof. X.Y. Li for the allowance of use of the HONDO 99 package and thank Prof. X.Y. Li for his constructive suggestion and helpful discussion. S.H. Ma thanks Dr. Wang Yanni for her help in the calculation in the beginning of the project.

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