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Using ab initio and density functional calculations, we studied photoexcitation of a charge-balanced electron donor–acceptor (DA) complex comprised of tetracyanoethylene (TCE) and tetramethylethylene (TME). We considered both the TCE-TME stacked conformer and a possible conformer with a solvent molecule (dichloromethane) inserted between TCE and TME. The photoexcitation of the DA complex can directly form a charge transfer (CT) state. Our theoretical investigations show that the CT state can also be produced from the decay of higher excited states. Using the continuum model, we investigated the solvent effects on CT absorption, local excitation, and CT emission in the polar solvent. The equilibrium solvation energies of the ground and excited states of the DA complex were calculated using the self-consistent reaction field method, and then the correction of nonequilibrium solvation energies for the vertical transitions was made. The transition energies (i.e., CT absorption for the DA complexes and CT emission for the contact ion pair complexes) in the polar solvent show redshifts relative to those in the gas phase. © 2003 American Institute of Physics. [DOI: 10.1063/1.1613252]

I. INTRODUCTION

Photoinduced electron transfer (ET) has attracted much interest in both experimental and theoretical studies. In particular, the dynamics of the photoinduced charge separation has been extensively studied based on the current ET theory for the last decades.1–4 It is well known that an acceptor and a donor can form a charge-balanced DA complex, and the photoexcitation of this complex can lead to charge transfer (CT) absorption.1–8 The structures of such complexes tend to have two types: coplanar and face-to-face stacked conformations.9 Although charge separations and solvent effects upon CT transitions have been extensively studied, little attention has been paid to the conformations of charge-balanced DA complexes which are very critical in the complexes involving π electrons. In the π complexes, the dispersion energy is important, and so in the study of structure of the complex, Møller-Plesset second order perturbation (MP2) calculations are more reliable than the density functional theory (DFT). In addition, Gould and Kochi10,11 have shown that steric effects tend to increase the distance between the acceptor and donor. Therefore, the accurate study of geometries of charge-balanced DA complexes is of importance. Since the relaxation of these CT excited states will lead to the formation of ion pair complexes, there are two kinds of ion pair complexes, i.e., contact ion pair (CIP) and solvent separated ion pair (SSIP) complexes. An important difference between CIP and SSIP complexes is that CIP complexes show characteristic CT emissions, whereas the SSIP complexes do not.3,7

In the present study, we investigated photoexcitation of the charge-balanced DA complex comprised of TCE and TME. After obtaining reasonably accurate structure of the DA complex using MP2 calculations, we studied the CT ab-
The absorption of DA complex and CT emission of CIP complex using both the configuration interaction method by single excitation (CIS) with the GAUSSIAN suite of programs,\textsuperscript{12} and the complete active space self-consistent-field (CASSCF) method with the MOLPRO package\textsuperscript{13} at the MP2 optimized geometries. In this work, solvation energies and dipole moments of the ground and excited states were estimated by Onsager self-consistent reaction field (SCRF) method.\textsuperscript{14,15}

A few solvation models have been developed by Tomasi, Perscino, and Truhlar et al.\textsuperscript{16–18} However, the theoretical estimation of solvent effects on the properties of molecules remains as a challenging subject. Since the CT transition of the DA complex involves a large change of dipole moment, compared with the absorption in the gas phase, a redshift of the DA complex remains as a challenging subject. Since the CT transition of the solute molecule is calculated by solving the one-electron Fock equation in a self-consistent scheme. When the solute polarization energy is included, the total energy of the system is given by

$$E = \langle \psi | H_0 | \psi \rangle - \frac{1}{2} \mu \cdot R,$$

where $\mu$ is the dipole moment of ground state.

However, according to the Franck–Condon principle, during the vertical transition from the ground to excited state, only the electronic response of the solvents can keep up with the change of the solute charge distribution, while the orientational polarization of the solvent cannot adjust to the change of solute dipole. Therefore, the nonequilibrium solvation energy correction needs to be made. Compared with the transition energy obtained by SCRF calculation, in the absorption process the nonequilibrium solvation energy correction results in blue-shift, and the transition energy in polar solvent is

$$\Delta E^{\text{Sol}} = \hbar \nu_0 + \Delta (h \nu)^{\text{neq}},$$

where $\Delta E^{\text{Sol}}$ is the transition energy for the Frank–Condon transition, $\hbar \nu_0$ is the transition energy between two equilibrium states, and $\Delta (h \nu)^{\text{neq}}$ is the nonequilibrium solvation energy correction.

Since in the vertical transition only the electronic response of the solvent can keep up with the change of the solute charge distribution, the reaction field felt by the excited state is usually treated as the sum of two parts: the orientational (slow) and the electronic (fast) components.\textsuperscript{14,21–24} According to the treatment of Newton and Friedman,\textsuperscript{25} the solvation of the vertical excited state is defined as a reversible path connecting the ground and excited states, and thus the nonequilibrium solvation energy in the vertical transition can be written as:

$$E^{\text{neq}} = - \left( \frac{e - 1}{2 e + 1} \right) \frac{2 n^2 - 1}{2 n^2 + 1} \frac{2 (\mu_x - \mu_y) \mu_y}{1} \frac{a^3}{a_0^3},$$

$$- \left( \frac{e - 1}{2 e + 1} \right) \frac{2 n^2 - 1}{2 n^2 + 1} \frac{\mu_x^2}{a_0^3}.$$

In the equilibrium case, both the orientational and electronic polarizations of solvent are fully equilibrated with the solute dipole. In the framework of Onsager model, the equilibrium solvation energy of excited state is

$$H_1 = - \mu \cdot R,$$

while the reaction field $R$ is

$$R = \frac{2}{a_0} \frac{\mu}{2 e + 1} \left( e - 1 \right).$$

where $a_0$ is the radius of the spherical cavity. The total energy of a solute molecule is calculated by solving the one-electron Fock equation in a self-consistent scheme. When the solute polarization energy is included, the total energy of the system is given by

$$E = \langle \psi | H_0 | \psi \rangle - \frac{1}{2} \mu \cdot R,$$

where $\psi$ is the total wave function of the solute molecule. Thus, the equilibrium solvation energy of the ground state can be expressed as

$$E^{\text{eq}} = - \left( \frac{e - 1}{2 e + 1} \right) \frac{2 n^2 - 1}{2 n^2 + 1} \frac{2 (\mu_x - \mu_y) \mu_y}{1},$$

where $\mu_x$ is the dipole moment of ground state.

In the framework of Onsager model, the equilibrium solvation energy of excited state is

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$$E = \langle \psi | H_0 | \psi \rangle - \frac{1}{2} \mu \cdot R,$$

where $\psi$ is the total wave function of the solute molecule. Thus, the equilibrium solvation energy of the ground state can be expressed as

$$E^{\text{eq}} = - \left( \frac{e - 1}{2 e + 1} \right) \frac{2 n^2 - 1}{2 n^2 + 1} \frac{2 (\mu_x - \mu_y) \mu_y}{1},$$

where $\mu_x$ is the dipole moment of ground state.
\[ E^q_e = -\frac{1}{a_0} \mu_{e^*} \mu_e \left[ \frac{1}{2} e + 1 \right]. \]  

Under the framework of the Onsager model, the nonequilibrium solvation energy correction is

\[ \Delta(h \nu)^{neq} = E^{neq}_e - E^q_e = \frac{(\mu_{e^*} - \mu_e)^2}{a_0^2} \left[ \frac{1}{2} e + 1 \right]. \]

Compared to the case of the absorption, the situation is reversed in the emission process. Assuming that the solvent relaxation time is much shorter than the lifetime of the \( S_1 \) state, the excited state will be fully relaxed and equilibrated in the solvent. In the emission process, the ground state experiences the orientation-related interaction for the reaction field corresponding to the dipole moment of the \( S_1 \) state. The correction of the nonequilibrium solvation energy can be obtained from Eq. (9) by exchanging “e” and “g.” In the emission process, the nonequilibrium solvation energy correction results in redshift, and the transition energy in polar solvent is

\[ \Delta E^\text{red} = h \nu^0 - \Delta(h \nu)^{neq}. \]

We use this equation to obtain the nonequilibrium solvation energy correction.

### III. RESULTS AND DISCUSSION

#### A. Isolated donor and acceptor (TME and TCE) and the gas-phase absorption

TCE is a ubiquitous organic oxidant, and frequently acts as a strong electron acceptor in ET reactions, while TME is an electron donor. The ground state geometries of TCE and TME were optimized at the MP2/6-31G** level. The structure of \( D_{2h} \) symmetry of TCE is a minimum energy geometry, and the calculated geometrical parameters agree well with the values obtained by electron diffraction and neutron diffraction [Fig. 1(a)].\(^{26-28}\) The most stable conformer of TME has \( C_2 \) symmetry [Fig. 1(b)], whereas the conformation of \( D_{2h} \) symmetry is a transition state at the MP2/6-31G** level.

Since the correlation energy is important for these structures, it is desirable to carry out the multiple reference (MR) CI type calculations\(^{29}\) and complete active space SCF-second order perturbation theory (CAS-PT2).\(^{30}\) However, these calculations are feasible only for relatively small molecules at the present status. Time-dependent density-functional theory (TD-DFT) with the adiabatic approximation employing the exchange-correlation functionals appears to work very well for low-lying valence excitations.\(^{31-33}\) However, we find that these methods give somewhat small values for the transition energy of the CT state for the DA complex because the DA complex is a \( \pi \)-complex involving \( \pi-H \) interactions,\(^{34,35}\) and so the dispersion energy which the DFT calculation cannot take into account is important in the DA complex. Therefore, we used the MP2/6-31G** optimized geometries for the TCE and TME complexes. The excited states were investigated using CIS, TD-DFT, and CASSCF methods with the 6-31+ + G** basis set. Some investigations showed that some low-lying excited states of TME are probably Rydberg states.\(^{36}\) The excited states of TME and TCE were investigated both using CIS and TD-DFT methods with 6-31+ + G** and SVP+Diffuse+Ryderberg [SVP(D, R)] basis sets.

The energies, the transition dipole moments, and the oscillator strengths of the excited singlet states of TME and TCE are listed in Table I. The excitation from \( S_0 \) to \( S_1 \) results from the electron transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). HOMO and LUMO of the ground states of TME and TCE were obtained using the SVP(D, R) basis set, and are shown in Fig. 2. The excited state of TME for the transition \( S_0 \to S_1 \) yields a transition energy of 6.104 eV at the CIS/6-31+ + G** level, and 5.546 eV at the level of Becke–Lee–Yang–Parr exchange functionals (BLYP) with the 6-31+ + G** basis set. Both CIS and TD-DFT calculations show that the oscillator strength of the transition is small. From the CIS and TD-DFT calculations, we find that the \( 3^1A, 1^1B, 2^1B \) states are nearly degenerate in energy. The \( 3^1B \) state, the fifth singlet excited state, arises from the...
TABLE I. Low-lying excited states of TME and TCE by CIS, TD-DFT/BHLYP, and CASSCF calculations using the 6-31 + + G** and SVP(D,R) basis sets.*

<table>
<thead>
<tr>
<th>State</th>
<th>Transition</th>
<th>CASSCF</th>
<th>TD-BHLYP/SVP(D,R)</th>
<th>TD-BHLYP/6-31++G**</th>
<th>CIS/SVP(D,R)</th>
<th>CIS/6-31++G**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E</td>
<td>m_o</td>
<td>E</td>
<td>m_o</td>
<td>E</td>
</tr>
<tr>
<td>TME</td>
<td>2 1A</td>
<td>HOMO→LUMO+3</td>
<td>6.104(0.001)</td>
<td>0.20</td>
<td>6.004(0.001)</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>3 A</td>
<td>HOMO→LUMO+3</td>
<td>6.861(0.001)</td>
<td>0.00</td>
<td>6.593(0.000)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1 1B</td>
<td>HOMO→LUMO+6</td>
<td>6.934(0.001)</td>
<td>0.17</td>
<td>6.719(0.001)</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>2 1B</td>
<td>HOMO→LUMO+6</td>
<td>6.945(0.003)</td>
<td>0.34</td>
<td>6.723(0.001)</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>3 1B</td>
<td>HOMO→LUMO+6</td>
<td>7.233(0.021)</td>
<td>4.76</td>
<td>7.076(0.035)</td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>4 1A</td>
<td>HOMO→LUMO+6</td>
<td>7.500(0.005)</td>
<td>0.42</td>
<td>7.083(0.014)</td>
<td>0.71</td>
</tr>
<tr>
<td>TCE</td>
<td>1 1B1u</td>
<td>HOMO→LUMO</td>
<td>4.865(0.059)</td>
<td>5.55</td>
<td>4.871(0.050)</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td>1 1B1g</td>
<td>HOMO→LUMO</td>
<td>5.321(0.000)</td>
<td>0.00</td>
<td>5.322(0.000)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1 1B2u</td>
<td>HOMO→LUMO</td>
<td>5.715(0.000)</td>
<td>0.02</td>
<td>5.222(0.000)</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>1 1B2g</td>
<td>HOMO→LUMO</td>
<td>5.725(0.000)</td>
<td>0.00</td>
<td>5.720(0.000)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1 1A1u</td>
<td>HOMO→LUMO</td>
<td>5.737(0.000)</td>
<td>0.00</td>
<td>5.736(0.000)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1 1B2a</td>
<td>HOMO→LUMO</td>
<td>6.229(0.102)</td>
<td>2.08</td>
<td>6.567(0.147)</td>
<td>2.62</td>
</tr>
</tbody>
</table>

*a The experimental transition energy (\(\lambda_{exp}\)) of TME is 6.633 eV (53 500 cm⁻¹) (Ref. 36), and that of TCE is 4.592 eV (33 800 cm⁻¹) (Ref. 37).

*b \(E\) is the relative energy (eV) of the excited state with the ground state \(S_0\) being taken zero. The oscillator strength \(f\) is given in parentheses.

*c \(m_o\) is the transition dipole moment between \(S_0\) and the \(i\)th excited state.

*d According to the TD-DFT/(B3LYP)/6-31+ + G** calculations (not listed in the table), the \(S_0→S_1\) transition energy of TME is 6.432 eV, and the \(S_0→S_1\) transition energy of TCE is 4.119 eV. This has been slightly underestimated possibly because the dispersion energy is not properly correlated.

HOMO→LUMO+5 transition. The transition energies from \(S_0\) to \(S_5\) are 7.233 eV at the CIS/6-31+ + G** level, and 6.613 eV at the BHLYP/6-31+ + G** level, respectively. The transition energy of the maximum absorption obtained from the experimental observation is 6.633 eV. The oscillator strength obtained at the CIS/6-31+ + G** and BHLYP/6-31+ + G** calculations, are \(f=0.621\) and \(f=0.435\), respectively. The transition dipole moments and oscillator strengths show that the excitations from \(S_0\) to \(S_1, S_2, S_3, S_4, S_5\) states are very weak. Therefore, the transition of the maximum absorption may arise from the transition from \(S_0\) to \(S_5\). The transition dipole moments obtained by CIS calculations agree with those by the TD-DFT calculations. The directions of transition dipole moments are shown in Fig. 3(a).

In the CASSCF calculations, eight active electrons and ten active orbitals were considered in the optimization of the excited state of TME. The transition energies obtained from CASSCF/6-31+ + G** calculations are between those of the CIS and TD-DFT calculations. The gas-phase UV absorption spectrum of TME shows a strong band with maximum at 6.633 eV (53 500 cm⁻¹) and a weak low-energy band starting around 5.344 eV (43 100 cm⁻¹). The intense band at 6.633 eV is generally accepted as the \(\pi→\pi^*\) transition of TME. Since the 3 1A, 1 1B, 2 1B states are nearly degenerate in energy, the broad band absorption starting at 5.344 eV may probably attribute to the transitions from ground state to the \(S_2, S_3, S_4, S_5\) states. However, there is a controversy as to whether the broad low-energy band is associated with the \(\pi→\pi^*\) transition or \(\pi→3\delta\) transition. In this work, the orbital analyses from the CASSCF calculations show that the broadband absorption arise mainly from \(\pi→3\delta\) Rydberg transitions, while \(S_5\) (3 1B) arises from \(\pi→\pi^*\) transition (Table II).

In the case of TCE, the transition energies for \(S_0→S_1\) at the CIS/6-31+ + G** and BHLYP/6-31+ + G** levels are 4.865 and 4.365 eV, respectively. Both CIS and TD-DFT methods show that the intensity for \(S_0→S_1\) transition is very strong. The CIS calculations show that the 1 1B2u, 1 1B2g, 1 1A2 states are nearly degenerate, and so are the TD-DFT calculations. However, the transition energy of the 1 1B3u state obtained by CIS calculation is slightly lower than the TD-DFT calculations.

FIG. 2. HOMO (lower) and LUMO (upper) of the ground states of TME (a) and TCE (b). HOMO and LUMO of TME and TCE were obtained from the calculations using SVP(D,R) basis set.

FIG. 3. Orientations of transition dipole moments of the low-lying excited states of TME (a) and TCE (b).
than that of the $1^1B_{2g}$ state, while the order is reversed for the TD-DFT calculations, namely, the $1^1B_{3u}$ state lies below the $1^1B_{2g}$ state. Since both methods indicate that such three low-lying states are nearly degenerate, the different order for the three states may be acceptable. The CIS and TD-DFT calculations show that the intensity for $S_0\rightarrow S_6$ transition is also strong. The orbital energy analysis by CI density and TD-DFT density shows that the orbitals from the HOMO-6 to HOMO-2 are nearly degenerate, explaining that the energies of the excited states $1^1B_{3u}$ and $1^1B_{2g}$ for the transitions from lower orbitals are lower than those of the excited states $1^1A_u$ and $1^1B_{2g}$ for the transitions from higher orbitals. The transition dipole moments by CIS calculations agree with those by the TD-DFT calculations. The directions of transition dipole moments for TCE are shown in Fig. 3 with those by the TD-DFT calculations. The directions of the transition dipole moments by CIS calculations agree with the experimental result. Since both methods indicate that such three low-lying states are nearly degenerate, the different order for the three states may be acceptable.

<table>
<thead>
<tr>
<th>Transition</th>
<th>CIS $E$</th>
<th>CIS $f$</th>
<th>CIS $m_0$</th>
<th>CIS $\mu$</th>
<th>CIS $E$</th>
<th>CIS $\mu$</th>
<th>CIS $\mu_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>3.292</td>
<td>0.015</td>
<td>1.08</td>
<td>12.46</td>
<td>2.930</td>
<td>16.01</td>
<td>14.51</td>
</tr>
<tr>
<td>$S_2$</td>
<td>4.903</td>
<td>0.419</td>
<td>4.75</td>
<td>1.84</td>
<td>1.95</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>$S_3$</td>
<td>5.323</td>
<td>0.000</td>
<td>0.06</td>
<td>0.89</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>

$^a$E is relative energy with the state energy of $S_0$, being zero, and in eV. The CIS calculations were performed at the 6-31+G** level, but the basis set was reduced to 6-31+G* for the CASSCF calculation.

$^b$Transition dipole moments $m_0$ and dipole moments ($\mu$) are given in D. Dipole moments are at the direction from the center of TCE to that of TME. The CIS calculations of conformer $I$ show that the transition dipole moment $m_{21}$ is 3.94 D and the oscillator strength of the $S_2\rightarrow S_1$ transition is 0.095, while the transition dipole moment $m_{31}$ is 0.08 D and the oscillator strength of the $S_2\rightarrow S_1$ transition is less than 0.001.

$^c$In this work, SCRF calculations were performed based on CIS/6-31G** method. The dipole moments of $S_0$ of conformer $I$ by SCRF calculations is 0.93 D, and that of conformer $II$ is 3.60 D.

### B. Photoexcitation of the charge-balanced DA complex

#### 1. Geometry optimizations

Experiments and theoretical calculations all have shown that the stacked conformation of the charge-balanced DA complex is the most stable, resulting in the maximum overlap between the $\pi$-type molecular orbitals in the isolated species. The DA structure was previously investigated using HF calculations. However, since this system is a $\pi$ complex in which the electron correlation is critical, here we fully optimized the geometry using MP2/6-31+G* calculations (Fig. 4). The stabilization energy of the charge-balanced DA complex was calculated without and with basis set superposition error (BSSE) correction by counterpoise method. Since the present basis set is the mid-size, the electron correlation tends to be underestimated, while the complexation energy is overestimated due to the BSSE. For this mid-size basis set, the 50% BSSE correction tends to be more realistic. Thus, the complexation energies are reported with the median value ($\Delta E^\text{H}$) between the BSSE-uncorrected ($\Delta E^\text{H}^\text{unc}$) and BSSE-corrected ($\Delta E^\text{H}^\text{corr}$) values, while the 50% BSSE error is given as the error bar. The MP2/6-31+G* complexation energies ($\Delta E^\text{H}$) for I and II are 9.30 and 10.37 kcal-mol$^{-1}$, respectively. For conformer I, the center-to-center distance is $d = 3.26$ Å. The center-to-center distance is much closer than that obtained from HP/6-31+G** methods (4.5 Å). The complexation energies of I and II are 9.30 ± 3.12 and 10.37 ± 4.50 kcal-mol$^{-1}$, respectively, where the median value between the BSSE-uncorrected and BSSE-corrected values (i.e., the half BSSE corrected value) is given as a more realistic value.
conformer I shows that the charge (in a.u.) located on the TME and TCE moieties are 0.95 and $-0.95$, respectively. One of the singly occupied molecule orbitals (SOMOs) in $S_1$ state is $\pi$-type orbital located on TME moiety, and the other is a $\pi^*$-type orbital of TCE, as shown in Fig. 5. Therefore, the $S_1$ of conformer I is a CT excited state resulted from an electron being out of the $\pi$-type HOMO (located on the TME moiety) into the $\pi^*$-type LUMO (located on the TCE moiety). The transition energy for $S_0\rightarrow S_1$ at the CIS/6-31$^+ + G^*$ level is 3.292 eV, and the dipole moment in the gas phase is 12.46 D and that in dichloromethane is 14.51 D. The transition dipole moment was calculated to be 1.08 D, with an oscillator strength $f=0.015$. The oscillator strength of the $S_0\rightarrow S_1$ transition indicates that the intensity of such CT absorption is weak. We have also carried out CASSCF calculations. Since the CT transitions involve with the frontier orbitals, we have considered four HOMOs and four LUMOs in the CASSCF calculations. Due to the limitation of the choice of the active orbitals, only the CT states were investigated.

The $S_2$ state of conformer I shows the characteristics of locally excited (LE) state, arising from an electron being out of the $\pi$-type HOMO-1 into the $\pi^*$-type LUMO. The NBO analysis shows that one of SOMOs in $S_2$ state is $\pi$-type orbital located on the TCE moiety, and the other is a $\pi^*$-type orbital contributed also from TCE. The CIS/6-31$^+ + G^*$ calculation gives a large transition dipole moment, $m = 4.75$ D, and a large oscillator strength, $f=0.419$. This indicates that the intensity of the transition from $S_0$ to $S_2$ is much stronger than that of the CT absorption. The energy for the $S_0\rightarrow S_2$ transition is 4.903 eV, which is very close to the calculated value of the first excitation of TCE. The CIS calculations show that the $S_3$ state is also a LE state located on TCE moiety. The small transition dipole moment of the $S_0\rightarrow S_3$ transition and the negligible oscillator strength obtained from our calculations indicate that such transition is very weak.

At the CIS/6-31$^+ + G^*$ level, the excitation energy of the $S_0\rightarrow S_1$ transition of conformer II is 4.839 eV, close to the value of the first excitation of TCE, 4.865 eV. The NBO analysis shows that the $S_1$ state has the LE state characteristics, and the $S_1$ state results from a $\pi-\pi^*$ excitation in the TCE moiety. The calculation shows that the $S_2$ state is also a LE state in the TCE moiety, with negligibly small oscillator strength. From the oscillator strength and transition dipole moment, we find that the intensity of the $S_0\rightarrow S_1$ transition

FIG. 4. Two conformations of the charge-balanced DA complex obtained at the MP2/6-31$^+ + G^*$ level (the center-to-center distances are given in angstrom).

In consideration that the conformational change due to the presence of solvent may lead to different conclusion, we investigated conformer II that the acceptor and donor are separated by a solvent molecule. Conformer II is a stacked structure of $C_2$ symmetry, and the center-to-center distance between the donor and acceptor is $d=7.66$ Å (Fig. 4). Although this complexation energy is comparable to (or slightly larger than) conformer I, conformer II may be less stable than conformer I when the extra binding energy for conformer I by the presence of a solvent molecule is considered.

2. Electronic structures of the ground states and vertical excited states

We carried out the natural bond orbital (NBO) population charge analysis of excited state at the CIS/6-31$^+ + G^*$ level. The NBO population analysis of $S_1$ state of
of conformer II is very strong, while that of the $S_0 \rightarrow S_2$ transition is very weak. The $S_1$ state arises from the HOMO-1→LUMO transition, and the $S_2$ state, from the HOMO-7→LUMO transition. The NBO population analysis shows that the $S_3$ state is a CT state, with the net charges 0.99, 0.01, and $-1.00$ a.u. on the TME, the inserted solvent molecule, and the TCE, respectively. The CT from the inserted solvent molecule to the electron donor is apparently negligible. The orbital analysis shows that the $S_3$ state of conformer II arises from the HOMO→LUMO transition. The transition energies obtained from the CIS/6-31+ +G** and CASSCF/6-31+G* calculations are 5.554 and 5.129 eV, respectively. However, owing to the small transition dipole moment and the negligible oscillator strength for the $S_0 \rightarrow S_1$ transition, this CT absorption of conformer II is very weak.

The transition energy increases when a solvent molecule is inserted between the donor and acceptor, and its intensity of CT absorption is much weaker. Therefore, the CT absorption observed in experiments would arise from the photoexcitation of conformer I, while not from the excitation of conformer II. The CT state can also be produced through another pathway, e.g., a decay of higher excited states. The CIS calculations of conformer I show that the transition dipole moment of the $S_2 \rightarrow S_1$ transition is 3.94 D and the oscillator strength is 0.095, while the transition dipole moment of the $S_3 \rightarrow S_1$ transition is 0.08 D and the oscillator strength is less than 0.001. Since the intensity of the $S_0 \rightarrow S_2$ transition is very strong, and the $S_0 \rightarrow S_1$ transition is also strong, we can predict that the CT state of conformer I can also be produced from the decay of $S_2$ state. From the SCRF calculations, the dipole moments for both ground and excited states increase in magnitude by approximately 10% in going from the gas-phase to solution-phase.

C. Charge recombination of ion pair complex

In general, the geometry of the ground state remains unchanged during the photoexcitation of the charge-balanced DA complex. However, if the lifetime of the CT excited state $S_1$ is much longer than the solvent relaxation time, the $S_1$ state at the equilibrium geometry of charge-balanced DA complex would relax to the equilibrium geometry of CIP complex. The investigation of the CT transitions of the two conformations of the charge-balanced DA complex shows that the photoexcitation of conformer I would lead to the formation of CIP complex, while the excitation of conformer II would not lead to the formation of CIP complex. In this work, optimization of the CIP complex was performed at the CIS/6-31+G* level. The full optimized structures of CIP complex are shown in Fig. 6. A frequency analysis at the same level shows that the optimized geometry is a minimum energy configuration. The stabilization energy of the CIP complex is defined as

$$E_s = \sum M E^{DA}(M) - E(D^+\cdots A^-),$$

(11)

where $E_s$ is the stabilization energy, $E(D^+\cdots A^-)$ is the total energy of CIP complex, and $E^{DA}(M)$ is the energy of the monomeric species calculated with the whole basis set of CIP complex. The stabilization energy ($E_s$) of CIP complex reaches a maximum value of 20.35 kcal mol$^{-1}$ at $d = 3.13$ Å. In contrast to the charge-balanced DA complex, the CIP complex has extremely large stabilization energy, due to the Coulomb interaction.

After the geometry optimizations of CIP complex, the electronic states at the equilibrium geometry of CIP complex with $C_2$ symmetry were investigated using CIS and CASSCF methods. The CIS calculation was performed at the 6-31+G** level, but the basis set was reduced to 6-31+G* for the CASSCF calculation. In the CASSCF calculations, eight active electrons and eight active orbitals are included. The ground state and $S_1$ state are presented in Table III, along with their dipole moments. The NBO analysis of the $S_1$ state at the equilibrium geometry of the CIP complex shows that the net charges of the donor and acceptor moieties are 0.92 and $-0.92$ a.u., respectively. The $S_1$ state with $A$ symmetry is charge-separated like a diradical. The dipole moment of the $S_1$ state of CIP complex is 12.02 D at the CIS/6-31+G* level, and 15.17 D at the CASSCF/6-31+G* level. The orientation of the dipole moment of $S_1$ is along the

![Fig. 6. Conformation of CIP complex obtained at the level of CIS/6-31+G*. The center-to-center distance is given in angstrom.](image)

<table>
<thead>
<tr>
<th>Sym</th>
<th>CIS</th>
<th>CASSCF</th>
<th>SCRF</th>
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<tr>
<td></td>
<td>$E$</td>
<td>$m_{01}$</td>
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<tr>
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<td>A</td>
<td>0.00</td>
<td>1.11</td>
</tr>
<tr>
<td>$S_1$</td>
<td>B</td>
<td>2.481</td>
<td>0.92</td>
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$^a$ $E$ is in eV. The $S_0$ state of CIP is charge-balanced. Transition dipole moment and dipole moments are given in D. Dipole moments are at the direction from the center of TCE to that of TME.

$^b$ $\mu$ is the dipole moments in dichloromethane.
direction from TCE to TME in the gas phase, as shown in Fig. 6, and 13.81 D by the SCRF calculation. Since CIP complexes can be identified by the characteristic CT emissions,3,7 we will take into account the solvent effect on the CT emission of the CIP complex in the following section.

D. Solvent effects in the CT transition

Our results for the solvent effects on the transition energies of vertical absorption and emission processes are given in Table V. For comparison with experimental observation, dichloromethane (\( \varepsilon = 9.08, \mu = 1.425 \)) was chosen as the solvent. In this work, SCRF calculations were performed based on CIS/6-31+ + G** method.

The transition energies in gas-phase and in dichloromethane are listed in Table IV. Redshifts of CT absorption and emission in dichloromethane are predicted in our work. The redshift of transition energy is 0.508 eV for the \( S_1 \) CT state of conformer I and its vertical transition energy is 2.784 eV, while the experimental value is 2.296 eV in dichloromethane. Our theoretical result of the transition energy of the CT absorption is overestimated by about 0.5 eV. Since the dipole moment of the LE states of conformer I is very small, the transition energy changes for these LE states are negligibly small in dichloromethane. As shown in Table III, the \( S_1 \) and \( S_2 \) states in the conformer II are LE states. Solvation energies of \( S_1 \) and \( S_2 \) states of the conformer II were also considered. The shifts of transition energies are negligibly small in the polar solvent of dichloromethane. Since the CT state \( S_3 \) in the conformer II has a much larger dipole moment, nearly 40 D, a large red shift in CT transition energy is noted. In dichloromethane, the red shift of transition energy for the CT state of conformer II is predicted to be 2.402 eV, and the vertical transition energy for the CT state is 3.152 eV, while those of the two LE states are 4.839 eV and 5.335 eV, respectively. Therefore, in dichloromethane the transition energy of CT state falls below those of the LE states. In the polar solvent of dichloromethane, the transition energy from \( S_1 \) to \( S_0 \) at the equilibrium geometry of the CIP complex was calculated to be 1.672 eV. The transition energy of the CIP complex in the polar solvent produces a large red shift. The red shift of transition energy in emission process estimated by the present method is 0.809 eV.

Since the result of solvent effects obtained in the framework of Onsager model is qualitative, small discrepancy on the transition energy of the CT absorption between our calculation and experiment could be caused from the inaccuracy of theoretical calculations. Since both equilibrium solvation energy and nonequilibrium solvation energy are considered with the same Onsager model, there is no inconsistency problem. Further investigation on this system is needed, since the realistic environment is much more complicated.
than what we can theoretically simulate in the framework of continuum model.

We now consider the solvent effect on the decay rate of vertical excited state $S_1$ at the equilibrium geometry of ground state, and that at the equilibrium geometry of CIP complex. On the basis of Fermi’s Golden rule, the ET rate constant $k$ is proportional to the square of the electron coupling matrix element. The generalized Mulliken–Hush (GMH) theory for the nonperturbative calculation of the electronic coupling matrix element $\tilde{H}_{12}$ of ET reactions was developed by Cave and Newton. The GMH expression for $\tilde{H}_{12}$ can be written as

$$\tilde{H}_{12} = \frac{E_{12}m_{12}}{\sqrt{\Delta \mu_{12}^2 + 4m_{12}^2}},$$  \hspace{1cm} (12)$$

where $E_{12}$ is the energy gap between the initial adiabatic state and the final one, $\Delta \mu_{12}$ is the dipole moment difference between the two states, and $m_{12}$ is the transition dipole moment connecting the two states. According to Eq. (12) and the results from the CIS/6-31+$\text{+G}^{*\ast}$ calculations, the value of $\tilde{H}_{12}$ for the CT transition between CT state and ground states at the equilibrium geometry of DA complex is estimated to be 6.94 kcal mol$^{-1}$ and 4.76 kcal mol$^{-1}$ at the geometry of the CIP complex. The investigation based on the SCRF calculations shows that the electron coupling matrix elements between CT state and ground state decrease to 3.11 and 2.33 kcal mol$^{-1}$ in dichloromethane. Since ET rate constants are proportional to the squares of the electron coupling matrix element, the decay rate of CT state will be slower in dichloromethane than that in gas phase. According to the theoretical calculations, we can predict that the lifetime of CT state will be longer in dichloromethane than that in gas phase. The electron coupling matrix element of the $S_2 \rightarrow S_1$ transition in dichloromethane is not so different from that in the gas-phase.

IV. CONCLUSION

Using the MP2 method, we investigated the structures of TME, TCE, and two different conformers of the charge-balanced DA complex. The electronic excited states were investigated by using CIS, TD-DFT, and CASSCF methods. An obvious limitation for CIS is the improper treatment of electron correlation. Although the CIS method tends to overestimate transition energies, it may be an appropriate choice in the calculations of low-lying excited states of mid-sized organic systems, since most low-lying excited states of mid-sized organic systems are generally dominated by single excitations. While the TD-DFT method fails to give accurate transition energies for the CT excited states, the CIS and CASSCF methods provide reasonable results for the low-lying excitations of the charge-balanced DA complexes and ion pair complexes. We have compared both CASSCF and CIS calculated CT state results of DA and CIP complexes. We find the CIS method is reliable in photo-induced electron transfer study in the present mid-sized organic systems. The investigations of the low-lying excited states of the charge-balanced DA complex by employing CIS method show that a weak CT absorption observed in experiments may arise from the photoexcitation of the DA complex (conformer I), while the CT absorption arising from the photoexcitation of the solvent separated DA complex (conformer II) is very weak. Our theoretical investigations show that the CT state ($S_1$) of conformer I can also be produced through other pathways, e.g., a decay of higher excited states. The CT state of conformer I can also be produced from the decay of the $S_2$ state.

In a CT transition, charge transfer results in a large change of dipole moment and thus the solvation energy arises mainly from electrostatic interaction. Therefore, it is still appropriate to estimate solvent effects on CT transition by using the continuum model. The SCRE calculation shows that the dipole moments for both ground states and excited states increase in magnitude by approximately 10% in going from gas-phase to solution. In this work, the equilibrium solvation energies of the ground and CT excited states were calculated using the SCRF method, and then the correction of nonequilibrium solvation energies for the vertical transitions was made. The red shifts of the CT absorption of DA complex and CT emission of CIP complex are predicted in dichloromethane. Compared with the experimental value, our theoretical result of the transition energy of the CT absorption is overestimated by about 0.5 eV. Since CIS overestimates the transition energies by 0.3–0.6 eV for the low-lying excited states of our systems, our treatment of solvent effects on CT transition is appropriate in the present mid-sized organic systems.

According to GMH theory, theoretical calculations show that the electron coupling is stronger in the equilibrium geometry of DA complex than in the equilibrium geometry of CT state. Based on the Golden rule and GMH model, the solvent effect on the charge recombination of CT state was also investigated in this work. The theoretical investigation based on SCRF calculations shows that the charge recombination of CIP complex will be slower in dichloromethane than that in gas phase.