Bull. Chem. Soc. Jpn., 63, 516—519 (1990) [Vol. 63, No. 2

Oxidation and Reduction Potentials and Electron-Transfer Interactions in Photoexcited States[1)]

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(Received August 3, 1989)

In this paper we discuss the oxidation and reduction potentials of a solvated redoxcouple in photoexcited states, these being the extension of our foregoing theoretical treatment pertinent to the energetics of sequential electrooxidation ($E^{\text{oxd}}_{1/2}$) and reduction ($E^{\text{red}}_{1/2}$) steps. After formulating the ionization potential and electron affinity of solvated molecules by using the $E^{\text{oxd}}_{1/2}$ and $E^{\text{red}}_{1/2}$ values, the equations on the oxidation ($E^{\text{oxd}}_{1/2\cdot\text{exc}}$) and reduction ($E^{\text{red}}_{1/2\cdot\text{exc}}$) potentials in excited states are derived. From these the important relation ($E^{\text{oxd}}_{1/2\cdot\text{exc}}+E^{\text{red}}_{1/2\cdot\text{exc}}$)=($E^{\text{oxd}}_{1/2}+E^{\text{red}}_{1/2}$) is obtained. For the case of a benzenoid alternant hydrocarbon (BAH) the above left-hand-side summation would become constant. Also, the mutual correlation of the $E^{\text{oxd}}_{1/2\cdot\text{exc}}$ or $E^{\text{red}}_{1/2\cdot\text{exc}}$ value at ^1L_a excited state to the $E^{\text{red}}_{1/2}$ or $E^{\text{oxd}}_{1/2}$ potential at ground state is discussed for BAH's. Finally the electron-transfer interaction between an electron donor and an electron acceptor has been considered in photoexcited states by virtue of oxidation and reduction potentials. The equation thus obtained is of the same type as that formulated semiempirically by Rehm and Weller. Our treatment provides theoretical background for the Rehm and Weller equation.

In previous papers we reported the general treatment of the energetics of sequential electroreduction and electrooxidation steps of organic substances by applying thermodynamic energy cycles and SCFMO calculations.[2–4)] In this paper we have extended this procedure to electronic excited states to derive the general formulas of oxidation ($E^{\text{oxd}}_{1/2\cdot\text{exc}}$) and reduction ($E^{\text{red}}_{1/2\cdot\text{exc}}$) potentials in excited states. Using the equations thus obtained the mutual relation of $E^{\text{oxd}}_{1/2\cdot\text{exc}}$ and $E^{\text{red}}_{1/2\cdot\text{exc}}$ is discussed and also electron-transfer interactions between electron donors and acceptors at photoexcited states are formulated and discussed in comparison with the semiempirical equation proposed by Rehm and Weller.[5)]

Results and Discussion

Ionization Potential and Electron Affinity in Solvents and at Excited Electronic States. From the foregoing papers[2–4)] we know that the first oxidation ($E^{\text{oxd}}_{1/2}$) and reduction ($E^{\text{red}}_{1/2}$) potentials for reversible redox systems in the ground state are given by Eqs. 1 and 2 in eV unit, respectively.

$$E^{\text{oxd}}_{1/2}(\text{R}^+/\text{R}) = \Delta G^\circ - \varepsilon_{\text{ho}} + \Delta E^+_{\text{solv}} \tag{1}$$

$$E^{\text{red}}_{1/2}(\text{R}^-/\text{R}) = \Delta G^\circ - \varepsilon_{\text{lu}} - \Delta E^-_{\text{solv}} \tag{2}$$

where the absolute potential of a reference electrode is expressed by ΔG° and where $\Delta E^-_{\text{solv}}=(E^-_{\text{solv}}-E_{\text{solv}})$ and $\Delta E^+_{\text{solv}}=(E^+_{\text{solv}}-E_{\text{solv}})$ are the solvation energy differences (negative values) between monoanion or monocation and neutral species. Under the Koopmans theorem[6)] electron affinity (EA) equals $-\varepsilon_{\text{lu}}$ and ionization potential (IP) equals $-\varepsilon_{\text{ho}}$, where ε_{lu} and ε_{ho} are respectively LUMO and HOMO energies. We can now rewrite the Eqs. 1 and 2 as Eqs. 3 and 4, respectively.

$$IP_{\text{solv}} = E^{\text{oxd}}_{1/2} - \Delta G^\circ = IP + \Delta E^+_{\text{solv}} \tag{3}$$

$$EA_{\text{solv}} = E^{\text{red}}_{1/2} - \Delta G^\circ = EA - \Delta E^-_{\text{solv}} \tag{4}$$

Here, it is easily understood that the ($E^{\text{oxd}}_{1/2}-\Delta G^\circ$) should correspond to IP in solvents (IP_{solv}), and the ($E^{\text{red}}_{1/2}-\Delta G^\circ$) to EA in solvents (EA_{solv}). Since $\Delta G^\circ=-4.40$ eV,[4)] IP_{solv} and EA_{solv} would be easily evaluated by measuring the $E^{\text{oxd}}_{1/2}$ and the $E^{\text{red}}_{1/2}$ values, respectively; i.e., IP_{solv} decreases by $|\Delta E^+_{\text{solv}}|$ from the IP in a gas phase, but EA_{solv} increases by $|\Delta E^-_{\text{solv}}|$ from the gas phase EA.

Let us now consider the ionization potential (IP^{exc}) and electron affinity (EA^{exc}) in an excited stage (ΔE^{UV}). We can write as $\Delta E^{\text{UV}}=(E^{\text{exc}}_{\text{t}}-E_{\text{t}})$ by employing the total energies in the ground (E_{t}) and excited states ($E^{\text{exc}}_{\text{t}}$), so this ΔE^{UV} value means the adiabatic 0–0 transition energy. Since the gas-phase ionization potential (IP^{exc}) in the excited state of ΔE^{UV} may be given by $IP^{\text{exc}}=(E^+_{\text{t}}-E^{\text{exc}}_{\text{t}})$ in the total energy expression, and since $E^{\text{exc}}_{\text{t}}=E_{\text{t}}+\Delta E^{\text{UV}}$, $IP^{\text{exc}}=(IP-\Delta E^{\text{UV}})$ because of $(E^+_{\text{t}}-E_{\text{t}})=IP$ in a ground gas state. Of course, as stated before, the IP equals $-\varepsilon_{\text{ho}}$ in the approximation of Koopams' theorem (Eq. 1).

Alternatively, ε_{lu} in Eq. 2 corresponds to the total energy difference written as $(E^-_{\text{t}}-E_{\text{t}})$ so that the $EA=(E_{\text{t}}-E^-_{\text{t}})$ in the ground state.[2–4)] This treatment may lead to the expression $EA^{\text{exc}}=(E^{\text{exc}}_{\text{t}}-E^-_{\text{t}})$, then the relation of $EA^{\text{exc}}=(EA+\Delta E^{\text{UV}})$ is clear. The values of IP, IP_{solv}, EA, and EA_{solv}, as well as $E^{\text{oxd}}_{1/2}$ and $E^{\text{red}}_{1/2}$, are listed in Table 1 for benzenoid alternant hydrocarbons (BAH), these being assessed on the basis of our foregoing studies.[2–4,7)]

Oxidation and Reduction Potentials in Excited States. Referring to the Eqs. 3 and 4 we can now formulate the oxidation ($E^{\text{oxd}}_{1/2\cdot\text{exc}}$) and reduction ($E^{\text{red}}_{1/2\cdot\text{exc}}$) potentials in the ΔE^{UV} excited state as follows:

$$E^{\text{oxd}}_{1/2\cdot\text{exc}} = \Delta G^\circ + IP - \Delta E^{\text{UV}} + \Delta E^{+\cdot\text{exc}}_{\text{solv}} \tag{5}$$

$$E^{\text{red}}_{1/2\cdot\text{exc}} = \Delta G^\circ + EA + \Delta E^{\text{UV}} - \Delta E^{-\cdot\text{exc}}_{\text{solv}} \tag{6}$$

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Table 1. Electrochemical Data, *IP*, and *EA* of Benzenoid Alternant Hydrocarbons in the Ground State and the ^1L_b and ^1L_a Excited States[a)]

Compound	Ground state						Excited state ($^1L_a/^1L_b$)[b)]				
	$E^{oxd}_{1/2}$	$E^{red}_{1/2}$	IP	EA	IP_{solv}	EA_{solv}	ΔE^{UV}	IP^{exc}	EA^{exc}	$E^{oxd}_{1/2\cdot exc}$	$E^{red}_{1/2\cdot exc}$
	V vs. SCE	V vs. SCE	eV	eV	eV	eV	eV	eV	eV	V vs. SCE	V vs. SCE
Benzene	(2.68)	(−3.58)	9.52	−1.12	7.08	0.82	6.21	3.04	5.09	−3.53	2.63
							4.76	4.49	3.64	−2.08	1.18
Naphthalene	(1.81)	−2.56	8.15	0.152	6.21	1.84	4.35	3.80	4.50	−2.54	1.79
							4.17	3.98	4.32	−2.36	1.61
Anthracene	1.32	−1.99	7.47	0.552	5.72	2.41	3.31	4.16	3.86	−1.99	1.32
							—	—	—	—	—
Naphthacene	0.98	−1.60	7.04	—	5.38	2.80	2.60	4.44	—	−1.62	1.00
							—	—	—	—	—
Pentacene	(0.78)	−1.33	6.74	—	5.18	3.07	2.13	4.61	—	−1.35	0.80
							2.90	3.84	—	−2.12	1.57
Phenanthrene	(1.74)	−2.48	7.86	0.308	6.14	—	4.23	3.63	4.54	−2.49	1.75
							3.59	4.27	3.90	−1.85	1.11
Benz[*a*]-anthracene	1.39	−2.03	7.47	0.696	5.79	2.37	3.49	3.98	4.19	−2.10	1.46
							3.22	4.25	3.92	−1.83	1.19
Chrysene	1.59	−2.30	7.60	0.419	5.99	2.10	3.89	3.71	4.31	−2.30	1.59
							—	—	—	—	—
Dibenz[*a*,*h*]-anthracene	1.43	−2.07	7.38	—	5.83	2.33	3.54	3.84	—	−2.11	1.47
							3.15	4.23	—	−1.72	1.08
Perylene	1.04	−1.69	7.00	—	5.44	2.71	2.86	4.14	—	−1.82	1.17
							3.67	3.33	—	−2.63	1.98
Pyrene	1.28	−2.09	7.41	0.579	5.68	2.31	3.72	3.69	4.30	−2.44	1.63
							3.34	4.07	3.92	−2.06	1.25
Benz[*a*]pyrene	1.16	−1.87	7.12	—	5.56	2.53	3.23	3.90	—	−2.07	1.36
							3.08	4.04	—	−1.92	1.26
Coronene	1.35	−2.08	7.36	—	5.75	2.32	3.63	3.73	—	−2.28	1.55
							2.90	4.46	—	−1.55	0.82

a) Data were taken from Ref. (4), (15, 16), (17, 18), (7, 19, 20) for electrochemical data, *IP*, *EA*, and UV (in organic solvents) energies, respectively. Data in parentheses for $E^{oxd}_{1/2}$ and $E^{red}_{1/2}$ were the calculated values using the relation between electrochemical potentials and molecular orbital energies.[4)] b) The upper and the lower side numbers for each substance are for the ^1L_a and ^1L_b excited states, respectively.

The solvation energy difference between a monocation in the ground state and a neutral species in a ΔE^{UV} excited state is denoted by $\Delta E^{+\cdot exc}_{solv}$. Also, $\Delta E^{-\cdot exc}_{solv}$ has a meaning similar to the $\Delta E^{+\cdot exc}_{solv}$ except for replacing the monocation by the monoanion. We now calculate the values of $(E^{oxd}_{1/2\cdot exc}-E^{oxd}_{1/2})$ and $(E^{red}_{1/2\cdot exc}-E^{red}_{1/2})$ by using the Eqs. 3 and 5 for the former and Eqs. 4 and 6 for the latter. The Eqs. 7 and 8 are finally obtained.[8)]

$$E^{oxd}_{1/2\cdot exc}=E^{oxd}_{1/2}-(\Delta E^{UV}+E^{exc}_{solv}-E_{solv})=E^{oxd}_{1/2}-\Delta E^{UV}_{solv} \quad (7)$$

$$E^{red}_{1/2\cdot exc}=E^{red}_{1/2}+(\Delta E^{UV}+E^{exc}_{solv}-E_{solv})=E^{red}_{1/2}+\Delta E^{UV}_{solv} \quad (8)$$

It should be noted here that, as mentioned above, $\Delta E^{+\cdot exc}_{solv}=(E^{+}_{solv}-E^{exc}_{solv})$ and $\Delta E^{+}_{solv}=(E^{+}_{solv}-E_{solv})$, so, $(\Delta E^{+\cdot exc}_{solv}-\Delta E^{+}_{solv})=-(E^{exc}_{solv}-E_{solv})$. Because of $\Delta E^{UV}=E^{exc}_{t}-E_{t}$ in the vapor state, the value of the term $(\Delta E^{UV}+E^{exc}_{solv}-E_{solv})$ turns out to be $[(E^{exc}_{t}+E^{exc}_{solv})-(E_{t}+E_{solv})]=\Delta E^{UV}_{solv}$, which corresponds to the 0-0 transition energy in solvents,[13)] this solvent being recommended as the same employed for the potential measurement. We now do a treatment similar to the derivation of Eq. 7 for the evaluation of the term of $(E^{red}_{1/2\cdot exc}-E^{red}_{1/2})$. When one calculates the value of $(\Delta E^{-}_{solv}-\Delta E^{-\cdot exc}_{solv})$ using the relation of $\Delta E^{-\cdot exc}_{solv}=(E^{-}_{solv}-E^{exc}_{solv})$ and $\Delta E^{-}_{solv}=(E^{-}_{solv}-E_{solv})$, the value comes out to be $(E^{exc}_{solv}-E_{solv})$. Accordingly the extreme right hand term of Eq. 8 is easily derived. The sum of Eqs. 7 and 8 leads to Eq. 9. This is an interesting and important relation.

$$(E^{oxd}_{1/2\cdot exc}+E^{red}_{1/2\cdot exc})=(E^{oxd}_{1/2}+E^{red}_{1/2}) \quad (9)$$

It is well-known that the sum $(E^{oxd}_{1/2}+E^{red}_{1/2})$ becomes constant in the case of BAH.[2,4)] Therefore it is interesting that this constancy is also true for the oxidation and reduction potentials in photoexcited states of BAH. In Table 1 are listed the potentials of $E^{oxd}_{1/2\cdot exc}$ and $E^{red}_{1/2\cdot exc}$ calculated at the ^1L_a and ^1L_b excited states of BAH and also the other physical constants necessary for evaluating those potentials. The following is an important property of BAH. As was verified in the forementioned papers,[2,7,9,10)] Eq. 10 connecting oxidation-reduction potentials and singlet or triplet electronic transition energies is generally valid.[11)]

$$(E^{oxd}_{1/2}-E^{red}_{1/2})=k_1\,{}^{1,3}\Delta E^{UV}_{ho\rightarrow lu}+k_2 \quad (10)$$

For the case of BAH Eq. 10 was surprisingly satisfactory for the correlation of $(E^{oxd}_{1/2}-E^{red}_{1/2})$ to the ^1L_a excitation energy $(\Delta E^{UV}_{ho\rightarrow lu})$, and the constant terms k_1 and k_2 were 1.011 and −0.001, respectively.[2,7)] Here, the spectral data employed for BAH were those in organic solvents.[7,19] Now, within the experimental error $(E^{\mathrm{oxd}}_{1/2}-\Delta E^{\mathrm{UV}}_{\mathrm{solv}}\ (^1\mathrm{L_a}))=E^{\mathrm{red}}_{1/2}$. Equation 7 indicates $(E^{\mathrm{oxd}}_{1/2}-\Delta E^{\mathrm{UV}}_{\mathrm{solv}}\ (^1\mathrm{L_a}))=E^{\mathrm{oxd}}_{1/2\cdot\mathrm{exc}}\ (^1\mathrm{L_a})$, so that $E^{\mathrm{oxd}}_{1/2\cdot\mathrm{exc}}$ at the $^1\mathrm{L_a}$ state is equal to $E^{\mathrm{red}}_{1/2}$ in the ground state in a good approximation. Also, we can write $(E^{\mathrm{red}}_{1/2}+\Delta E^{\mathrm{UV}}_{\mathrm{solv}}\ (^1\mathrm{L_a}))=E^{\mathrm{oxd}}_{1/2}$ from Eq. 10 and $(E^{\mathrm{red}}_{1/2}+\Delta E^{\mathrm{UV}}_{\mathrm{solv}}\ (^1\mathrm{L_a}))=E^{\mathrm{red}}_{1/2\cdot\mathrm{exc}}\ (^1\mathrm{L_a})$ from Eq. 8, thus $E^{\mathrm{red}}_{1/2\cdot\mathrm{exc}}$ at the $^1\mathrm{L_a}$ state is close to the $E^{\mathrm{oxd}}_{1/2}$ value in the ground state. Inspection of Table 1 clearly reveals the above mutual correlation between $E^{\mathrm{oxd}}_{1/2}$ and $E^{\mathrm{red}}_{1/2\cdot\mathrm{exc}}\ (^1\mathrm{L_a})$ values and between the $E^{\mathrm{red}}_{1/2}$ and $E^{\mathrm{oxd}}_{1/2\cdot\mathrm{exc}}\ (^1\mathrm{L_a})$ values. Of course, these relations are not held on the $^1\mathrm{L_b}$ excited state of BAH, for which the relation of Eq. 10 is not good because of a larger CI effect.[7]

Electron-Transfer Interaction in Photoexcited States. Let us now consider the electron-transfer interaction from an excited donor molecule D* to a ground state acceptor A. This interaction may cause an ion-pair formation $^2\mathrm{D}^+\cdots{}^2\mathrm{A}^-$ in solution occuring through an intermediate encounter complex. Referring to the Mulliken type CT process[12,13] this energy (ΔF) may be expressed by

$$\Delta F = IP^{\mathrm{D\cdot exc}}_{\mathrm{solv}} - EA^{\mathrm{A}}_{\mathrm{solv}} - e^2/\varepsilon\cdot a \qquad (11)$$

where the term $-e^2/\varepsilon\cdot a$ is the Coulombic stabilization energy of the ion-pair in solution with the dielectric constant ε, a being the cavity radius. Keeping in mind the aforementioned equations that are $IP^{\mathrm{exc}}=IP-\Delta E^{\mathrm{UV}}$ and Eq. 3, we can easily derive the equation $IP^{\mathrm{exc}}_{\mathrm{solv}}=(IP_{\mathrm{solv}}-\Delta E^{\mathrm{UV}}_{\mathrm{solv}})$ (see the Appendix for details). Also, starting from the Eq. 4 and $EA^{\mathrm{exc}}=EA+\Delta E^{\mathrm{UV}}$ we can obtain the equation $EA^{\mathrm{exc}}_{\mathrm{solv}}=(EA_{\mathrm{solv}}+\Delta E^{\mathrm{UV}}_{\mathrm{solv}})$ by a treatment similar to the derivation of $IP^{\mathrm{exc}}_{\mathrm{solv}}$ (see Appendix). Let us now modify the Eq. 11 by introducing the relation $IP^{\mathrm{D\cdot exc}}_{\mathrm{solv}}=IP^{\mathrm{D}}_{\mathrm{solv}}-\Delta E^{\mathrm{D\cdot UV}}_{\mathrm{solv}}$ for $IP^{\mathrm{D\cdot exc}}_{\mathrm{solv}}$ to get $\Delta F=IP^{\mathrm{D}}_{\mathrm{solv}}-EA^{\mathrm{A}}_{\mathrm{solv}}-\Delta E^{\mathrm{D\cdot UV}}_{\mathrm{solv}}-e^2/\varepsilon\cdot a$, which follows Eq. 12 by the application of Eqs. 3 and 4.

$$\Delta F = E^{\mathrm{D\cdot oxd}}_{1/2} - E^{\mathrm{A\cdot red}}_{1/2} - \Delta E^{\mathrm{D\cdot UV}}_{\mathrm{solv}} - e^2/\varepsilon\cdot a \qquad (12)$$

When an electron transfer from a ground state donor D to an excited acceptor A* occurs, ΔF is written as

$$\Delta F = IP^{\mathrm{D}}_{\mathrm{solv}} - EA^{\mathrm{A\cdot exc}}_{\mathrm{solv}} - e^2/\varepsilon\cdot a \qquad (13)$$

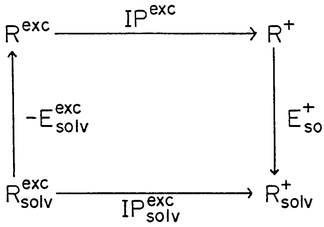
Applying the formula $EA^{\mathrm{A\cdot exc}}_{\mathrm{solv}}=EA^{\mathrm{A}}_{\mathrm{solv}}+\Delta E^{\mathrm{A\cdot UV}}_{\mathrm{solv}}$ and Eqs. 3 and 4 to the Eq. 13 it is also possible to derive Eq. 14

$$\Delta F = E^{\mathrm{D\cdot oxd}}_{1/2} - E^{\mathrm{A\cdot red}}_{1/2} - \Delta E^{\mathrm{A\cdot UV}}_{\mathrm{solv}} - e^2/\varepsilon\cdot a \qquad (14)$$

which has the same form as that of Eq. 12, except for the difference of $\Delta E^{\mathrm{D\cdot UV}}_{\mathrm{solv}}$ and $\Delta E^{\mathrm{A\cdot UV}}_{\mathrm{solv}}$ It is a surprising result that in spite of the photoexcitation of different molecular species, i.e., electron donor or acceptor, the equation finally obtained has the same form. Note that this equation is of the same type as that employed by Rehm and Weller.[5] They first gave this type of equation from the semiempirical concept in order to interpret the fluorescence quenching phenomena through an electron transfer immediately following an encounter complex formation in photoexcited states.[14] Accordingly our derivation of Eqs. 12 and 14 has turned out to verify theoretically the above Rehm and Weller's empirical equation.

Appendix

Considering the energy cycle shown in Scheme 1 the $IP^{\mathrm{exc}}_{\mathrm{solv}}$ is given by $IP^{\mathrm{exc}}_{\mathrm{solv}}=IP^{\mathrm{exc}}+E^{+}_{\mathrm{solv}}-E^{\mathrm{exc}}_{\mathrm{solv}}$, in which the term of $(E^{+}_{\mathrm{solv}}-E^{\mathrm{exc}}_{\mathrm{solv}})$ is rewritten like $[(E^{+}_{\mathrm{solv}}-E_{\mathrm{solv}})-(E^{\mathrm{exc}}_{\mathrm{solv}}-E_{\mathrm{solv}})]=[\Delta E^{+}_{\mathrm{solv}}-\Delta E_{\mathrm{solv}}]$, so that $IP^{\mathrm{exc}}_{\mathrm{solv}}=IP^{\mathrm{exc}}+\Delta E^{+}_{\mathrm{solv}}-\Delta E_{\mathrm{solv}}$. Since $IP^{\mathrm{exc}}=IP-\Delta E^{\mathrm{UV}}$, $IP^{\mathrm{exc}}_{\mathrm{solv}}=IP-\Delta E^{\mathrm{UV}}+\Delta E^{+}_{\mathrm{solv}}-\Delta E_{\mathrm{solv}}$, thus $IP^{\mathrm{exc}}_{\mathrm{solv}}=(IP+\Delta E^{+}_{\mathrm{solv}})-(\Delta E^{\mathrm{UV}}+\Delta E_{\mathrm{solc}})$. The first term of the right-hand-side equation equals IP_{solv} (Eq. 3), and the second term is expressed by $(E^{\mathrm{exc}}_{\mathrm{t}}-E_{\mathrm{t}}+E^{\mathrm{exc}}_{\mathrm{solv}}-E_{\mathrm{solv}})=(E^{\mathrm{exc}}_{\mathrm{t}}+E^{\mathrm{exc}}_{\mathrm{solv}})-(E_{\mathrm{t}}+E_{\mathrm{solv}})=\Delta E^{\mathrm{UV}}_{\mathrm{solv}}$. We can then obtain $IP^{\mathrm{exc}}_{\mathrm{solv}}=IP_{\mathrm{solv}}-\Delta E^{\mathrm{UV}}_{\mathrm{solv}}$.



Scheme 1.

The development of this work is due to much valuable discussion pertinent to the electron-transfer interactions in photoexcited states with Professor Yoshifumi Maki of Gifu Pharmaceutical University and Professors Noboru Mataga and Tadashi Okada of Department of Chemistry, Faculty of Engineering Science, Osaka University. The autors wish to express their sincere thanks to them.

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11) In principle, ${}^{1,3}\Delta E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}}$ values measured in vapour and solution are both applicable to Eq. 10 based on the procedure for the derivation.[2,7,9,10] For the solution data, however, it is recommended that the solvent effect on the spectral data should be taken into account.

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