Supporting Information

Computational Study of Photocatalytic CO₂ Reduction by a Ni(II)

Complex Bearing an S₂N₂-Type Ligand

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Methods	${}^{3}{[NiLX_{2}]^{2+}} \rightarrow X + {}^{3}{[NiLX]^{2+}}$	${}^{3}{[NiLX]^{2+}} \rightarrow X + {}^{3}{[NiL]^{2+}}$
B3LYP ^a	0.0	1.8
B3LYP/BSSE ^b	1.7	3.4
B3LYP-D3	5.4	6.4
B3LYP-D3/BSSE ^b	7.2	8.1
M06-L	7.3	7.4
M06-L/BSSE ^b	8.9	9.0

Table S1. The free energy changes (kcal/mol) for the dissociation of acetonitrile ligands from ${}^{3}{[NiLX_2]^{2+}}$ calculated by using different methods

^a The data are listed for comparison; ^b The basis set superposition error (BSSE) was considered.

Comments: For the dissociation of acetonitrile ligands, there is a difference of about 5.0 kcal/mol for the reaction free energies without dispersion correction. By contrast, the deviation caused by not considering BSSE is less than 2.0 kcal/mol. With the corrections of dispersion and BSSE, the reaction free energies for the two processes are both less than 9.0 kcal/mol. Owing to the fact that the formed ³{[NiLX]²⁺} or ³{[NiL]²⁺} readily obtains an electron to generate the more stable Ni^I species, therefore, the dissociation of acetonitrile ligands is favorable.

It	tems	−ОСОН	a-Int1	b-Int1	c-Int1
Bond lengths	C1-O1	1.237	1.241	1.217	1.222
(Å)	C1-O2	1.446	1.347	1.384	1.374
	Ni-C1	<i>a</i>	1.988	2.014	2.006
Bond angles (°)	∠01C102	112.1	117.6	116.5	119.2
Charges (a)	O1C1O2 moiety	-1.000	-0.776	-0.845	-0.892
	H1	0.420	0.523	0.504	0.511

Table S2. The key structure parameters and charges in protonated $t-\eta^2_{CO}$

^{*a*} There is no Ni-C1 bond in ⁻OCOH.

Comments: In **a-Int1**, the C1-O1 and C1-O2 bond lengths and the O1C1O2 bond angle are predicted to be 1.241 Å, 1.347 Å and 117.6°, respectively, nearing those in -OCOH (1.237 Å, 1.446 Å and 112.1°). The charges on the O1C1O2 and H1 moieties of **a-Int1** are -0.776 (-0.718 in **t-\eta^2co**, see Figure S6) and 0.523 e, respectively. These changes indicate that this protonation is accompanied by

the further electron transfer from catalyst to CO_2 moieties. By contrast, the O1C1O2 moieties in **b-Int1** and **c-Int1** carry more negative charges, being -0.845 and -0.892 e, respectively, and the H1 atoms carry fewer positive charges, being 0.504 and 0.511 e, respectively, which suggests an increase in the degree of electron transfer.

The formations of H ₂ and HCOO (HCOOH) starting from {[NL] ⁻ }								
Doutitions	Ni	CAT	U 1	u٦	H ₃ O	HCOO		
	INI	moiety	111	112	moiety	moiety		
³ {[NiL] ⁰ }	0.379	0.000	a	<i>a</i>	<i>a</i>	<i>a</i>		
h-Int	0.384	1.236	-0.236	<i>a</i>	<i>a</i>	<i>a</i>		
h-TS	0.397	1.294	-0.287	0.617	0.993	<i>a</i>		
i-TS1	0.534	1.498	-0.159	a	<i>a</i>	-0.498		
i-Int1-1	0.545	1.519	-0.130	<i>a</i>	<i>a</i>	-0.519		
i-TS2-1	0.603	1.634	-0.019	<i>a</i>	<i>a</i>	-0.634		
i-Int2	0.648	1.563	0.181	<i>a</i>	<i>a</i>	-0.563		
i-TS1'	0.343	1.273	-0.202	<i>a</i>	<i>a</i>	-0.273		

Table S3. The charge (e) distributions on the structures of the key stationary points along the pathways of the formations of H₂ and HCOO⁻ (HCOOH) starting from ${}^{3}{[NiL]^{0}}$

^{*a*} There is no such moiety in the corresponding structure.

Table S4. The total charge decomposition analysis (CDA) results for Ni⁰ species with different ligands

Catalysts	d	b	d-b	r
O-containing	0.343	0.026	0.317	-0.061
S-containing	0.493	0.019	0.474	-0.128
Se-containing	0.491	0.043	0.448	-0.105

Comments: We defined ligand and Ni⁰ as fragments 1 and 2, respectively, and carried out the charge decomposition analysis. The Ni⁰ is in high-spin configuration while the ligand is in low-spin state, thus we need to analyze alpha and beta spins separately. Here, the listed data are the total results of alpha and beta spins, and d (donation) denotes the amount of electron transfer from fragment 1 to 2, b (back-donation) stands for the amount of electron back-donation from fragment 2 to 1, r (charge polarization) represents the charge polarization of occupied orbitals. For three different catalysts, the b values are all small, which indicates that the back-donation from Ni center to ligand is weak.

Calaulatad itama	O coordination		S coordination		Se coordination	
	o-TS1	0-t-η ² co	TS1	t-η²co	se-TS1	se-t-η ² co
ΔG_{gas1} a	12.6	9.5	12.5	7.7	12.5	10.2
$\Delta { m G}_{ m gas2}$ b	13.8	13.5	13.6	12.2	14.5	15.8
$\Delta G_{sol} (DMA = 37.8)^{c}$	13.1	3.1	6.1	-5.0	10.1	-2.0
$\Delta G_{sol} (H_2O_{\epsilon=78.4})$	11.4	-7.0	4.9	-17.4	8.5	-13.9
$\Delta G_{sol} (DMF = 37.2)$	13.0	3.1	6.0	-5.0	10.1	-2.0
ΔG_{sol} (MeCN $\epsilon=35.7$)	13.0	2.1	6.2	-6.3	10.0	-3.1
ΔG_{sol} (Acetone $\epsilon=20.5$)	13.1	3.0	6.6	-5.0	10.3	-1.8
ΔG_{sol} (Benzene $\epsilon=2.3$)	12.3	6.9	9.8	3.1	11.5	6.1

Table S5. The free energies (kcal/mol) for the key structures along the formation of CO_2 adducts via the η^2_{CO} mode starting from different catalysts in different solvents. The free energy of Ni⁰ species plus CO_2 is set to zero

^{*a*} The value is calculated at the level of geometry optimization without the solvent correction;

^b The data is obtained through single-point energy calculation at high-level basis set in gas phase;

^c The solvent correction was considered in DMA solvent.



Figure S1. Free energy profile for the oxidation and deprotonation of sacrificial electron donor (BIH). The geometry optimizations were carried out in DMA solvent, the free energy of BIH plus $3-Ru^*$, 2DMA·H₂O, 1-Ru and OH⁻ is set to zero, and the distances are given in Å.



Figure S2. Predicted processes for the formation of the Ni¹ and Ni⁰ species. The geometry optimizations were carried out in DMA solvent, the free energy of ${}^{3}{[NiLX_2]^{2+}}$ plus two 2-Ru molecules and BI is set to zero, and the distances are given in Å.



Figure S3. Predicted processes for the reduction of Ni center from Ni^{II} to Ni⁰ without the dissociation of acetonitrile ligands (a) and with one acetonitrile molecule losing (b). The free energy of ${}^{3}{[NiLX_{2}]^{2+}}$ plus 2-Ru and BI is set to zero, and the distances are given in Å.

Comments: Unlike $[NiLX_2]^0$ and $[NiL]^0$, the species $[NiLX]^0$ in singlet state is more stable than that in triplet state, and the difference in free energy is 2.6 kcal/mol in DMA solvent. Similar to the process which undergoes two acetonitrile ligand detachment, the Ni¹ species is also readily formed and the formation of the Ni⁰ species requires to overcome a slightly high free energy barrier for both the processes. Compared with the case of the formation of ${}^{3}{[NiL]^{0}}$, the free energy barriers of the second electron transfer mediated by BI[•] along the pathways without the loss of acetonitrile ligand and with one acetonitrile ligand losing are 3.3 kcal/mol lower and 6.1 kcal/mol higher, respectively, and the corresponding overall reaction free energies for the generations of ${}^{3}{[NiLX_2]^0}$ and ${}^{1}{[NiLX]^0}$ are 8.9 and 1.1 kcal/mol higher. These results further indicate that the two acetonitrile molecules tend to be lost in the reduction process of ${}^{3}{[NiLX_2]^2}$.



Figure S4. The combinations of water molecules with Ni^{x+} (x=0-2) species in DMA solvent. The free energies are given in kcal/mol and the bond lengths are shown in Å.

Comments: The reaction free energies for these processes range from 2.2 to 10.8 kcal/mol, suggesting that water molecule coordination to Ni^{x+} (x=0-2) center might be unfavorable from the thermodynamic viewpoint.



Figure S5. The binding processes of CO₂ with Ni⁰ species ${}^{3}{[NiL]^{0}}$. The free energy of ${}^{3}{[NiL]^{0}}$ plus CO₂ is set to zero. The data in square bracket with blue italic are the results without the solvent corrections and the bond lengths are shown in Å.

Comments: The CO₂ adduct t- η^2 _{CO} (η^2 _{CO} binding mode) is generated via a transition state TS1 with a free energy barrier of 6.1 kcal/mol, and the reaction free energy of this process is -5.0 kcal/mol, which indicates that the formation of $t-\eta^2_{CO}$ is facile both kinetically and thermodynamically. By contrast, the free energy barrier for the formation of $t-\eta^{1}_{C}$ through a transition state TS1' is 13.0 kcal/mol higher, and the corresponding reaction free energy is 7.3 kcal/mol, suggesting that CO₂ binding to ³{[NiL]⁰} by the η^{1}_{C} mode is at a significant disadvantage. The formed t- η^{2}_{CO} could convert to t- η^{1}_{O} $(\eta^{1}_{0} \text{ binding mode})$ via a transition state **TS2** with a free energy barrier of 6.8 kcal/mol, while the reaction free energy is 5.8 kcal/mol, showing that the reverse conversion is more favorable and the t- η^{1}_{0} may be absent. Besides, we also located a t- $\eta^{2}_{0,0}$ with the $\eta^{2}_{0,0}$ mode. For its formation, an intermediate t- $\eta^2_{0,0}$ -int is firstly formed via a transition state TS1" with a free energy barrier of 13.9 kcal/mol. Then t- $\eta^2_{0,0}$ -Int further converts to t- $\eta^2_{0,0}$ by a second transition state TS2'', while the free energy of TS2" is 1.3 kcal/mol lower than that of $t-\eta^2 o_0$ -Int after the solvent effect is considered, showing that the DMA solvent is more beneficial to lower the free energy of TS2" and the isomerization could occur readily. The free energy of t- $\eta^2_{0,0}$ is 5.5 kcal/mol lower than that of t- η^1_{C} , while 1.0 and 6.8 kcal/mol higher than that of $t-\eta^1_{O}$ and $t-\eta^2_{CO}$, respectively. Overall, $t-\eta^2_{CO}$ has the lowest free energy among the four CO_2 adducts and its formation only needs to surpass a low free energy barrier. Therefore, the $t-\eta^2 c_0$ should be the available species to participate in the subsequent CO formation.

Compared with the structure of the free CO₂ molecule, the significant geometric features of the CO₂ moiety in CO₂ adducts are that it has bending structure and elongated C-O bond. From Figure S5, we can see that the O1C1O2 angles in $t-\eta^1c$, $t-\eta^2co$, $t-\eta^1o$ and $t-\eta^2o$, are 133.5, 134.0, 133.8 and 111.1°, respectively, and the C1-O1 and C1-O2 bond lengths are all in the range from 1.219 to 1.315 Å. These changes indicate that the coordinated CO₂ shows some features of CO₂⁻⁻ (the O1C1O2 angle and C-O bond length are predicted to be 137.1° and 1.240 Å, respectively) and the electron transfer from Ni⁰ species to the anti-bonding π^* orbital of CO₂ occurs.



Figure S6. Molecular orbitals of CO_2 with different OCO angles (a) and the four CO_2 adducts (b).

Comments: The NBO analysis shows that the charges on the CO₂ moieties of $\mathbf{t}-\eta^{1}_{C}$, $\mathbf{t}-\eta^{2}_{CO}$, $\mathbf{t}-\eta^{1}_{O}$ and $\mathbf{t}-\eta^{2}_{O,O}$ are all close to -1 e, which just confirms the occurrence of electron transfer from the ³{[NiL]⁰} to CO₂ moieties. Among these CO₂ adducts, $\mathbf{t}-\eta^{2}_{O,O}$ carries the most negative charges on the CO₂ moiety, while $\mathbf{t}-\eta^{2}_{CO}$ carries the least, being -1.165 and -0.718 e, respectively. Molecular orbital analysis shows that the CO₂ π^* orbitals overlaps with the nickel d orbital by the two oxygen lobes in SOMO (singly occupied molecular orbital) of $\mathbf{t}-\eta^{2}_{O,O}$, and its most negative charges on the CO₂ moiety should be attributed to the strong electronegativity of the oxygen atoms. In $\mathbf{t}-\eta^{2}_{CO}$, there is an interaction between the terminal oxygen p orbital of CO₂ and the d orbital of Ni in the SOMO-1. Obviously, the electron back-donation from oxygen p orbital to nickel vacant d orbital should be

existed, which leads to the least negative charge on the CO₂ moiety in $t-\eta^2_{CO}$. Moreover, the back-interaction could further activate the CO₂ and stabilize the CO₂ adduct, this might be a major reason that the free energy of $t-\eta^2_{CO}$ is the lowest among the four CO₂ adducts.



Figure S7. The formation of CO along the singlet potential energy surface starting from ${}^{1}{[NiL]^{0}}$. The free energy of ${}^{1}{[NiL]^{0}}$ plus CO₂ and 2H₃O⁺ is set to zero. The bond lengths are shown in Å.

Comments: The results show that only a CO₂ adduct in the η_{C}^{1} binding mode (denoted as $\mathbf{s}-\eta_{C}^{1}$, "s" stands for the singlet state) was located. The formation of $\mathbf{s}-\eta_{C}^{1}$ requires to overcome a free energy barrier of 9.4 kcal/mol, which is 9.7 kcal/mol lower than that of $\mathbf{t}-\eta_{C}^{1}$ but 3.3 kcal/mol higher than that of $\mathbf{t}-\eta_{C}^{2}$. The C-O bond cleavage after the first protonation needs to surpass a high free energy barrier of 37.9 kcal/mol, indicating that this pathway is unfeasible. The free energy barrier of the C-O bond cleavage after the second protonation is slightly lower than that along path 1, while being 5.6 kcal/mol higher relative to the case along path 3. Owing to that the concentration of proton is low and the path 3 is dominant in this system, thus these results further confirm that the CO₂ reduction to CO proceeds on the triplet potential energy surface.



Figure S8. Several key structures of the stationary points along the pathway of HCOOH formation. The distances are shown in Å.



Figure S9. The formation of H₂ along the singlet potential energy surface starting from ${}^{1}{[NiL]^{0}}$. The free energy of ${}^{1}{[NiL]^{0}}$ plus 2H₃O⁺ is set to zero. The bond lengths are shown in Å.

Comments: The H_2 formation process along the singlet potential energy surface is similar to that along the triplet potential energy surface, while the free energy barrier and reaction free energy for the Ni-H1 bond cleavage, by contrast, are 1.3 and 15.9 kcal/mol higher, respectively. Thus, the reaction for the H_2 evolution along the triplet potential energy surface is dominant, just like the generation of CO.



Figure S10. The protonation process of ${}^{2}{[NiL]^{+}}$. The free energy of ${}^{2}{[NiL]^{+}}$ plus H₃O⁺ and 2-Ru is set to zero. The bond lengths are shown in Å.

Comments: Proton attacking the Ni¹ species ${}^{2}{[NiL]^{+}}$ is feasible based on our calculations despite the existence of Coulomb repulsion between them (both with positive charges). Firstly, H₃O⁺ reacts with the S atom of ${}^{2}{[NiL]^{+}}$ to produce a S-protonated species, then the Ni-hydride complex ${}^{2}{[HNiL]^{2+}}$ is generated via the hydrogen transfer. The overall free energy barrier and reaction free energy for the formation of ${}^{2}{[HNiL]^{2+}}$ are 5.2 and -12.7 kcal/mol, respectively. Subsequent single electron transfer from ${}^{2}{[Ru(bpy)_{2}(bpy^{-})]^{+}}$ to ${}^{2}{[HNiL]^{2+}}$ are 1.7 and -41.0 kcal/mol, respectively. These results show that the Ni-hydride intermediate **h-Int** could be also formed from the Ni¹ species.



Figure S11. Calculated processes for the reduction of Ni center from Ni^{II} to Ni⁰ with oxygen-containing ligand (a) and selenium-containing ligand (b). The free energy of ${}^{3}{[NiL'X_2]^{2+}}$ (a) or ${}^{3}{[NiL'X_2]^{2+}}$ (b) plus 2-Ru and BI is set to zero. The bond lengths are shown in Å.

Comments: Compared with the sulfur-containing catalyst, the free energy barriers of the single electron transfer from ${}^{2}\{[Ru(bpy)_{2}(bpy^{-})]^{+}\}$ to Ni^{II} species and from BI[•] to Ni^I species are both lower for the oxygen-containing catalyst, while are slightly higher when sulfur atom is replaced by selenium atom. The overall reaction free energies for the formation of ${}^{3}\{[NiL']^{0}\}$ and ${}^{3}\{[NiL'']^{0}\}$ are -6.8 and -6.7 kcal/mol, respectively, both being lower than that of sulfur-containing catalyst. Taken together, sulfur coordination seems to have no advantage over oxygen or selenium coordination in stabilizing the Ni⁰ species.



Figure S12. The decomposition analysis of complex orbital contribution to the value of b for oxygen-containing (a), sulfur-containing (b) and selenium-containing (c) catalysts. The data in red font denotes the back-donation from the d orbital of Ni center to the pyridine ring moiety of ligand, while the blue font to the sulfur-containing moiety.

Comments: Owing to the fact that the Ni⁰ species is predicted to be a triplet ground state, the HOMO of alpha electron in (b) is also the SOMO in Figure S6.



Figure S13. The binding of CO₂ to Ni⁰ species with oxygen-containing ligand. The free energy of ${}^{3}{[NiL']^{0}}$ plus CO₂ is set to zero and the bond lengths are shown in Å.

Comments: For ³{[NiL']⁰}, only two CO₂ adducts binding with the η^2_{CO} and η^1_O modes (denoted as **o-t-\eta^2_{CO}** and **o-t-\eta^1_O**) were located. The formation of **o-t-\eta^2_{CO}** through a transition state **o-TS1** requires to overcome a free energy barrier of 13.1 kcal/mol, and the reaction free energy of this process is 3.1 kcal/mol. The free energy of **o-t-\eta^1_O** is 3.4 kcal/mol higher than that of **o-t-\eta^2_{CO}**, and the former could convert to the latter with a low free energy barrier of 1.6 kcal/mol.



Figure S14. The binding of CO_2 to Ni⁰ species with selenium-containing ligand. The free energy of ³{[NiL"]⁰} plus CO₂ is set to zero and the bond lengths are shown in Å.

Comments: For ${}^{3}{[NiL"]^{0}}$, three CO₂ adducts were obtained except for the structure of the η^{1}_{C} mode which is always rearranged to the η^{2}_{CO} mode during geometry optimization. The free energy barrier

and the reaction free energy for the generation of se-t- η^2_{CO} are 10.1 and -2.0 kcal/mol, respectively, indicating that this process is feasible both kinetically and thermodynamically. The free energy of se-t- η^2_{CO} is 5.0 kcal/mol lower than that of se-t- η^1_O , and the free energy barrier of the conversion from the former to the latter is 6.0 kcal/mol, showing that se-t- η^1_O more readily converts to se-t- η^2_{CO} . Additionally, the adduct se-t- $\eta^2_{O,O}$ was also obtained and its formation process is similar to that of t- $\eta^2_{O,O}$. The formation of se-t- $\eta^2_{O,O}$ needs to surpass a slightly higher free energy barrier of 18.2 kcal/mol and the overall reaction free energy of this process is 4.9 kcal/mol, suggesting that CO₂ binding to ³{[NiL"]⁰} by the $\eta^2_{O,O}$ mode is less stable relative to those by the η^2_{CO} and η^1_O modes.

S.2 The C-O bond cleavage calculated by using M06-L and B3LYP-D3 functionals

Considering the weak interactions, we used M06-L and B3LYP-D3 functionals to calculate some key processes along pathways of the C-O bond cleavage (paths 1 and 3), respectively. The calculated results indicate that the reaction processes are consistent under the three different functionals (see Tables S6 and S7). Besides, the difference of the key bond lengths in the structures of the key stationary points between the three methods are within 0.1 Å (see Figure S15). Therefore, the chosen B3LYP functional is appropriate here.

Functionals	h-Int1+ H ₂ O ⁺	h-Int?	b-TS1	h-Int3+2H ₂ O
	b Inti (11)0	0 11102	0 101	
B3LYP ^a	0.0	-28.3	-12.5	-52.5
M06-L	0.0	-26.4	-12.7	-48.2
B3LYP-D3	0.0	-31.0	-14.9	-50.1

Table S6. The free energies (kcal/mol) for the key structures along path 1 of CO_2 reduction calculated by different functionals

^{*a*} The data are listed here for comparison.

Functionals	c-Int1	c-TS1	c-Int2	c-TS2	c-Int3+CO
B3LYP ^a	0.0	9.7	1.4	1.6	-5.6
M06-L	0.0	8.3	-0.2	1.7	0.5
B3LYP-D3	0.0	8.6	0.0	0.2	-3.1

Table S7. The free energies (kcal/mol) for the key structures along path 3 of CO₂ reduction calculated by different functionals

^{*a*} The data are listed here for comparison.



Figure S15. The key structures along paths 1 and 3 of CO_2 reduction calculated by M06-L and B3LYP-D3 functionals. The bond lengths are shown in Å.

S.3 Translational entropy correction

One thinks that the free energy change directly obtained from the DFT calculation without translational entropy correction in solvent is not adequate, thus we performed the correction of translational entropy in DMA solvent with the method reported by Whitesides et al¹ for the pathway of CO₂ reduction including the formation of $t-\eta^2_{CO}$ and the C-O bond cleavage along path 3. The results indicate that the reaction free energies have only minor change which is negligible.

Table S8. The free energy changes (kcal/mol) with translational entropy correction for the key reaction processes of the CO₂ reduction (contains the formation of $t-\eta^2_{CO}$ and the C-O bond cleavage along path 3) calculated by B3LYP

Species Reactants ^c	TS1	t-η²co	c-Int1	c-TS1	c-Int2	c-TS2	c-Int3	
	$+H_3O^+$	$+H_3O^+$	+H ₂ O	$+H_2O$	+H ₂ O	+H ₂ O	+H ₂ O+CO	
$\Delta G_{sol}(1)^{a}$	0.00	6.07	-5.00	-65.89	-56.22	-64.49	-64.32	-71.48
$\Delta G_{sol}(2)^{b}$	0.00	6.08	-4.99	-65.87	-56.21	-64.48	-64.30	-71.48

 a The $\Delta G_{sol}(1)$ denotes the reaction free energy without the translational entropy correction;

^b The $\Delta G_{sol}(2)$ denotes the reaction free energy with the translational entropy correction;

 c The reactants include $^{3}\{[NiL]^{0}\},$ CO₂ and H₃O⁺.

S.4 Single electron transfer

We used the Marcus theory^{2,3} to estimate the barriers of the single electron transfer processes, and the energy barrier ΔG^{\neq} for a single electron transfer reaction could be obtained using equation (1).

$$\Delta G^{\neq} = \frac{\left(\Delta G + \lambda\right)^2}{4\lambda} \tag{1}$$

Here, the ΔG is the reaction free energy for the single electron transfer process, and the λ is the reorganization energy from all involved nuclei and solvent molecules. The nuclear reorganization energy (λ_N) was obtained through calculating the energy difference between the initial and final electronic states while keeping the geometries of reactants unchanged. For the reaction between a donor D and an acceptor A, the λ_N is numerically shown in equation (2), where the numbers 1 and 2 denote the initial and finial electronic state of each species, respectively.

$$\lambda_{N} = D2 + A2 - D1 - A1 \tag{2}$$

The solvent reorganization energy (λ_s) was calculated using the non-equilibrium solvent cage, which was carried out via the "scrf=read" keyword together with the "NonEq=write/read" in input option in Gaussian 09. The λ_s is numerically shown in equation (3), where the [α] and [β] represent the unpolarized and polarized solvent cages when maintaining the same geometries of reactants, respectively.

$$\lambda_s = D2[\alpha] + A2[\alpha] - D2[\beta] - A2[\beta]$$
(3)

The above methods for the estimations of λ_N and λ_S are reasonable according to the reports of Maseras. $^{4-6}$

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