Electronic Supporting Information for

Vibronic Coupling Effects in the Photoelectron Spectra of LiB_6^-

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Table S.I. **Normal-mode combinations, primitive basis dimensions, and single-particle functions (SPFs) employed in uncoupled and coupled (TD and TI) MCTDH calculations for LiB_6^-**

Combination of normal modes	Primitive basis	SPF
ν_1	18	[14,14,14,14,14,14]
ν_2	16	[12,12,12,12,12,12]
ν_3	15	[10,10,10,10,10,10]
ν_4	13	[8,8,8,8,8,8]
ν_5	10	[6,6,6,6,6,6]
ν_1,ν_7,ν_{11}	18,18,18	[14,14,14,14,14,14]
ν_2,ν_8,ν_9	16,16,16	[12,12,12,12,12,12]
ν_3,ν_6,ν_{12}	15,15,15	[10,10,10,10,10,10]
ν_4,ν_{10},ν_{13}	13,13,13	[8,8,8,8,8,8]
ν_5,ν_{14},ν_{15}	10,10,10	[6,6,6,6,6,6]
ν_1	18	
ν_2	16	
ν_3	15	
ν_4	13	
ν_5	10	
ν_2,ν_4,ν_{15}	4,4,4,4	
ν_7,ν_9,ν_{11},ν_{14}	3,3,3,3	
ν_1,ν_3,ν_5,ν_6,ν_8,ν_{10},ν_{12},ν_{13}	2,2,2,2,2,2,2,2	

Table S.II. **Higher-order terms concerning the non-totally symmetric modes of LiB_6^- involved in the model vibronic Hamiltonian**

Mode	$\gamma_i^{(j)}$	$D_i^{(j)}$	Mode	$\gamma_i^{(j)}$	$D_i^{(j)}$
	$\widetilde{X}$			$\widetilde{C}$	
ν_6	-0.0473	0.0003	ν_6	-0.0216	0.0000
ν_7	-0.0085	0.0000	ν_7	-0.0101	0.0000
ν_8	-0.0022	0.0000	ν_8	-0.0109	0.0000
ν_9	-0.0098	0.0000	ν_9	-0.3734	0.0838
ν_{10}	0.0004	0.0000	ν_{10}	-0.6617	0.1626
ν_{11}	-0.0026	0.0000	ν_{11}	-0.8999	0.2670
ν_{12}	-0.0037	0.0000	ν_{12}	0.0020	0.0000
ν_{13}	0.0025	0.0000	ν_{13}	-0.0060	0.0000
ν_{14}	0.0037	0.0000	ν_{14}	0.0034	0.0000
ν_{15}	-0.0115	0.0000	ν_{15}	0.0132	0.0000
	$\widetilde{A}$			$\widetilde{D}$	
ν_6	-0.0275	0.0003	ν_6	-0.0064	0.0000
ν_7	-0.0206	0.0002	ν_7	0.0519	-0.0004
ν_8	-0.0016	0.0000	ν_8	0.0029	0.0000
ν_9	-0.0095	0.0000	ν_9	0.0086	0.0000
ν_{10}	-0.0038	0.0000	ν_{10}	-0.0032	0.0000
ν_{11}	-0.0002	0.0000	ν_{11}	0.0049	0.0000
ν_{12}	0.0011	0.0000	ν_{12}	0.0022	0.0000
ν_{13}	0.0072	0.0000	ν_{13}	-0.0035	0.0000
ν_{14}	0.0010	0.0000	ν_{14}	0.0238	-0.0002
ν_{15}	-0.0148	0.0000	ν_{15}	0.0097	0.0000
	$\widetilde{B}$			$\widetilde{E}$	
ν_6	0.0673	-0.0005	ν_6	0.00724	-0.0002
ν_7	0.0238	-0.0001	ν_7	-0.0484	0.0004
ν_8	0.0077	0.0000	ν_8	-0.0058	0.0000
ν_9	0.3082	-0.0385	ν_9	-0.0159	0.0000
ν_{10}	0.4787	-0.0633	ν_{10}	-0.0012	0.0000
ν_{11}	0.9169	-0.2718	ν_{11}	-0.0010	0.0000
ν_{12}	-0.0031	0.0000	ν_{12}	-0.0041	0.0000
ν_{13}	-0.0242	0.0000	ν_{13}	0.0040	0.0000
ν_{14}	-0.0630	0.0002	ν_{14}	-0.0029	0.0000
ν_{15}	-0.0105	0.0000	ν_{15}	0.0200	0.0000

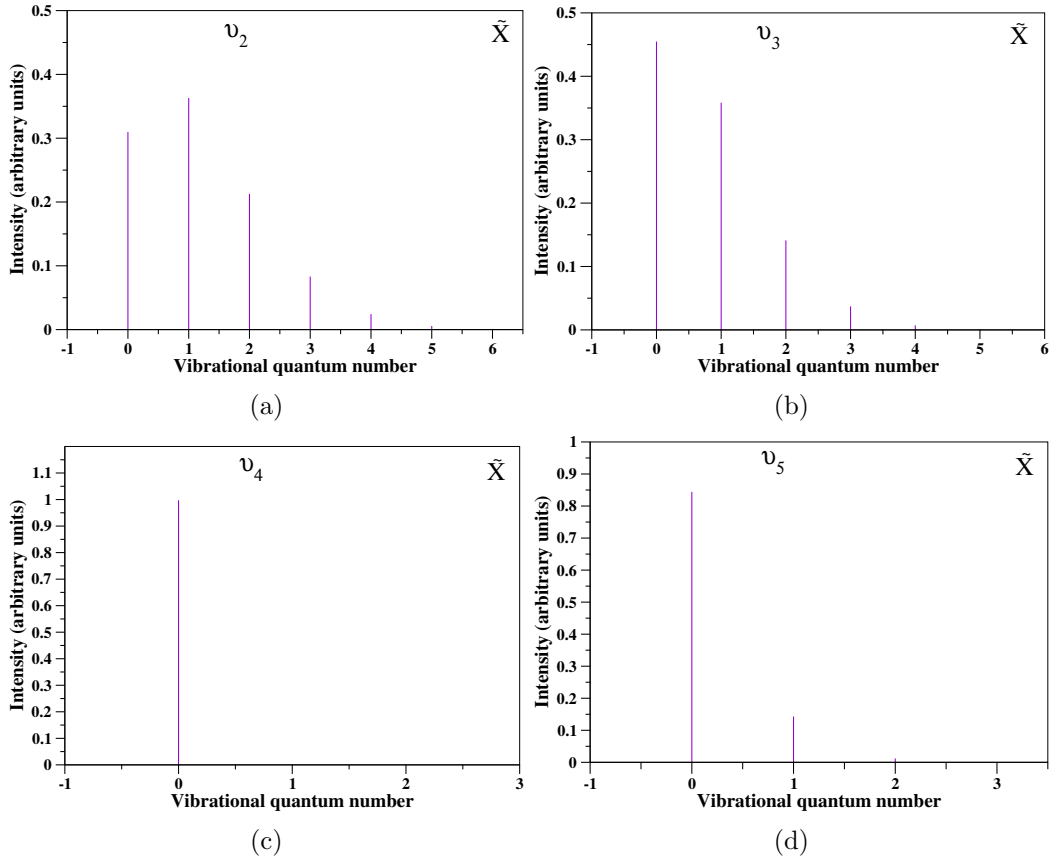

Figure S1. Poisson intensity distribution for totally symmetric modes concerning the $\tilde{X}$ state of LiB_6.

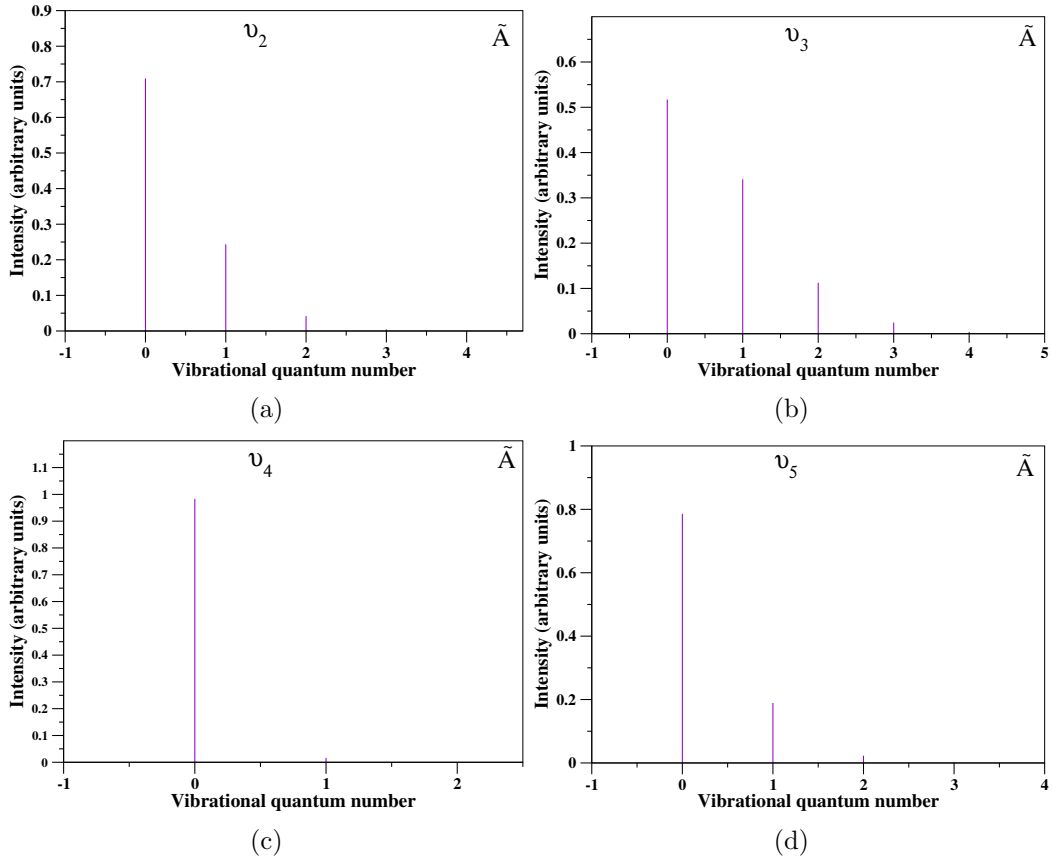

Figure S2. Poisson intensity distribution for totally symmetric modes concerning the $\tilde{A}$ state of LiB_6.

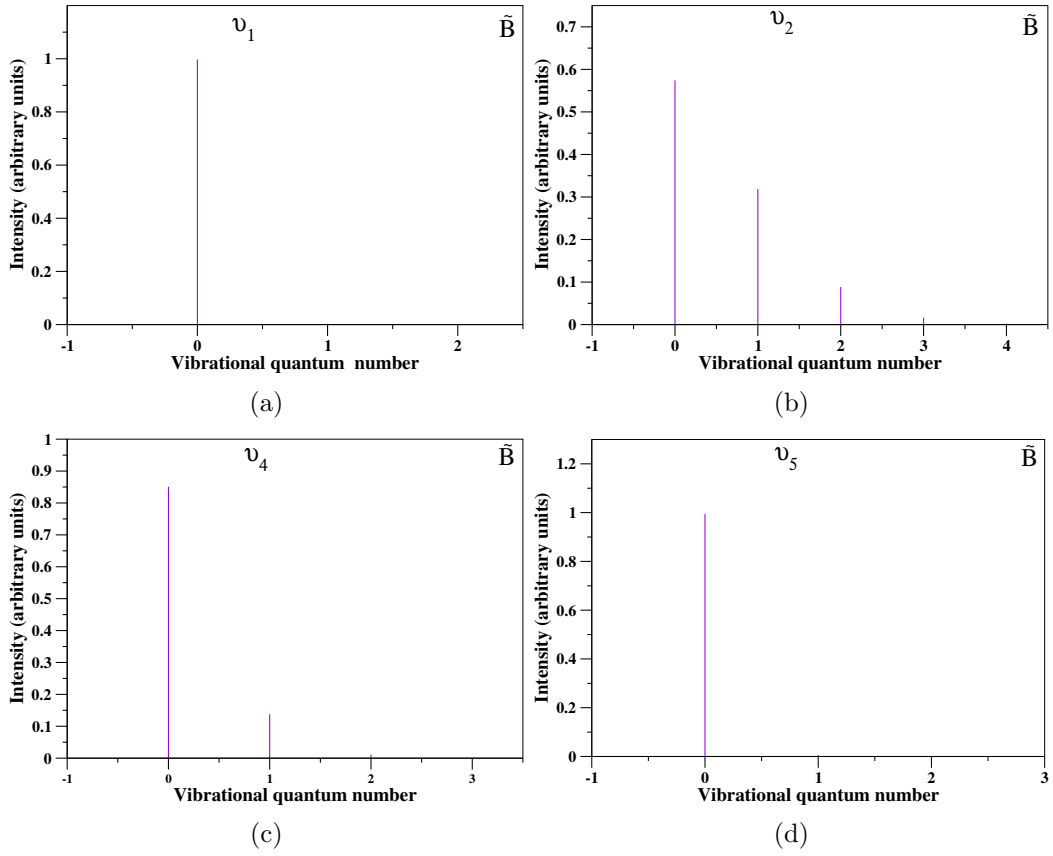

Figure S3. Poisson intensity distribution for totally symmetric modes concerning the $\tilde{B}$ state of LiB_6.

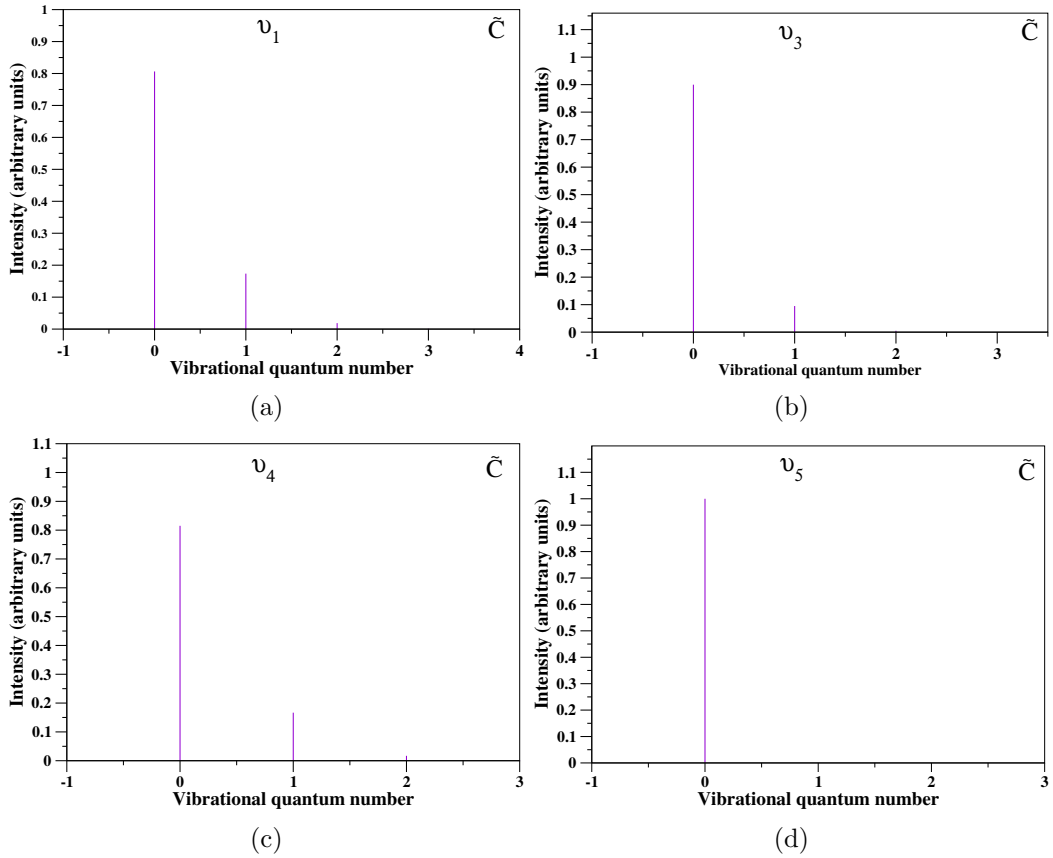

Figure S4. Poisson intensity distribution for totally symmetric modes concerning the $\tilde{C}$ state of LiB_6.

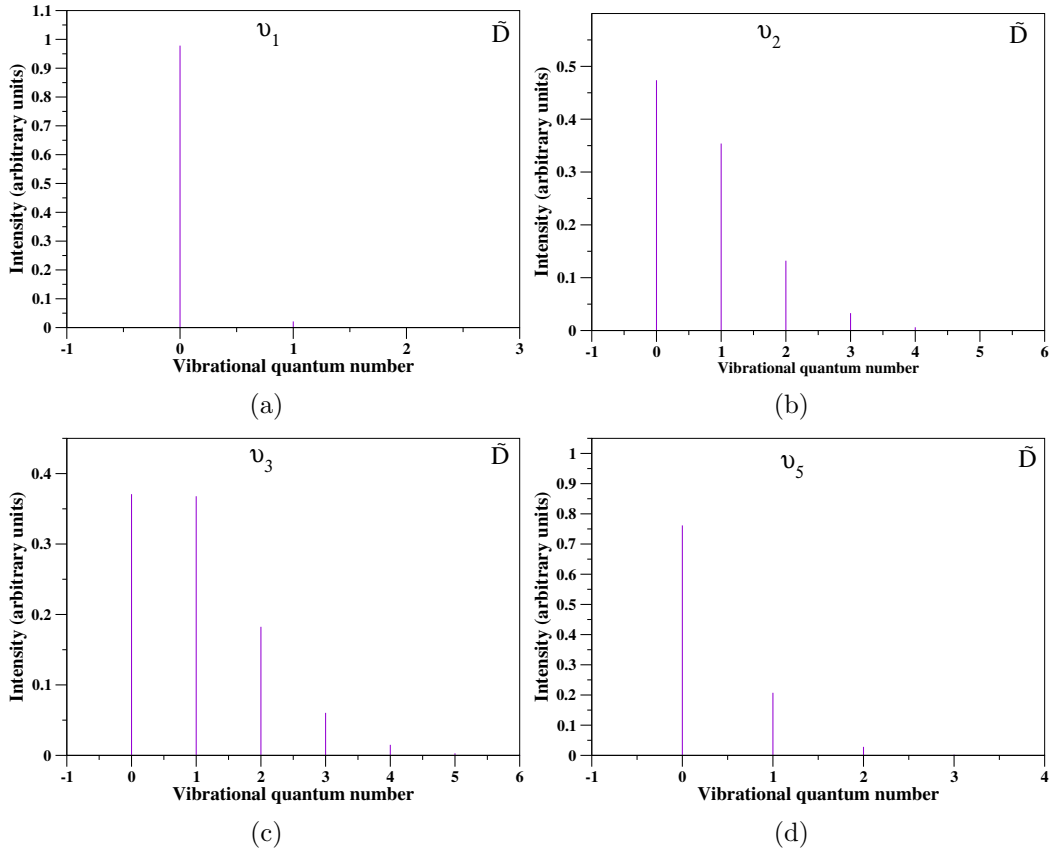

Figure S5. Poisson intensity distribution for totally symmetric modes concerning the $\tilde{D}$ state of LiB_6.

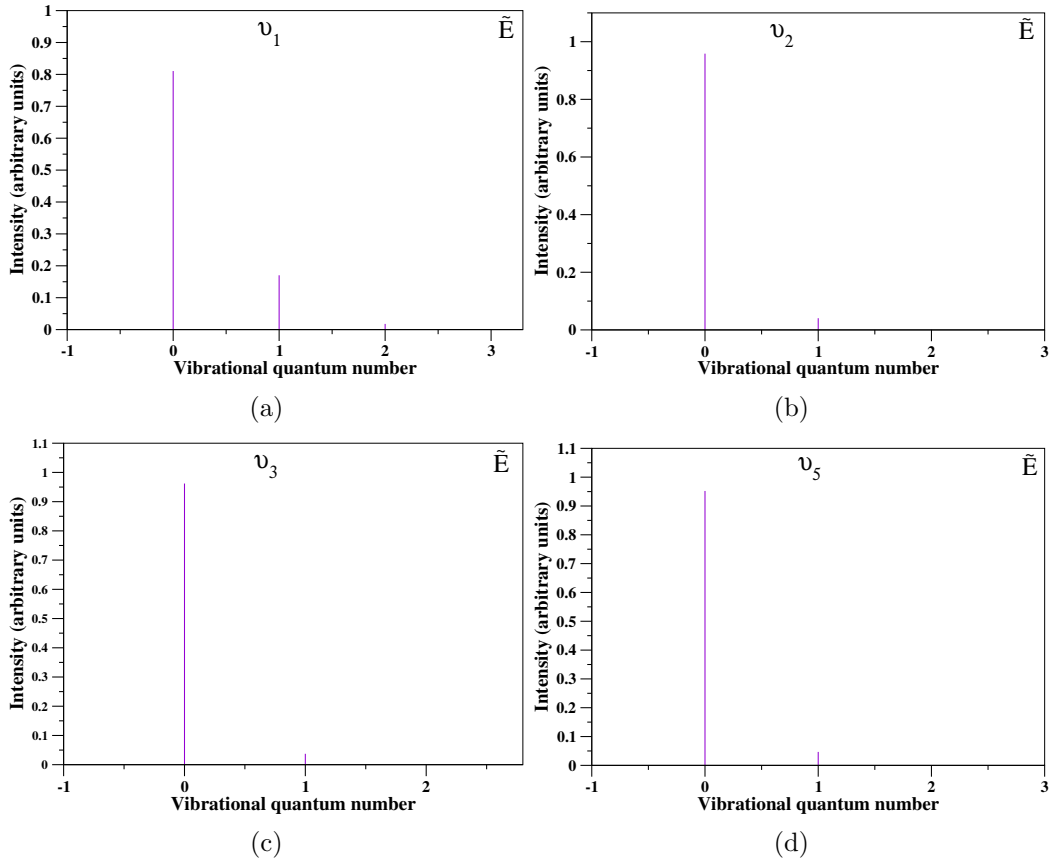

Figure S6. Poisson intensity distribution for totally symmetric modes concerning the $\tilde{E}$ state of LiB_6.

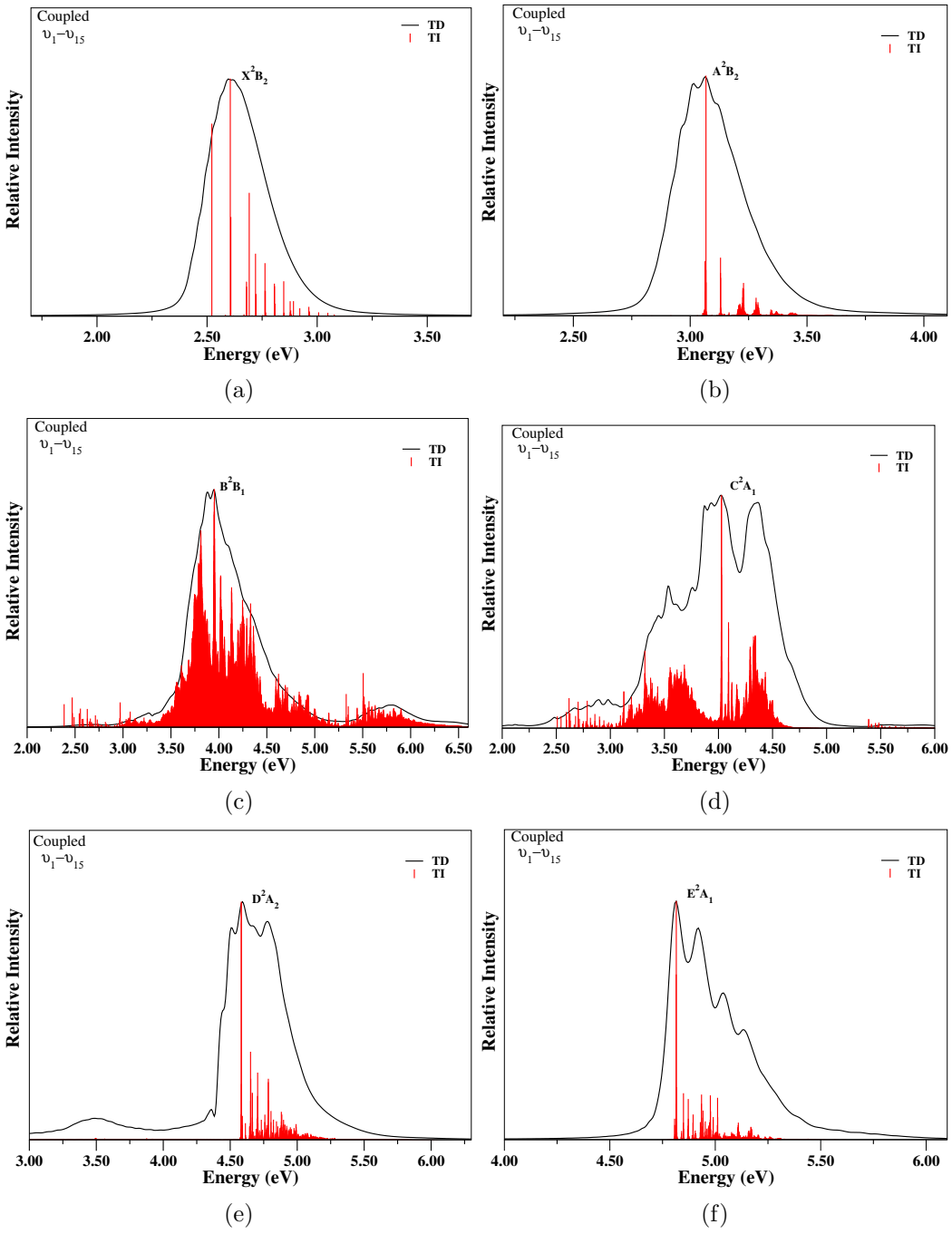

Figure S7. Comparison of theoretically calculated TD and TI coupled spectral peaks for $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, $\tilde{D}$ and $\tilde{E}$ states of LiB_6. In this figure, the black curves and the red stick lines are estimated from the TD and TI methodologies, respectively.