ADDITIONS AND CORRECTIONS

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Hung-Chen Chen and Chao-Ping Hsu*: Ab initio Characterization of Electron Transfer Coupling in Photoinduced Systems: Generalized Mulliken−Hush with Configuration-Interaction Singles

Page 11989. We have recently found a problem in our program that calculates configuration interaction singles (CIS) excited-state charge densities. As a result, the Mulliken charges and permanent dipole moments of excited states are affected, which in turn affect the image charges and the generalized Mulliken−Hush (GMH) coupling values. Correct values are now included in Tables 1−5 and Figures 1 and 2. It is seen that the coupling values obtained using the solvation model, the image charge approximation (ICA), remain very similar to the original values. The couplings with an acetonitrile model solvent for **1** series were changed by less than 10%, while those obtained in a vacuum was affected more. In one case (**1**[**10**] in a vacuum with 6-31G* basis) it was increased by more than a factor of 2. Therefore, the main conclusion that, with a model solvent we can improve and verify the GMH coupling values, is still valid. All of the original discussions and conclusions are not affected.

TABLE 1: Electron-Transfer Coupling (in cm^{-1}) of the 1[n] Series

solvent	basis set	bridge σ bond numbers (n)				
		4	6	8	10	12
		full molecules				
vacuum	3-21G	2164	1050	584	725	170
	6-31G*	2340	1022	737	950	74.0
benzene	3-21G	2031	745	293	109	43.5
	6-31G*	2089	736	279	92.0	32.6
acetonitrile	3-21G	1946	655	271	79.8	35.0
	6-31G*	1938	618	249	73.6	28.8
CNDO/S/CI[a]		533	119	34[b]		
CNDO/S/CI[c]		507	112	35		
experimentally inferred[d]		1830	660			
		Without the spacer: disconnected model				
vacuum	6-31G*	405	0.575	0.00852	< 0.007	< 0.007

[a] Reference 6. [b] This value was inferred from Figure 11 of ref 6. [c] Reference 5. [d] Reference 4.

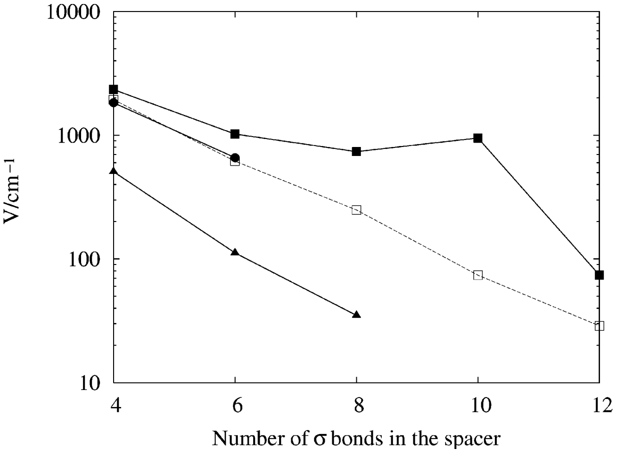
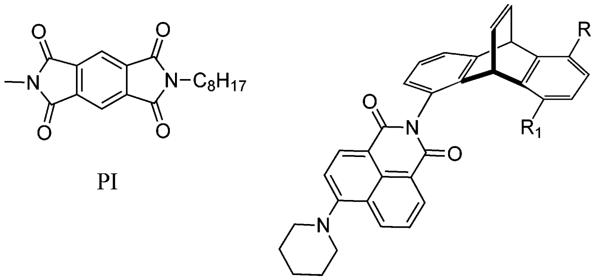


Figure 1. Calculated ET coupling strengths compared with experimental estimates and other previous results. Data with squares are CIS-GMH results with the 6-31G* basis. Filled squares are calculated in a vacuum, while open squares are calculated using a solvent model with $\epsilon = 37.5$ (mimicking acetonitrile). Filled circles are values inferred from experimental results.[4] Filled triangles represent results from a CNDO Hamiltonian.[5]

CHART 2: A pair of molecules where through-space ET coupling was studied. 2a: R_1=PI, R_2=H; 2b: R_1=H, R_2=PI. A third molecule 2′, was used to find the structure of the LE state, where R_1 = R_2=H.



Fitting the new data to eq 2 in the original paper, we obtained a β value of 1.05 bond^{-1} (=0.95 Å^{-1}) in acetonitrile with the 6-31G* basis set. This new value still agrees well with β' from the experimentally observed ET reaction rate, which was found

TABLE 2: Major Excitations and Their Amplitudes (in parentheses) of the First Excited State (LE) and the Lowest Charge-Transfer (CT) State for 1[6] in a Vacuum and in Two Solvents (basis set: 6-31G*)

states	vacuum	benzene	acetonitrile
LE	HOMO→LUMO+1 (0.90)[a] HOMO-1→LUMO+2 (−0.34)[a]	HOMO→LUMO+1 (0.91)[a] HOMO-1→LUMO+2 (−0.34)[a]	HOMO→LUMO+1 (0.91)[a] HOMO-1→LUMO+2 (−0.34)[a]
E/eV[b]	4.64	4.65	4.65
CT	HOMO→LUMO (0.83)[c] HOMO→LUMO+1 (−0.27)[a]	HOMO→LUMO (0.92)[c]	HOMO→LUMO (0.98)[c]
E/eV[b]	7.26	6.95	6.10
θ[b]	24.6	12.8	2.98

[a] Excitation localized in donor. [b] Vertical excitation energy. [c] Charge-transfer excitation. [d] Angle (in degrees) between $\Delta \vec{\mu}_{ij}$ and $\vec{\mu}_{ij}$, in a transition from the LE to the CT state.

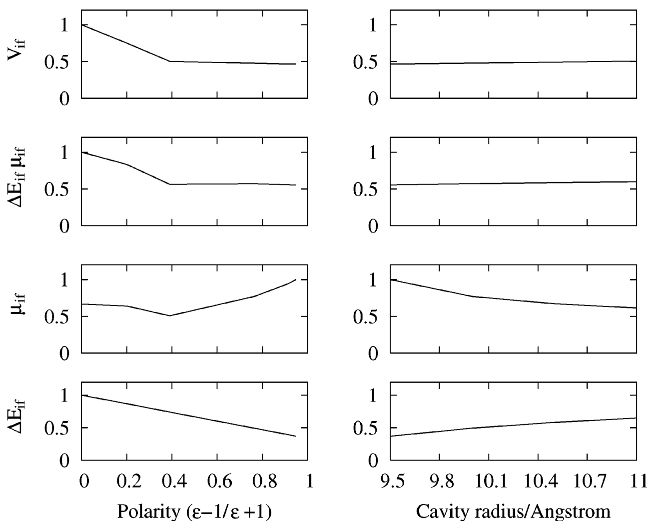


Figure 2. Effects of solvent polarity (left) and cavity radii (right) on quantities determining ET coupling of **1**[**8**]. The values are normalized to 1 for the maximum values in both panels. For testing solvent polarity, a cavity radius of 10.5 Å was used. For the cavity radius data, the dielectric constant was fixed at 37.5.

TABLE 3: Iterations toward Self-Consistency in ICA[a]

	solvent: benzene ($\epsilon = 2.28$)				solvent: acetonitrile ($\epsilon = 37.5$)			
cycle	ΔE/ eV[b]	$\Delta\mu$/ a.u.[c]	μ_{if}/ a.u.[d]	V/ cm^{-1} [e]	ΔE/ eV[b]	$\Delta\mu$/ a.u.[c]	μ_{if}/ a.u.[d]	V/ cm^{-1} [e]
1	2.096	18.92	0.328	293	1.046	20.09	0.647	271
2	1.986	19.70	0.369	299	1.036	19.99	0.645	269
3	1.951	19.78	0.376	299	1.037	19.99	0.645	269
4	1.950	19.79	0.375	298	1.035	19.99	0.645	269
5	1.955	19.68	0.369	295	1.035	19.99	0.645	269
6	1.955	19.68	0.369	295	1.035	19.99	0.645	269

[a] Shown are CIS/3-21G results with **1**[**8**]. In each cycle, the Mulliken charges of the CT state from the previous cycle were used to generate the image charges. Image charges of the first cycle were generated from a calculation in a vacuum. [b] Differences in vertical excitation energies. [c] Differences in permanent dipole moments. [d] Transition dipole moments. [e] Electronic couplings.

to be 0.92 − 1.25 bond^{-1}, or 0.82 − 1.11 Å^{-1}, depending on the solvent.[1−3]

We also wish to take this chance to include the correct structure for 4-piperidinyl-naphthalene-1,8-dicarboximide fragment in Chart 2, and the correct expression of eq 5.

$$q_A^{im} = -\frac{\epsilon - 1}{\epsilon + 1}\frac{R}{|r_A|}q_A \tag{5}$$

For the latter, the correct expression was used for both previous and current calculations.

TABLE 4: A test of electronic coupling with a rectangular cavity in a dielectric solvent, with molecule 1[8][a]

solvent	e	d/Å[b]	ΔE/eV	$\Delta\mu_{if}$/a.u.	μ_{if}/a.u.	V/cm^{-1}
acetonitrile	37.5	3.0	0.490	20.09	1.357	265
		3.5	0.866	19.99	0.787	274
		4.0	1.117	19.87	0.617	279
ethyl acetate	6.0	3.5	1.340	19.87	0.512	278
tetrahydrofuran	7.5	3.5	1.180	19.83	0.567	272
dichloromethane	9.1	3.5	1.117	19.77	0.587	267

[a] Shown are results from CIS/ 3-21G calculations. The definition of symbols follow those of Table 3. [b] When the center of nuclear charges of the molecule is set to origin, the two planar boundaries of the cavity in the x (y,z) coordinate are placed at ± ($d+|x_{\max}|$) [± ($d+|y_{\max}|$), ± ($d+|z_{\max}|$))] where $x_{\max}$ ($y_{\max}$, $z_{\max}$) is the largest atomic x (y,z) coordinate in their absolute values.

TABLE 5: Electronic Coupling (in cm^{-1}) of ANI*−DBO−PI → ANI^{+}−DBO−PI^{-}

system	solvent	V/cm^{-1} [a]
1,5-substituted ANI-DBO-PI (**2a**)		
full molecule	vacuum	217/250[b]/240[c]
	benzene	191
	acetonitrile	190
without DBO fragment	vacuum	180/235[b]/220[c]
experiments[d]		207
1,8-substituted ANI-DBO-PI (**2b**)		
full molecule	vacuum	1.82/2.32[b]/3.85[c]
	benzene	1.75
	acetonitrile	1.48
without DBO fragment	vacuum	0[e]/0.091[b]/0[c,e]
experiments[d]		0

[a] Obtained with 3-21G basis set unless otherwise noted. [b] 3-21+G basis set. [c] 6-31G* basis set. [d] Reference 7. [e] Coupling is smaller than 0.005 cm^{-1}.

References and Notes

(1) Oevering, H.; Paddon-Row, M. N.; Heppener, H.; Oliver, A. M.; Cotaaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258.

(2) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958.

(3) Oliver, A. M.; Craig, D.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366.

(4) Bixon, M.; Jortner, J.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 7349.

(5) Larsson, S.; Volosov, A. *J. Chem. Phys.* **1986**, *85*, 2548.

(6) Clayton, A.; Ghiggino, K. P.; Wilson, G. J.; Paddon-Row, M. N. *J. Phys. Chem.* **1993**, *97*, 7962.

(7) Gosztola, D.; Wasielewski, B. W. M. J. *J. Photochem. Photobiol. A* **1996**, *102*, 71.

10.1021/jp0670440