

## Electronic Couplings in Organic Mixed-Valence Compounds: The Contribution of Photoelectron Spectroscopy

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**Abstract:** We show that the electronic coupling in strongly coupled organic mixed-valence systems can be effectively probed by means of gas-phase ultraviolet photoelectron spectroscopy (UPS). Taking six diamines as examples, the UPS estimates for the electronic couplings  $H_{ab}$  are compared with the corresponding values determined from the intervalence charge-transfer absorption bands and from electronic structure calculations. Similar trends are observed for the  $H_{ab}$  values estimated from UPS and optical spectra; this provides support for the applicability of Hush theory to strongly coupled organic mixed-valence systems. The UPS electronic couplings are found to be somewhat smaller than those from optical spectroscopy, which is attributed to the role of vibronic coupling to symmetrical modes; when corrected for this vibronic coupling, the UPS  $H_{ab}$  estimates confirm that triarylamine-based mixed-valence systems are close to the class-II/class-III borderline.

### Introduction

Organic mixed-valence (MV) systems are receiving increasing attention because of the insight they provide into the understanding of electron-transfer phenomena.<sup>1–8</sup> They are also of interest due to their relevance to organic electronic materials;

for example, bis(diaryl-amino)biphenyl<sup>9</sup> derivatives are commonly used as hole transport agents in organic light-emitting diodes where the charge carrier is the corresponding mixed-valence cation. Switching devices based on organic mixed-valence systems have also been proposed.<sup>10</sup> The properties of MV systems strongly depend on the extent of electronic coupling between charge-bearing subunits. The magnitude of this interaction is defined by the matrix element  $H_{ab} = \langle \Psi_a | H | \Psi_b \rangle$ , where  $H$  is the molecular Hamiltonian and  $\Psi_a$  and  $\Psi_b$  are the wave functions of the diabatic states, corresponding in dimeric MV systems to the two possible valence structures  $M_a^+ - BR - M_b$  or  $M_a - BR - M_b^+$  (with  $M$  denoting a redox site and  $BR$  the bridge).

The electronic couplings are usually estimated from the analysis of the intervalence charge-transfer (IV-CT) transition. A simple model that has been extensively verified for transition-metal MV compounds and is now increasingly applied to organic MV systems was elaborated by Hush.<sup>11</sup> Using a semiclassical formalism, Hush showed that the electronic coupling is related to the maximum,  $E_{op}$ , and transition dipole moment,  $\mu_{ab}$ , of the IV-CT band as<sup>11</sup>

$$H_{ab} = \frac{\mu_{ab} E_{op}}{eR} \quad (1)$$

Here,  $R$  is the effective separation distance between the donor and acceptor sites (diabatic states).<sup>12</sup>

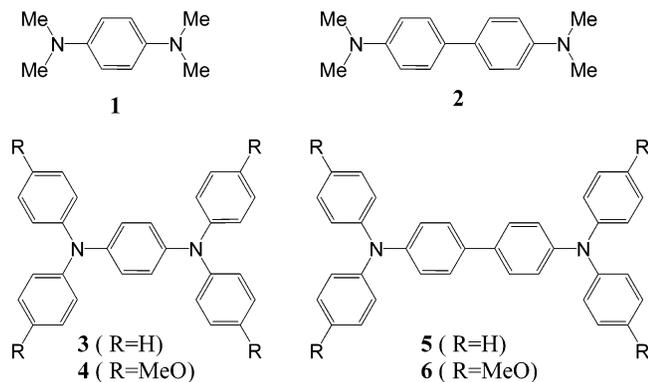
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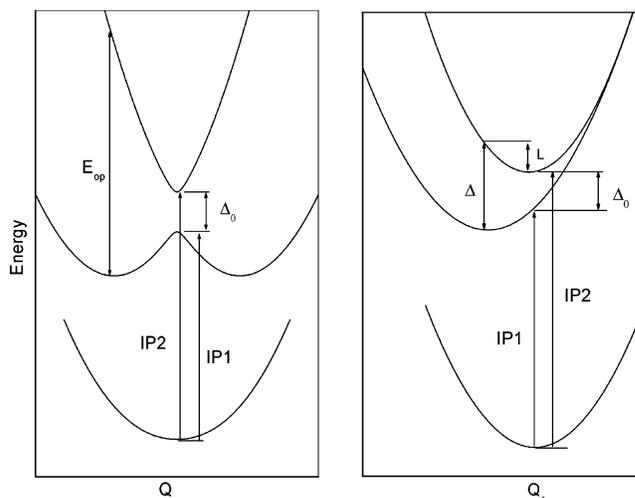


**Figure 1.** Chemical structures of 1,4-bis(dimethylamino)benzene (**1**); 4,4'-bis(dimethylamino)biphenyl (**2**); 1,4-bis(diphenylamino)benzene (**3**); 1,4-bis[di(4-methoxyphenyl)amino]benzene (**4**); 4,4'-bis(diphenylamino)biphenyl (**5**); and 4,4'-bis[di(4-methoxyphenyl)amino]biphenyl (**6**).

Another widely applied experimental method to probe the electronic coupling in organic MV systems is based on the rate of electron exchange between redox centers measured by electron spin resonance (ESR) spectroscopy.<sup>1–3</sup> It has been recently shown that in bis(hydrazine) radical cations<sup>3b</sup> the  $H_{ab}$  values obtained from optical data accurately predict the intramolecular electron-transfer rate constants determined by ESR. However, in several other MV systems, such as those including perchlorinated triphenylmethyl redox sites, interpretation of ESR results requires markedly larger values for  $H_{ab}$  than those obtained from optical measurements.<sup>1c</sup> While the discrepancy between the results might be simply due to the use of erroneous values for  $R$ , it has also been suggested that the use of Hush theory (eq 1) to calculate  $H_{ab}$  may not be correct for strongly coupled organic compounds.<sup>1c</sup>

Many organic MV systems, such as triarylamine-based compounds, have been found to display significant electronic couplings and are intermediate between class II and class III or even belong to class III in the classification scheme of Robin and Day.<sup>13</sup> Such strong electronic interactions generally give rise to electron-transfer rates much faster than the typical time scales of magnetic resonance; as a result, the electronic coupling in these systems can often be obtained only from IV-CT band measurements. Thus, in such instances, it is important to obtain an alternative experimental estimate of the electronic couplings. This would not only provide a better understanding of the electron-transfer phenomena but will help to establish the reliability of the results derived from IV-CT bands.

In this contribution, we report the results of direct measurements of the electronic coupling parameters in amine-based MV systems (see Figure 1) using gas-phase ultraviolet photoelectron spectroscopy (UPS); **1**<sup>+</sup> and **2**<sup>+</sup> are examples of class-III



**Figure 2.** Sketch of typical adiabatic energy surfaces for (a, left) a class-II system in which the horizontal axis represents the antisymmetric vibrational mode  $Q_-$  (in a class-III system, all three surfaces exhibit only one minimum at  $Q_- = 0$ ) and (b, right) a class-II or -III system as a function of the symmetric vibrational coordinate  $Q_+$ .

systems, and **3**<sup>+</sup>–**6**<sup>+</sup> are class-II/class-III borderline systems (see Figure 2). The UPS results are compared with those derived previously from optical data and from electronic structure calculations.

## Experimental and Computational Section

Samples of **1** (98% purity) and **2** (97% purity) were purchased from Aldrich. Compounds **3**–**6** were synthesized according to published procedures.<sup>5,14</sup> Gas-phase photoelectron spectra of **1**–**6** were collected in the Center for Gas-Phase Electron Spectroscopy (Department of Chemistry, The University of Arizona), using an instrument and experimental procedures described in more detail elsewhere.<sup>15a</sup> The samples sublimed ( $10^{-4}$  Torr) at 28–36 (**1**), 130–146 (**2**), 180–200 (**3**), 230–270 (**4**), 220–250 (**5**), and 260–290 °C (**6**) with no evidence of contaminants present in the gas phase during data collection. Instrument resolution during data collection was better than 30 meV (measured using the full width at half-height for the  $^2P_{3/2}$  ionization of Ar). Figures 3 and 4 show the experimental data; in these figures the vertical length of each data mark represents the experimental variance of that point.<sup>15b</sup> The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks. Each Gaussian peak is defined by four degrees of freedom: position, intensity, half-width to the high-binding-energy side, and half-width to the low-binding-energy side. The widths listed in Table 1 are the sum of the two individual half-widths. The peak positions and half-widths are reproducible to about  $\pm 0.02$  eV.

Solutions containing **5**<sup>+</sup> were generated by the addition of excess solid **5** to solutions of  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}]^+[\text{SbCl}_6]^-$  (Aldrich). The IV-CT maximum was observed at 1395 nm ( $7166\text{ cm}^{-1}$ ;  $\epsilon_{\text{max}} = 27\,900\text{ M}^{-1}\text{ cm}^{-1}$ ) in dry dichloromethane, with an additional maximum at 484 nm ( $20\,667\text{ cm}^{-1}$ ;  $\epsilon_{\text{max}} = 20\,900\text{ M}^{-1}\text{ cm}^{-1}$ ). In acetonitrile, the maxima

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- (12) While the parameters  $\mu_{ab}$  and  $E_{op}$  are accessible from optical measurements, the diabatic transfer distance  $R$  cannot in principle be directly measured. Only significantly after the seminal work of Hush, Cave, and Newton<sup>11d</sup> was a prescription developed on how to obtain  $R$ . In addition to  $\mu_{ab}$ , this model requires knowledge of the adiabatic dipole moment shift that can be obtained, in principle, from Stark effect experiments or from quantum-mechanical calculations.
- (13) (a) Robin and Day classified the MV systems into three types: class I, completely valence-trapped (no electronic coupling between redox sites); class II, valence-trapped (weak coupling); and class III, delocalized valency (strong coupling).<sup>13b</sup> (b) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

- (14) The known compound **5** (Madelung, R. *Justus Liebigs Ann. Chem.* **1927**, *454*, 36) was prepared from diphenylamine and 4,4'-dibromobiphenyl using standard palladium-catalyzed methodology (Thayumanavan, S.; Barlow, S.; Marder, S. R. *Chem. Mater.* **1997**, *9*, 3231), and its identity and purity were checked by NMR and mass spectroscopy ( $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 300 MHz)  $\delta$  7.47 (d, 4H,  $J = 8.5$  Hz), 7.27 (t, 8H,  $J = 8.4$  Hz), 7.10 (m, 12H), 7.03 (t, 4H,  $J = 7.3$  Hz);  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 75 MHz)  $\delta$  148.1, 147.2, 135.0, 129.6, 127.6, 124.7, 124.4, 123.2; FAB HRMS calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_2$ : 488.2252; found: 488.2243).
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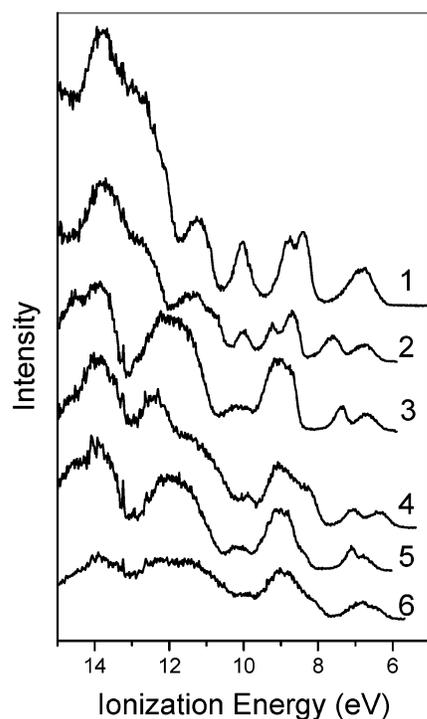


Figure 3. Gas-phase photoelectron spectra of systems 1–6.

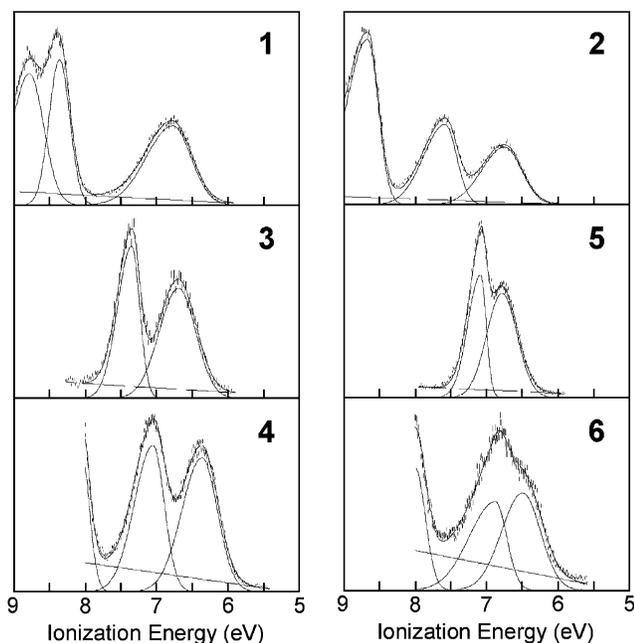


Figure 4. High-resolution close-up of the first ionizations of the benzene-bridged systems 1, 3, and 4, and the biphenyl-bridged systems 2, 5, and 6.

were observed at 1279 nm ( $7816\text{ cm}^{-1}$ ) and 479 nm ( $20861\text{ cm}^{-1}$ ), but the cation was too unstable to allow accurate determination of  $\epsilon_{\text{max}}$  values. The IV-CT data of  $1^+–4^+$  and  $6^+$  have been reported elsewhere.<sup>3,5–7</sup>

As in the case of our previous calculations on 3, 4, and 6,<sup>6,7</sup> the geometry of molecules 1, 2, and 5 were optimized at the density functional theory (DFT) level, using the B3LYP functionals, where Becke's three-parameter hybrid exchange functional is combined with the Lee–Yang–Parr correlation functional.<sup>16,17</sup> The electronic couplings

**Table 1.** Fit Parameters from a Deconvolution with Gaussians of the First Two UPS Ionizations and Experimental and KT-AM1 as Well as TD-DFT Theoretical Values (Obtained at the DFT-Optimized Geometries of the Neutral State) of the Parameter  $\Delta\text{IP}$  (All Values in electronvolts)

	IP <sub>1</sub> position (width)	IP <sub>2</sub> position (width)	$\Delta\text{IP}(\text{UPS})$	$\Delta\text{IP}(\text{KT-AM1})$	$\Delta\text{IP}(\text{TD-DFT})$
1	6.78 (0.74)	8.36 (0.34)	1.58	1.83	1.99
2	6.75 (0.65)	7.58 (0.54)	0.83	0.84	1.25
3	6.70 (0.60)	7.35 (0.36)	0.65	0.63	1.05
4	6.36 (0.59)	7.05 (0.49)	0.69	0.59	0.99
5	6.79 (0.50)	7.09 (0.30)	0.30	0.37	0.76
6	6.50 (0.64)	6.88 (0.62)	0.38	0.35	0.73

$H_{\text{ab}}$  were calculated by means of time-dependent DFT (TD-DFT)<sup>18</sup> at the same B3LYP level. In addition,  $H_{\text{ab}}$  was derived from Koopmans' theorem<sup>19</sup> using Kohn–Sham-type molecular orbitals and Hartree–Fock-type orbitals obtained at both ab initio and semiempirical Austin Model 1 (AM1) levels. All nonempirical calculations were carried out with the 6-31G\*\* split valence plus polarization basis set<sup>20</sup> using the Gaussian 98 suite of programs.<sup>21</sup>

## Results and Discussion

In a  $M_{\text{a}}–\text{BR}–M_{\text{b}}$  system, the splitting between the first and second ionization potentials (IP),  $\Delta\text{IP} = \text{IP}_2 - \text{IP}_1$ , is related to the strength of the electronic coupling in the MV  $M_{\text{a}}^+–\text{BR}–M_{\text{b}}$  state.<sup>11b,22,23</sup> Indeed, since  $\Delta\text{IP}$  is determined at the geometry of the neutral molecule, and consequently at a symmetric radical-cation geometry configuration, the first and second IPs correspond to creation of the delocalized electronic states:

$$\begin{aligned}\Psi_+ &= (1/\sqrt{2})(\Psi_{\text{a}} + \Psi_{\text{b}}) \\ \Psi_- &= (1/\sqrt{2})(\Psi_{\text{a}} - \Psi_{\text{b}})\end{aligned}\quad (2)$$

of the radical cation. Bearing in mind that, in the framework of the two-state model (see Figure 2a), the energy difference,  $\Delta_0 = \epsilon_+ - \epsilon_-$ , between the molecular electronic states  $\Psi_+$  and  $\Psi_-$ , is associated with  $2H_{\text{ab}}$ , then  $\Delta\text{IP}$  gives a direct estimate of the electronic coupling integral,  $H_{\text{ab}} = \Delta\text{IP}/2$ .

In triarylamine MV systems such as  $3^+–6^+$ , it has been shown that the electron-transfer (ET) process is significantly coupled not only to antisymmetric vibrations  $Q_-$  (which are the only vibrations that enter as reaction coordinate in the conventional Hush–Marcus model)<sup>11,24</sup> but also to the totally

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symmetric modes  $Q_+$ .<sup>6,7,25,26</sup> As a consequence, the effective electronic coupling depends on the coordinate of the symmetric vibration(s)<sup>7</sup> (see Figure 2b); therefore, using the  $\Delta IP$  value will give a lower limit estimate for  $H_{ab}$ .

The gas-phase photoelectron spectra of **1–6** are shown in Figure 3; the details of the first ionizations are shown in Figure 4. From these figures and Table 1, it is seen that replacing the methyl groups of **1** and **2** with phenyl groups in **3** and **5** has little effect on the first ionizations  $IP_1$  but leads to very significant reductions in  $\Delta IP$  splitting; on the other hand, methoxy substitution on the terminal rings when going to **4** and **6** causes a 0.3 eV decrease in  $IP_1$  but has little effect on  $\Delta IP$  with respect to **3** and **5**. The replacement of the benzene bridge with a biphenyl bridge of approximately twice the length reduces the  $\Delta IP$  splitting, and thus the electronic coupling, in the same proportion, i.e., by about 50%.

We have recently evaluated  $\Delta_0$  (and thus  $\Delta IP$ ) using several computational approaches: (a) from the energy spectrum obtained at the TD-DFT level, (b) from DFT calculations by computing the energy of the lowest state of each symmetry representation, and (c) by means of Koopmans' theorem (KT).<sup>6</sup> It was found that the best agreement with experimental data was obtained from KT-AM1 calculations; the KT-AM1 values are, therefore, given in Table 1. In the context of electronic structure calculations, it is also particularly interesting to examine the reliability of the TD-DFT results, since this method is currently widely used for excited-state computations. In contrast to the simple semiempirical AM1 calculations, B3LYP-TD-DFT overestimates the  $\Delta_0$  value for all systems; for instance in **5+** and **6+**, the TD-DFT estimates are about 100% larger than the experimental value. This result is in line with current findings that, due to inherent problems in the applied standard exchange-correlation functionals (see for instance ref 27 for detailed explanations), TD-DFT yields substantial errors for systems exhibiting charge-transfer states.<sup>27</sup> We note, however, that for all systems studied here, the error of the TD-DFT estimate is systematic, being about 0.4 eV; this finding suggests that it should be possible to obtain more accurate TD-DFT estimates via an empirical correction.<sup>28</sup>

We now turn to a comparison of the electronic couplings as derived from UPS measurements and obtained from optical data;<sup>29</sup> see Table 2.  $H_{ab}$  for **1+** and **2+** was determined as  $H_{ab} = E_{op}/2$ ,<sup>30</sup> while for systems **3+–6+**  $H_{ab}$  was derived using eq 1. In the latter cases, the question of the appropriate value of  $R$  arises; several experimental and theoretical studies<sup>3g,6,7,31</sup> indicate that the actual electron-transfer distances in organic systems are

**Table 2.** Electronic Coupling  $H_{ab}$  (eV) for Systems **1+–6+** As Obtained from Optical and UPS Measurements

	optical	$\Delta IP/2$	$(\Delta IP/2) + L^a$
<b>1+</b>	1.01 <sup>b,c</sup>	0.79	-
<b>2+</b>	0.61 <sup>b,c</sup>	0.42	-
<b>3+</b>	0.70 (0.45) <sup>d,e</sup>	0.33	0.66
<b>4+</b>	0.53 (0.40) <sup>d,f</sup>	0.35	0.55
<b>5+</b>	0.36 (0.20) <sup>d,g</sup>	0.15	0.30
<b>6+</b>	0.31 (0.19) <sup>d,h</sup>	0.19	0.34

<sup>a</sup> Using the following values of  $L$  (obtained either from electronic structure calculations or the fit of the profile of IV-CT bands): 0.3 eV (**3+**),<sup>7</sup> 0.2 eV (**4+**),<sup>6b</sup> 0.15 eV (**5+**), and 0.15 eV (**6+**).<sup>6b,7</sup> <sup>b</sup> Calculated taking  $H_{ab} = E_{op}/2$ . <sup>c</sup> From ref 3f; in  $CH_3CN$ . <sup>d</sup> Calculated according to eq 1 using  $R = R(TD-DFT)$  and, between parentheses,  $R = R(NN)$ ; both  $R(TD-DFT)$  and  $R(NN)$  values are obtained using the DFT-optimized geometries of the radical-cation state.<sup>6,7</sup> <sup>e</sup> From ref 7:  $E_{op} = 1.50$  eV;  $\mu_{ab} = 8.1$  D in propionitrile/0.2 M (TBA)H. <sup>f</sup> From ref 5b:  $E_{op} = 1.18$  eV;  $\mu_{ab} = 9.2$  D in  $CH_2Cl_2$ . <sup>g</sup> Present work:  $E_{op} = 0.89$  eV;  $\mu_{ab} = 11.0$  D in  $CH_2Cl_2$ . <sup>h</sup> From ref 5b:  $E_{op} = 0.79$  eV;  $\mu_{ab} = 11.6$  D in  $CH_2Cl_2$ .

significantly lower than the estimates based on the direct geometric distances between redox centers. For instance, it was shown very recently<sup>3g</sup> that in delocalized nitro-centered MV systems,  $R$  is only about 25–40% of the direct distance between the nitrogen atoms,  $R(NN)$ . Since for **3+–6+** there are no experimental electron-transfer distances available, Table 2 gives values of  $H_{ab}$  obtained using the following: (i) TD-DFT estimates for the ET distances  $R = R(TD-DFT)$ <sup>6,7</sup> and (ii) the commonly applied approach, where  $R$  is approximated to the nitrogen–nitrogen distance,  $R = R(NN)$ . In **3+–6+**, the ratio  $R(TD-DFT)/R(NN)$  is about 0.6;<sup>6,7</sup> we expect, therefore, the  $H_{ab}$  estimates based on the  $R(TD-DFT)$  values to be more realistic.

The data in Table 2 indicate that the  $H_{ab}$  values estimated optically show trends similar to the  $\Delta IP/2$  values and are comparable in magnitude. However, as expected from the neglect of the interaction with symmetric vibrations (see Figure 2b), the UPS data yield values lower than those derived from optical data. The strength of the electron-vibration couplings with symmetric modes can actually be estimated from the data for **1+** and **2+**: since **1+** and **2+** are class-III systems, the geometries of the ground states of both cation and neutral species possess a symmetric configuration; the difference<sup>32</sup> of 0.38–0.44 eV between  $E_{op}$  and  $\Delta IP$  can then be related to the relaxation processes along symmetric vibrations.

To obtain more accurate estimates of  $H_{ab}$  from UPS data, the  $\Delta IP/2$  values should be corrected to account for the interaction with symmetric vibrations. The most accurate way to accomplish such a correction would be to fit the shape of the ionization spectrum to a vibronic coupling model. However, a simple but effective estimate of the vibronic contribution can be provided by correcting the UPS values according to  $H_{ab} = (\Delta IP/2) + L$ , where  $L$  is the vibrational relaxation energy of the symmetric modes associated with the excitation of the cation from its ground state to its first excited state (see Figure 2b). This approximation assumes that the minimum of the cation

(25) Similar results have been recently found for other delocalized organic MV systems (see refs 3a,g and 8).

(26) (a) Interestingly, the fact that the interaction with symmetric vibrations could play a major role in the charge-transfer process in strongly delocalized MV systems was also predicted by Hush.<sup>26b,c</sup> (b) Hush, N. S. In *Mixed-Valence Compounds: Theory and Applications in Chemistry, Physics, Geology and Biology*; Brown, D. B., Ed.; D. Reidel Academic Publishers: Dordrecht, The Netherlands, 1980. (c) Reimers, R.; Hush, N. S. *Chem. Phys.* **1996**, *208*, 177.

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(28) (a) Recent<sup>28b</sup> investigations of (neutral) heterocyclic conjugated polymers show that after an empirical correction via a linear regression, TD-DFT yields accurate results for band gap. (b) Hutchison, G. R.; Ratner, M. A.; Marks, T. J., *J. Phys. Chem. A* **2002**, *106*, 1059.

(29) It should be noted that the optical values apply to solution, whereas the UPS values are determined in the gas phase. However, in strongly coupled systems, the IV–CT bands show typically little dependence on solvent polarity; this suggests that the medium has little effect on  $H_{ab}$  and, therefore, that solution and gas-phase values should be similar.

(30) (a) In the case of strongly coupled MV systems (class III), the energy of the intervalence transition becomes a direct measure of the electronic coupling:  $E_{op} = 2H_{ab}$ .<sup>10c</sup> The observed vibrational structure in the IV-CT band of **1+**<sup>3f</sup> and **2+**<sup>30b</sup> and the absence of solvent dependence<sup>3f</sup> are features characteristic of a class-III system. (b) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

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(32) A similar difference between  $E_{op}$  and  $\Delta IP$  values has been recently reported for a delocalized phthalocyanine MV dimer: Binstead, R. A.; Reimers, J. R.; Hush, N. S. *Chem. Phys. Lett.* **2003**, *378*, 654.

excited-state surface corresponds to a geometry similar to that of the neutral ground state and that the two cation potential surfaces have similar curvatures (this is justified by our previous work on triarylamine systems which suggests that the geometry of the cation in its first excited state is indeed similar to that of the neutral state).<sup>6</sup> The new estimates of  $H_{ab}$  derived in this manner are now in very good agreement with those calculated by a Hush analysis of the IV-CT bands using  $R(\text{TD-DFT})$ ; as expected, they are larger than the Hush values obtained by setting  $R$  to the nitrogen–nitrogen distance. The derived values (see Table 2) of 0.66, 0.55, and 0.32 eV for  $\mathbf{3}^+$ ,  $\mathbf{4}^+$ , and  $\mathbf{6}^+$  obtained using this approximation compare well with the estimates of 0.69, 0.60, and 0.38 eV obtained previously for these systems from the vibronic coupling simulations of the IV-CT bands.<sup>6,7</sup>

Assuming that  $\mathbf{3}^+ - \mathbf{6}^+$  are class-II systems, we have evaluated the activation barrier,  $\Delta G^\ddagger$  for the thermal electron transfer between the two redox centers of the triarylamine systems according to  $\Delta G^\ddagger = (E_{op} - 2H_{AB})^2/4E_{op}$ . Combining the IV-CT values for  $E_{op}$  with the UPS-corrected values of  $H_{ab}$ , we obtain for all systems rather small barrier estimates. For example,  $\Delta G^\ddagger$  is ca. 7 meV for  $\mathbf{6}^+$ , indicating that these species are close to the class-II/class-III borderline. However, due to the remaining uncertainties in estimating  $H_{ab}$ , the possibility that

$\mathbf{3}^+$  and  $\mathbf{4}^+$  are in fact class-III systems cannot be ruled out. The latter possibility is also supported by the vibronic coupling simulation of the IV-CT band;<sup>6,7</sup> in addition, very recent X-ray crystal structure studies of  $\mathbf{3}^+$  and a derivative of  $\mathbf{5}^+$  reveal that the ground state in both MV systems are characterized by a symmetric geometry.<sup>33,34</sup>

### Conclusions

In this work, we have demonstrated that the electronic coupling integrals in strongly coupled organic MV systems can be efficiently probed by means of gas-phase photoelectron spectroscopy. We expect, therefore, that this technique will receive more frequent applications in the investigations of ET processes.

Our results provide an important verification that the Hush model can be used to describe organic MV systems close to the class-II/class-III borderline. The present study also confirms the significant coupling of ET processes with symmetric modes in triarylamine-based mixed-valence systems.

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