Spectroscopic Study of δ Electron Transfer between Two Covalently Bonded Dimolybdenum Units via a Conjugated Bridge

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Supporting Information

Contents

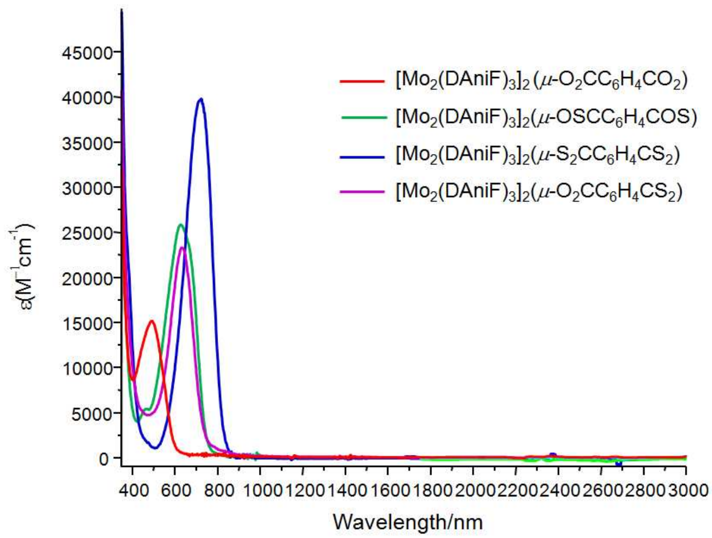

Figure S1. Vis-Near-IR spectra of the neutral dimolybdenum dimers, recorded in the CH_2Cl_2 solutions at room temperature.

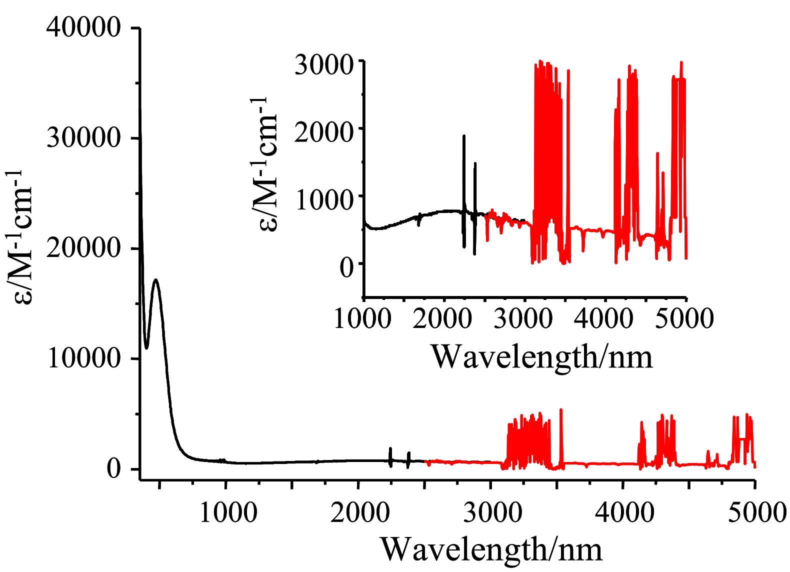

Figure S2. Combined Vis-Near-IR (black) and IR spectra (red) for {[Mo$_2$(DAniF)$_3$]$_2$(μ-O$_2$CC$_6$H$_4$CO$_2$)}PF$_6$ in CH_2Cl_2 solution at room temperature.

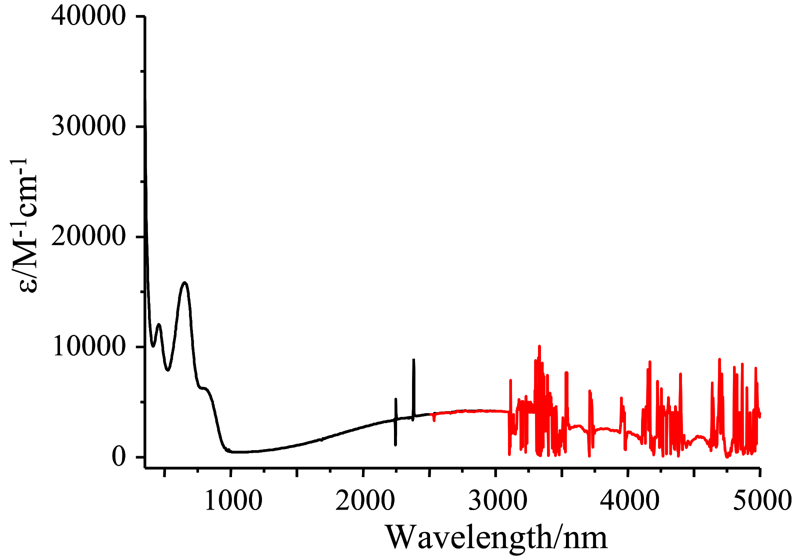

Figure S3. Combined Vis-Near-IR (black) and IR spectra (red) for $\{[Mo_2(DAniF)_3]_2(\mu\text{-}OSCC_6H_4COS)\}PF_6$ in CH_2Cl_2 solution at room temperature.

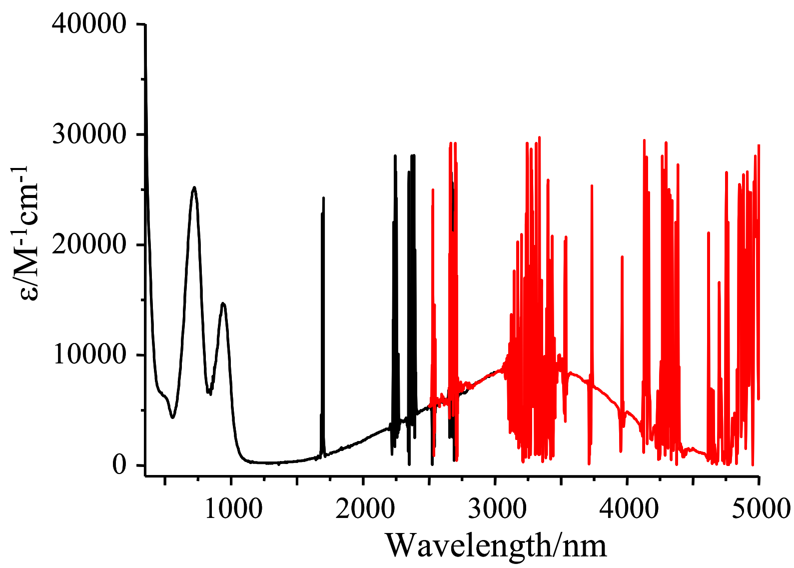

Figure S4. Combined Vis-Near-IR (black) and IR spectra (red) for $\{[Mo_2(DAniF)_3]_2(\mu\text{-}S_2CC_6H_4CS_2)\}$ PF_6 in CH_2Cl_2 solution at room temperature.

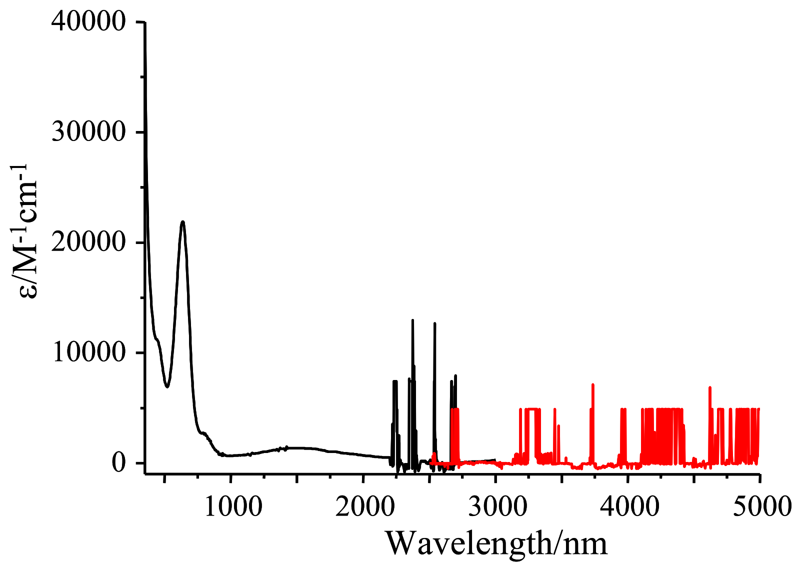

Figure S5. Combined Vis-Near-IR (black) and IR spectra (red) for $\{[Mo_2(DAniF)_3]_2(\mu\text{-}O_2CC_6H_4CS_2)\}PF_6$ in CH_2Cl_2 solution at room temperature.

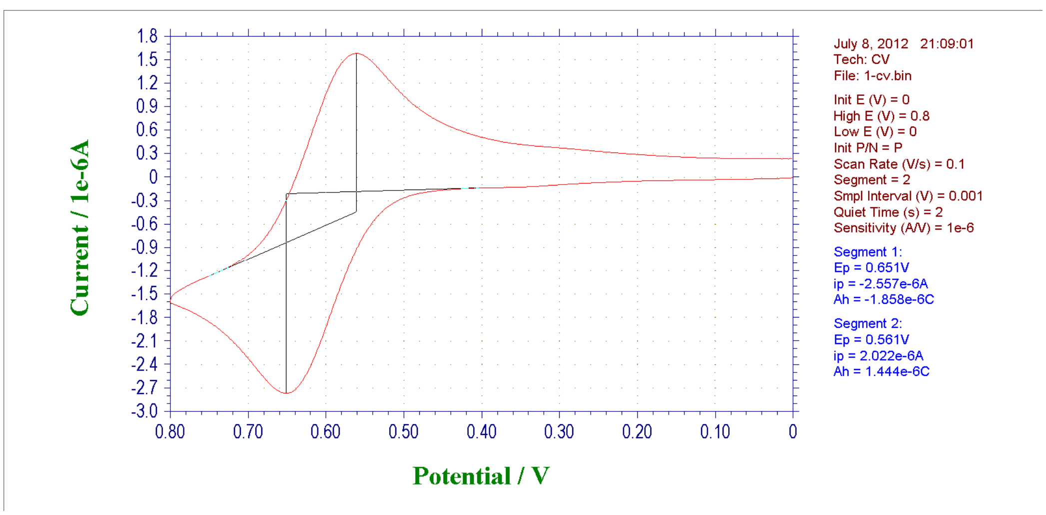

Figure S6. CV of $Mo_2(DAniF)_3(\mu\text{-}S_2CC_6H_5)$. E_{ox} = 0. 651 V, E_{red} = 0.561 V (vs Ag/AgCl).

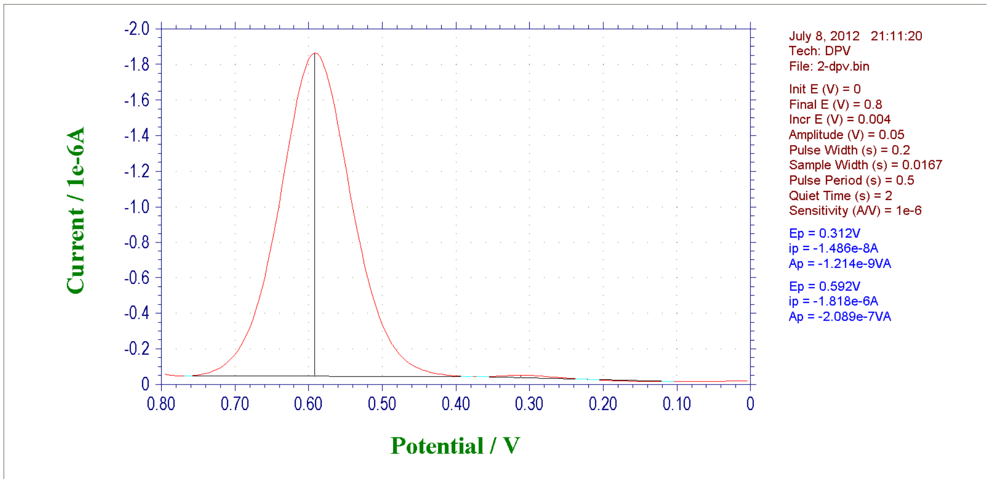

Figure S7. DPV of $Mo_2(DAniF)_3(\mu\text{-}S_2CC_6H_5)$. Half-wave potential E_p = 0.592 V (vs Ag/AgCl)

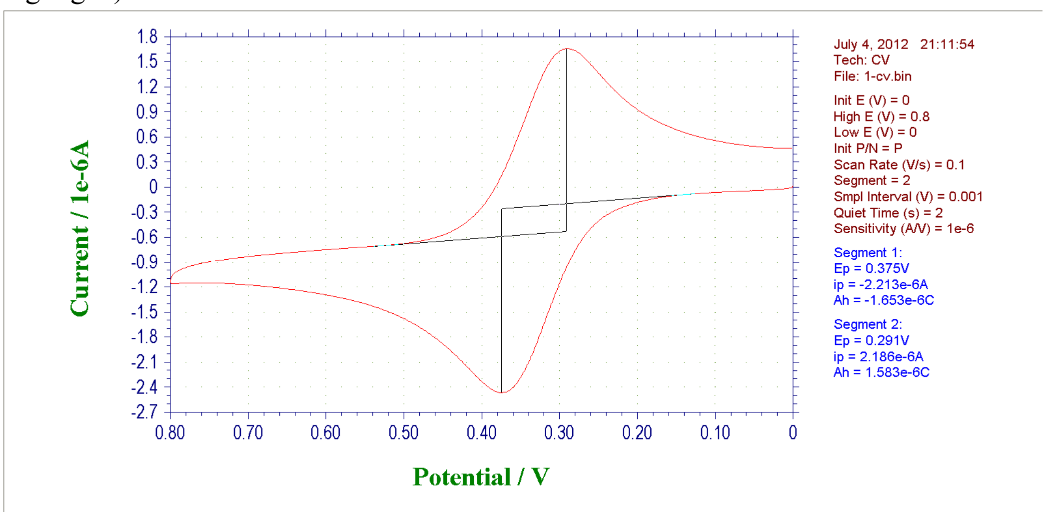

Figure S8. CV of $Mo_2(DAniF)_3(\mu\text{-}O_2CC_6H_5)$. E_{ox} = 0. 375 V, E_{red} = 0.291 V (vs Ag/AgCl)

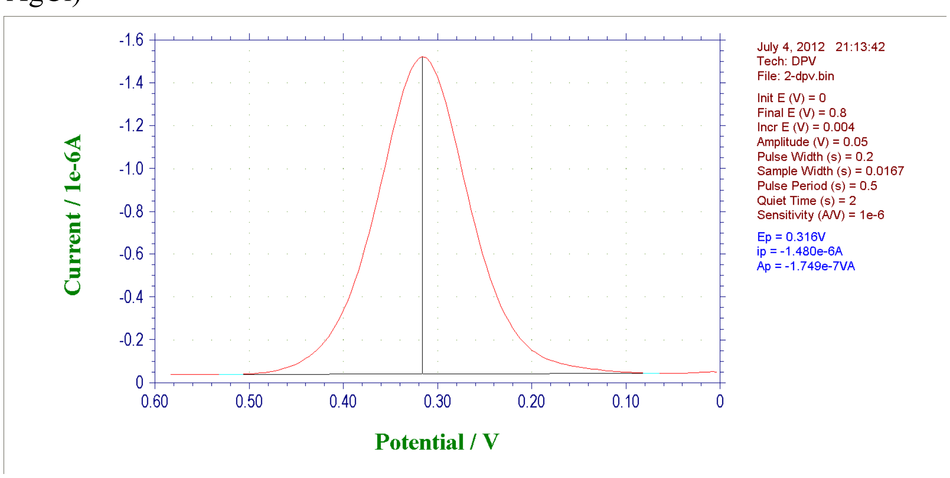

Figure S9. DPV of $Mo_2(DAniF)_3(\mu\text{-}O_2CC_6H_5)$. Half-wave potential E_p = 0.316 V (vs Ag/AgCl)

Table S1. Electronic coupling matrix elements from Mulliken-Hush equation.

complex	r_{ab} (Å)	r_{ab}' (Å)	E_{IT} (cm^{-1})	ε_{IT} ($M^{-1}cm^{-1}$)	cal.$\Delta\nu_{1/2}$ (cm^{-1})	exp.$\Delta\nu_{1/2}$ (cm^{-1})	H_{ab} (cm^{-1}) (r_{ab})	H_{ab} (cm^{-1}) (r_{ab}')
[$\mathbf{O_2}$-$\mathbf{O_2}$]$^+$	11.2	5.8	4240	1470	3190	4410	304	589
[**OS-OS**]$^+$	11.6	5.8	3440	3690	2820	3290	360	727
[$\mathbf{S_2}$-$\mathbf{S_2}$]$^+$	12.2	5.8	2640	12660	2470	1770	410	864
[$\mathbf{O_2}$-$\mathbf{S_2}$]$^+$	11.7	5.8	6560	2270	3890	4130	NA	NA

The H_{ab} values were calculated by Hush model (eq. 1). Calculated bandwidth at half-height, cal.$\Delta\nu_{1/2}$, was determined from eq. 2. Electron transfer distance r_{ab} was the [Mo_2]···[Mo_2] separation determined from the X-ray structure. Effective electron transfer distance, $r_{ab'}$ = 5.8 Å, was the geometrical length of the bridging group "-CC_6H_4C-". Spectroscopic data were extracted from the spectra of the mixed-valence complexes [Mo_2-Mo_2]$^+$ as seen in Figures 1, 2, 3 and 4.

$$Hab = \frac{2.06\times10^{-2}}{r}(\varepsilon_{IT}\Delta\nu_{1/2}E_{IT})^{1/2} \quad (1)$$

$$cal.\Delta\nu_{1/2} = (2310E_{IT})^{1/2} \quad (2)$$

Table S2. Effective energy gaps (ΔE_{ML}^{eff}) and effective coupling constants (H_{ML}^{eff}) for metal to ligand transition.

complex	r_{ML} (Å)	E_{ML} (cm^{-1})	ε_{ML} (M^{-1}cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	H_{ML} (cm^{-1})	ΔE_{ML}^{eff} (cm^{-1})	H_{ML}^{eff} (cm^{-1})
[**O_2-O_2**]	5.6	20600	15230	4770	4480	18230	551
[**OS-OS**]	5.8	16040	25870	3580	4300	14110	655
[**S_2-S_2**]	6.1	13850	39960	2800	4200	12390	708
[**O_2-S_2**]	5.8	15920	22500	3290	3820	11790	618

H_{ML} values were calculated using eq. 1. H_{ML}^{eff} values were calculated by eq. 2 and ΔE_{ML}^{eff} values were calculated by eq. 3.

Electronic coupling distances (r_{ML}) are the geometrical distances determined from the X-ray structures. Spectroscopic data were extracted from the spectra of the neutral complexes [Mo_2-Mo_2].

$$H_{ML}^{eff} = \frac{H_{ML}^2}{2\Delta E_{ML}^{eff}} \qquad (3)$$

$$\frac{1}{\Delta E_{ML}^{eff}} = 0.5 \times \left(\frac{1}{E_{MLCT} - E_{IT}} + \frac{1}{E_{MLCT}}\right) \qquad (4)$$

Table S3. Effective energy gaps (ΔE_{LM}^{eff}) and effective coupling constants (H_{LM}^{eff}) for ligand to metal transition.

complex	r_{LM} (Å)	ε_{LM} (M^{-1}cm^{1})	$\Delta\nu_{1/2}$ (cm^{-1})	E_{LM} (cm^{-1})	H_{LM} (cm^{-1})	ΔE_{LM}^{eff} (cm^{-1})	H_{LM}^{eff} (cm^{-1})
[**O_2-O_2**]$^+$	5.6	0	0	0	0	0	0
[**OS-OS**]$^+$	5.8	5450	2680	12330	1500	10330	109
[**S_2-S_2**]$^+$	6.1	17500	1350	10630	1700	9120	156
[**O_2-S_2**]$^+$	5.8	2780	3570	12970	1260	8580	93

H_{LM} values were calculated according to eq. 1. H_{LM}^{eff} values were calculated by eq. 4 and ΔE_{LM}^{eff} values were calculated by eq. 5. Spectroscopic data were extracted from the spectra of the mixed-valence complexes [Mo_2-Mo_2]$^+$. It is assumed that $r_{LM} \approx r_{ML}$ and $r_{LM'} \approx r_{M'L}$.

$$H_{LM}^{eff} = \frac{H_{LM}^2}{2\Delta E_{LM}^{eff}} \qquad (5)$$

$$\frac{1}{\Delta E_{LM}^{eff}} = 0.5 \times \left(\frac{1}{E_{LMCT} - E_{IT}} + \frac{1}{E_{LM}}\right) \qquad (6)$$

Table S4. Comparison between H_{ab} from Hush model and $H_{MM'}$ from CNS model.

complex	$H_{ab}(cm^{-1})^a$ (r_{ab}= $Mo_2\cdots Mo_2$)	$H_{ab}(cm^{-1})^b$ (r_{ab}'=5.8Å)	H^{eff}_{ML} (cm^{-1})	H^{eff}_{LM} (cm^{-1})	$H_{MM'}$ (cm^{-1})
[O_2-O_2]$^+$	304	589	551	0	551
[OS-OS]$^+$	360	727	655	109	764
[S_2-S_2]$^+$	410	864	708	156	864
[O_2-S_2]$^+$	NA	NA	618	93	711

$H_{MM'}$ values were calculated by summation of H^{eff}_{ML} and H^{eff}_{LM} (eq. 7).

$$H_{MM'} = H^{eff}_{ML} + H^{eff}_{LM} \qquad (7)$$

Table S5. Electron transfer kinetics for the symmetrical complexes based on the electronic coupling matrix elements from Hush and CNS methods.

complex	Hush			CNS		
	$\nu_{el}(s^{-1})$	ΔG^* (cm^{-1})	k_{et} (s^{-1})	$\nu_{el}(s^{-1})$	□G^* (cm^{-1})	k_{et} (s^{-1})
[O_2-O_2]$^+$	1.2×10^{14}	553	3.5×10^{11}	1.1×10^{14}	581	3.0×10^{11}
[OS-OS]$^+$	2.1×10^{14}	287	1.2×10^{12}	2.3×10^{14}	266	1.4×10^{12}
[S_2-S_2]$^+$	3.4×10^{14}	79	3.4×10^{12}	3.4×10^{14}	79	3.4×10^{12}

For the symmetrical complexes, $\lambda = E_{IT}$. The free energies of activation were calculated from eq. 7. Electronic frequencies calculated from eq. 8 are in order of 10^{14} s^{-1} and the rates of ET reactions were calculated from eq. 9, where κ=1 and $\nu_n = 5 \times 10^{12}$ s^{-1}.

$$\Delta G^* = \frac{(\lambda - 2H)^2}{4\lambda} \qquad (8)$$

$$\nu el = \frac{2H^2}{h}\sqrt{\frac{\pi^3}{\lambda RT}} \qquad (9)$$

$$k_{et} = \kappa \nu_n \exp(-\Delta G^* / k_B T) \qquad (10)$$

Table S6. Electron transfer kinetics for the unsymmetrical complexes based on the electronic coupling matrix elements from CNS methods.

complex	diabatic		adiabatic	
	ΔG* (dia) (cm^{-1})	k_{et} (s^{-1})	ΔG* (adia) (cm^{-1})	k_{et} (s^{-1})
[**O_2-S_2**]$^+$(forward)	2482	3.1×10^7	2430	4.1×10^7
[**O_2-S_2**]$^+$ (reverse)	256	1.5×10^{12}	364	8.6×10^{11}

For the unsymmetrical complex, the diabatic free energies of activation (ΔG_{dia}*) were calculated from eq.11 and the adiabatic ΔG_{adia}° and ΔG_{adia}* were calculated using eq. 12 and 13 based on the $H_{MM'}$ derived from the CNS equations (ref. 42 in the text).

$$\Delta G^* = \frac{\lambda}{4}(1+\frac{\Delta G^0}{\lambda})^2 \qquad (11)$$

$$\Delta G^{\mathrm{o}}_{\mathrm{ad}} = \Delta G^{\mathrm{o}}(1-\frac{2H^2_{\mathrm{ab}}}{(\lambda+\Delta G^{\mathrm{o}})(\lambda-\Delta G^{\mathrm{o}})}) \qquad (12)$$

With $\Delta G° = 2226\ cm^{-1}$, $H_{ab} = 711\ cm^{-1}$ and $\lambda = 4334\ cm^{-1}$

$\Rightarrow \Delta G^{\mathrm{o}}_{\mathrm{ad}} = 2063\ cm^{-1}$

$$\Delta G^*(adia) = \frac{\lambda}{4}+\frac{\Delta G^\circ}{2}+\frac{(\Delta G^\circ)^2}{4(\lambda-2H_{ab})}-H_{ab}+\frac{H^2_{ab}}{(\lambda+\Delta G^\circ)} \qquad (13)$$