Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

An unbiased confirmation of the participating isomers of $C_2B_5^-$ in the formation of its photo-detachment spectra, a theoretical study

Abhishek Kumar[1], T. Rajagopala Rao[1†] and Rudraditya Sarkar[2*]

[1] *Department of Chemistry, Indian Institute of Technology, Patna, Bihta, Bihar, 801103, India and*

[2] *CEISAM Lab, UMR 6230, University of Nantes, F-44000 Nantes, France*[*]

[*] rudra.smgr@gmail.com; Rudraditya.Sarkar@univ-nantes.fr; [†]rajgopal@iitp.ac.in

TABLE S1: Bond length($\mathring{A}$) at the equilibrium ground state configuration of $C_2B_5^-$ and C_2B_5 (isomer-I) belongs to C_{2v} point group symmetry. The geometry optimization is performed with Møller-Plesset perturbation (MP2) level of theory employing Dunning's correlation consistent polarized valence triple-zeta (cc-pVTZ) basis set. The schematic numbering of the atoms are shown in Fig. 1(a) in the main manuscript.

Bond length	$C_2B_5^-$	C_2B_5
$C_1 - B_6$	1.4398	1.3902
$C_1 - B_4$	1.5026	1.4447
$B_6 - B_4$	1.6793	1.7499
$B_4 - B_5$	1.5934	1.5745
$B_4 - B_3$	1.6204	1.6266
$B_5 - B_7$	1.6793	1.7499
$B_5 - C_2$	1.5026	1.4447
$c_2 - B_7$	1.4398	1.3902
$B_5 - B_3$	1.9346	2.1918

TABLE S2: Bond length($\mathring{A}$) at the equilibrium ground state configuration of $C_2B_5^-$ and C_2B_5 (isomer-II) belongs to C_s point group symmetry. The geometry optimization is performed with Møller-Plesset perturbation (MP2) level of theory employing Dunning's correlation consistent polarized valence triple-zeta (cc-pVTZ) basis set. The schematic numbering of the atoms are shown in Fig. 1(b) in the main manuscript.

Bond length	$C_2B_5^-$	C_2B_5
$B_7 - C_1$	1.4555	1.4263
$B_7 - B_4$	1.6853	1.6773
$C_1 - B_4$	1.5692	1.5956
$C_1 - B_3$	1.4571	1.4249
$B_4 - B_5$	1.6388	1.6266
$B_4 - B_3$	1.8306	1.7762
$B_5 - B_3$	1.9362	2.2686
$C_5 - B_6$	1.6747	1.6795
$B_3 - B_6$	1.6009	1.6234
$B_5 - C_2$	1.4811	1.4468
$C_2 - B_6$	1.4371	1.4284

TABLE S3: Frequencies (in eV) of both the isomers of $C_2B_5^-$ and C_2B_5 in their ground state equilibrium geometries.

C_{2v}			Cs		
Vibrational mode	Anionic frequencies	Neutral frequencies (Isomer-I)	Vibrational mode	Anionic frequencies	Neutral frequencies (Isomer-II)
$\nu_1(a_1)$	0.0496	0.0494	$\nu_1(a^{'})$	0.0417	0.0529
$\nu_2(a_1)$	0.0656	0.0715	$\nu_2(a^{'})$	0.0573	0.0687
$\nu_3(a_1)$	0.0835	0.0803	$\nu_3(a^{'})$	0.0651	0.0681
$\nu_4(a_1)$	0.1068	0.1112	$\nu_4(a^{'})$	0.0786	0.0877
$\nu_5(a_1)$	0.1613	0.1641	$\nu_5(a^{'})$	0.0950	0.1074
$\nu_6(a_1)$	0.1770	0.1732	$\nu_6(a^{'})$	0.1087	0.1091
$\nu_7(b_1)$	0.0226	0.0368	$\nu_7(a^{'})$	0.118	0.1233
$\nu_8(b_1)$	0.0570	0.0588	$\nu_8(a^{'})$	0.1461	0.1540
$\nu_9(b_2)$	0.0358	0.0511	$\nu_9(a^{'})$	0.1572	0.1603
$\nu_{10}(b_2)$	0.1010	0.0965	$\nu_{10}(a^{'})$	0.1728	0.1694
$\nu_{11}(b_2)$	0.1218	0.1224	$\nu_{11}(a^{'})$	0.1866	0.1866
$\nu_{12}(b_2)$	0.1478	0.1518	$\nu_{12}(a^{"})$	0.0217	0.0356
$\nu_{13}(b_2)$	0.1667	0.1724	$\nu_{13}(a^{"})$	0.0323	0.0384
$\nu_{14}(a_2)$	0.0325	0.0327	$\nu_{14}(a^{"})$	0.0566	0.0570
$\nu_{15}(a_2)$	0.0618	0.0615	$\nu_{15}(a^{"})$	0.0626	0.06242

TABLE S4: The vertical detachment energies (in eV) of the electronic states of isomer-I and isomer-II using different active spaces employing CASSCF and MRCI level of theories.

Isomer-I (CASSCF/cc-pVTZ)					
Active space	$\widetilde{X}^2A_1$	$\widetilde{A}^2B_2$	$\widetilde{B}^2A_2$	$\widetilde{C}^2B_1$	$\widetilde{D}^2A_1$
(10e,10o)	2.7775	3.9480	4.6621	5.1380	6.0722
(12e,10o)	2.3309	3.8251	3.8897	4.3261	5.4038
(10e,11o)	2.7443	4.3175	4.6352	4.8294	6.0855
(12e,11o)	2.4268	3.8719	3.9469	4.5451	5.4492
(10e,12o)	2.7880	4.2958	4.6525	4.9122	6.1513
(12e,12o)	2.3426	4.1629	3.9407	4.2637	5.4164
Isomer-I (MRCI/cc-pVTZ)					
(10e,10o)	3.2629	4.6906	5.1368	6.4018	6.5483
(12e,10o)	3.0552	4.5709	4.6840	5.4735	5.9838
(10e,11o)	3.2650	4.7457	5.1188	5.8789	6.5375
(12e,11o)	3.0497	4.6980	4.5816	5.5954	5.9987
(10e,12o)	3.2755	4.7470	5.1212	5.8994	6.5491
(12e,12o)	3.0345	4.7594	4.5604	5.4406	5.9718
Isomer-II (CASSCF/cc-pVTZ)					
Active space	$\widetilde{X}^2A'$	$\widetilde{A}^2A''$	$\widetilde{B}^2A'$	$\widetilde{C}^2A'$	$\widetilde{D}^2A'$
(10e,10o)	1.8395	3.5691	4.6525	5.2653	5.3492
(12e,10o)	1.6692	3.3517	4.3310	5.1361	5.2208
(10e,11o)	1.8859	3.5948	4.6132	5.3125	5.3581
(10e,12o)	1.9290	3.6557	4.6163	5.2617	5.3764
Isomer-II (MRCI/cc-pVTZ)					
(10e,10o)	2.4782	4.1752	5.3736	5.3916	5.7219
(12e,10o)	2.4045	4.1477	4.9871	5.8542	5.8657

TABLE S5: Comparison of experimental [1] vertical detachment energies with calculated MRCI(12e,10o)/cc-pVTZ level of theory in the present study and TD-B3LYP, OVGF and CCSD(T) level theories performed in the Ref. [1]. Here, (11) represents the electronic state of isomer-I (C_{2v}) and (12) represents the electronic state of isomer-II (C_s).

States	Ref. [1]	This study	Ref. [1]		
in Ref. [1]	exp	MRCI/cc-pVTZ	TD-B3LYP	OVGF	CCSD(T)
X(c_s)	2.61	2.40 (12)	2.54 (12)	2.74	2.63
A(C_{2v})	2.95	3.05 (11)	3.00 (11)	3.08	3.13
B(C_s)	4.06	4.15 (12)	4.13 (12)	4.47	...
C(C_{2v})	4.36	4.57 (11)	4.42 (11)	4.73	4.49
D(C_{2v})	4.93	4.68 (11)	4.79 (11)	4.90	4.97
E(C_s)	5.09	4.99 (12)	5.08 (12)	5.30	5.42
F(C_s)	5.62	5.98 (11), 5.85 (12)	5.57 (12)	5.86	...
G(C_s)	$\sim$6	5.87 (12)	...	...	...

TABLE S6: The frequencies of the reference state of the isomer-I and the intra-state coupling parameters of all vibrational modes of the $\widetilde{X}^2A_1$ state of isomer-I are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a_1)	0.0496	3.06188	-0.10417 (2.2054)	-0.00029	0.00080		
ν_2 (a_1)	0.0656	3.06312	-0.03814 (0.1690)	0.01228			
ν_3 (a_1)	0.0835	3.06305	0.10549 (0.7966)	-0.00638			
ν_4 (a_1)	0.1068	3.06050	-0.12287 (0.6617)	0.00903			
ν_5 (a_1)	0.1613	3.06118	0.00413 (0.0003)	0.00576	-0.00062	0.00001	0.00001
ν_6 (a_1)	0.1770	3.06045	-0.16019 (0.4095)	-0.00743			
ν_7 (b_1)	0.0226	3.00458		0.03756			
ν_8 (b_1)	0.0570	3.03779		0.00365			
ν_9 (b_2)	0.0358	3.00768		0.03701			
ν_{10} (b_2)	0.1010	3.01318		-0.00868			
ν_{11} (b_2)	0.1218	3.00902		0.00135			
ν_{12} (b_2)	0.1478	3.00810		0.00813		-0.00005	
ν_{13} (b_2)	0.1667	3.00922		0.01154			
ν_{14} (a_2)	0.0325	3.02865		0.00043		-0.00003	
ν_{15} (a_2)	0.0618	3.01258		-0.00063			

TABLE S7: The frequencies of the reference state of the isomer-I and the intra-state coupling parameters of all vibrational modes of the $\widetilde{A}^2B_2$ state of isomer-I are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a_1)	0.0496	4.57193	0.07140 (1.0361)	-0.00188			
ν_2 (a_1)	0.0656	4.57084	0.00358 (0.0015)	0.00083	0.00000	-0.00001	
ν_3 (a_1)	0.0835	4.57124	0.08572 (0.5269)	-0.00422			
ν_4 (a_1)	0.1068	4.57084	-0.08476 (0.3149)	-0.00591			
ν_5 (a_1)	0.1613	4.57253	0.04858 (0.0453)	-0.00293			
ν_6 (a_1)	0.1770	4.46938	0.01613 (0.0042)	-0.00493	-0.00061		
ν_7 (b_1)	0.0226	4.98253		0.07089			
ν_8 (b_1)	0.0570	5.48320		-0.02213			
ν_9 (b_2)	0.0358	4.54818		0.00326		-0.00004	
ν_{10} (b_2)	0.1010	4.54113		0.00408		-0.00013	
ν_{11} (b_2)	0.1218	4.54943		-0.00336			
ν_{12} (b_2)	0.1478	4.54635		-0.00740		0.00005	
ν_{13} (b_2)	0.1667	4.54637		0.01386		-0.00010	
ν_{14} (a_2)	0.0325	4.54660		-0.00227			
ν_{15} (a_2)	0.0618	4.53935		-0.00536			

TABLE S8: The frequencies of the reference state of the isomer-I and the intra-state coupling parameters of all vibrational modes of the $\widetilde{B}^2A_2$ state of isomer-I are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a_1)	0.0496	4.68139	-0.02469 (0.1238)	0.00174	0.00030		
ν_2 (a_1)	0.0656	4.68322	-0.01429 (0.0237)	-0.00868			
ν_3 (a_1)	0.0835	4.61263	-0.00285 (0.0006)	0.00115			
ν_4 (a_1)	0.1068	4.68458	-0.05193 (0.1182)	-0.00053			
ν_5 (a_1)	0.1613	4.68435	0.00947 (0.0017)	0.00522			
ν_6 (a_1)	0.1770	4.61329	0.19575 (0.6115)	0.00827			
ν_7 (b_1)	0.0226	4.48692		-0.02313			
ν_8 (b_1)	0.0570	4.55611		-0.04836		0.00042	
ν_9 (b_2)	0.0358	4.74553		-0.00145			
ν_{10} (b_2)	0.1010	4.74652		0.00058		-0.00005	
ν_{11} (b_2)	0.1218	-		-			
ν_{12} (b_2)	0.1478	4.74048		-0.02582			
ν_{13} (b_2)	0.1667	4.74681		0.01664			
ν_{14} (a_2)	0.0325	4.73017		-0.00753			
ν_{15} (a_2)	0.0618	4.72736		-0.01494			

TABLE S9: The frequencies of the reference state of the isomer-I and the intra-state coupling parameters of all vibrational modes of the $\widetilde{C}^2B_1$ state of isomer-I are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a_1)	0.0496	4.91959	-0.27967 (15.8963)	-0.03305	0.00383		
ν_2 (a_1)	0.0656	4.92512	-0.07239 (0.6088)	0.01776			
ν_3 (a_1)	0.0835	4.92384	0.12602 (1.1388)	-0.00866			
ν_4 (a_1)	0.1068	4.92244	-0.22057 (2.1326)	0.00725			
ν_5 (a_1)	0.1613	4.93629	-0.10890 (0.2279)	-0.01484	0.00173		
ν_6 (a_1)	0.1770	4.92064	-0.29784 (1.4157)	-0.01974			
ν_7 (b_1)	0.0226	4.67842		0.00392			
ν_8 (b_1)	0.0570	4.69083		0.04579		-0.00041	
ν_9 (b_2)	0.0358	5.43417		0.05623			
ν_{10} (b_2)	0.1010	5.39726		0.00126		-0.00008	
ν_{11} (b_2)	0.1218	-		-			
ν_{12} (b_2)	0.1478	5.38979		0.00770			
ν_{13} (b_2)	0.1667	5.42366		-0.02289		0.00012	
ν_{14} (a_2)	0.0325	5.32798		0.02151		-0.00018	
ν_{15} (a_2)	0.0618	5.35472		-0.03118			

TABLE S10: The frequencies of the reference state of the isomer-I and the intra-state coupling parameters of all vibrational modes of the $\widetilde{D}^2A_1$ state of isomer-I are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a_1)	0.0496	5.99131	0.06215 (0.7850)	-0.01430	-0.00061	-0.00024	
ν_2 (a_1)	0.0656	5.99127	0.00068 (0.0001)	-0.00170	-0.00004	-0.00002	
ν_3 (a_1)	0.0835	5.95735	-0.01440 (0.0149)	0.00414			
ν_4 (a_1)	0.1068	5.99029	-0.09777 (0.4184)	-0.00357	0.00173	-0.00025	
ν_5 (a_1)	0.1613	5.95146	-0.02718 (0.0142)	-0.01659	-0.00062		
ν_6 (a_1)	0.1770	5.95589	-0.04725 (0.0356)	0.00791			
ν_7 (b_1)	0.0226	5.95738		-0.00733			
ν_8 (b_1)	0.0570	6.00420		-0.01256			
ν_9 (b_2)	0.0358	5.98033		-0.03140		0.00026	
ν_{10} (b_2)	0.1010	5.98680		-0.03837			
ν_{11} (b_2)	0.1218	5.96342		-0.02255			
ν_{12} (b_2)	0.1478	5.97492		0.00459		-0.00018	
ν_{13} (b_2)	0.1667	5.98219		0.00988		-0.00013	
ν_{14} (a_2)	0.0325	5.96838		-0.01627			
ν_{15} (a_2)	0.0618	5.97780		-0.01030			

TABLE S11: The frequencies of the reference state of the isomer-II and the intra-state coupling parameters of all vibrational modes of the $\widetilde{X}^2A^{'}$ state of isomer-II are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a$^{'}$)	0.0417	2.40715	0.07336 (1.5474)	0.02557			
ν_2 (a$^{'}$)	0.0573	2.41135	0.05040 (0.3868)	0.02521	0.00034		
ν_3 (a$^{'}$)	0.0651	2.40277	0.03913 (0.1806)	0.00617			
ν_4 (a$^{'}$)	0.0786	2.41027	0.12192 (1.2030)	0.01945			
ν_5 (a$^{'}$)	0.0950	2.40627	0.00681 (0.0026)	0.02640	-0.00000	-0.00018	
ν_6 (a$^{'}$)	0.1087	2.40677	0.07975 (0.2691)	0.00075			
ν_7 (a$^{'}$)	0.1180	2.40343	0.06185 (0.1374)	0.01085	-0.00057		
ν_8 (a$^{'}$)	0.1461	2.40911	-0.00754 (0.0013)	0.01613	0.00033		
ν_9 (a$^{'}$)	0.1572	2.40629	0.00751 (0.0011)	0.00629	0.00005		
ν_{10} (a$^{'}$)	0.1728	2.38190	0.14746 (0.3641)	-0.00669			
ν_{11} (a$^{'}$)	0.1866	2.38235	-0.00822 (0.0010)	-0.00041			
ν_{12} (a$^{''}$)	0.0217	2.39606		0.03680			
ν_{13} (a$^{''}$)	0.0323	2.39652		0.01328			
ν_{14} (a$^{''}$)	0.0566	2.39646		0.00088			
ν_{15} (a$^{''}$)	0.0626	2.39643		-0.00035		0.00006	

TABLE S12: The frequencies of the reference state of the isomer-II and the intra-state coupling parameters of all vibrational modes of the $\widetilde{A}^2A^{'}$ state of isomer-II are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a$^{'}$)	0.0417	4.14209	-0.05716 (0.9395)	-0.00869	0.00124		
ν_2 (a$^{'}$)	0.0573	4.14423	0.02549 (0.0989)	-0.00382	-0.00046		
ν_3 (a$^{'}$)	0.0651	4.14622	0.03376 (0.1345)	0.00205	-0.00062		
ν_4 (a$^{'}$)	0.0786	4.14523	0.05165 (0.2159)	-0.01654			
ν_5 (a$^{'}$)	0.0950	4.14920	-0.07084 (0.2780)	-0.01470			
ν_6 (a$^{'}$)	0.1087	4.14832	0.10528 (0.4690)	0.00691			
ν_7 (a$^{'}$)	0.1180	4.15085	0.01313 (0.0062)	-0.00522	0.00046		
ν_8 (a$^{'}$)	0.1461	4.14394	0.03920 (0.0360)	0.00146			
ν_9 (a$^{'}$)	0.1572	4.14754	-0.00773 (0.0012)	0.00065	-0.00011	-0.00007	
ν_{10} (a$^{'}$)	0.1728	4.05981	-0.01702 (0.0049)	0.01422			
ν_{11} (a$^{'}$)	0.1866	4.14067	0.09141 (0.1200)	0.00016	-0.00048		
ν_{12} (a$^{''}$)	0.0217	4.13940		0.00676		-0.00014	
ν_{13} (a$^{''}$)	0.0323	4.13954		-0.00513			
ν_{14} (a$^{''}$)	0.0566	4.13930		-0.00948			
ν_{15} (a$^{''}$)	0.0626	4.13825		-0.01525			

TABLE S13: The frequencies of the reference state of the isomer-II and the intra-state coupling parameters of all vibrational modes of the $\widetilde{B}^2A''$ state of isomer-II are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a$'$)	0.0417	4.98375	-0.02939 (0.2484)	0.00075			
ν_2 (a$'$)	0.0573	4.98600	0.04334 (0.2860)	-0.00539			
ν_3 (a$'$)	0.0651	4.98531	0.01458 (0.0251)	-0.00343			
ν_4 (a$'$)	0.0786	4.98718	0.03054 (0.0755)	-0.00221	-0.00024		
ν_5 (a$'$)	0.0950	4.98789	0.05108 (0.1446)	-0.00023			
ν_6 (a$'$)	0.1087	4.98556	0.06558 (0.1820)	0.00265			
ν_7 (a$'$)	0.1180	4.98571	0.02056 (0.0152)	0.00372	-0.00014		
ν_8 (a$'$)	0.1461	4.98664	0.02873 (0.0193)	-0.01919	-0.00058		
ν_9 (a$'$)	0.1572	4.98832	-0.02229 (0.0101)	0.00499			
ν_{10} (a$'$)	0.1728	4.89533	-0.22228 (0.8273)	0.03666	0.00484	-0.00116	
ν_{11} (a$'$)	0.1866	4.98294	-0.05079 (0.0370)	0.01380			
ν_{12} (a$''$)	0.0217	4.96268		-0.01743			
ν_{13} (a$''$)	0.0323	4.96286		-0.02045			
ν_{14} (a$''$)	0.0566	4.96354		-0.00670			
ν_{15} (a$''$)	0.0626	4.96501		-0.0055		-0.00004	

TABLE S14: The frequencies of the reference state of the isomer-II and the intra-state coupling parameters of all vibrational modes of the $\widetilde{C}^2A^{'}$ state of isomer-II are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a$^{'}$)	0.0417	5.86834	0.02006 (0.1157)	-0.02626	-0.00389	0.00020	0.00008
ν_2 (a$^{'}$)	0.0573	5.83498	0.12084 (2.2237)	-0.00261			
ν_3 (a$^{'}$)	0.0651	5.84870	0.00464 (0.0025)	-0.02005			
ν_4 (a$^{'}$)	0.0786	5.84787	0.19709 (3.1438)	0.01567			
ν_5 (a$^{'}$)	0.0950	5.86349	0.20971 (2.4365)	-0.01001	-0.00341		
ν_6 (a$^{'}$)	0.1087	5.85446	0.10746 (0.4887)	-0.00122			
ν_7 (a$^{'}$)	0.1180	5.86186	0.04043 (0.0587)	-0.03827			
ν_8 (a$^{'}$)	0.1461	5.80910	0.08025 (0.1509)	-0.06145	-0.00078	0.00073	
ν_9 (a$^{'}$)	0.1572	5.85783	0.10328 (0.2158)	-0.01033			
ν_{10} (a$^{'}$)	0.1728	5.50398	-0.02102 (0.0074)	-0.00686	0.00147	0.00036	-0.00002
ν_{11} (a$^{'}$)	0.1866	5.83502	0.12921 (0.2397)	0.03780			
ν_{12} (a$^{''}$)	0.0217	5.83970		-0.01903			
ν_{13} (a$^{''}$)	0.0323	5.82847		-0.06050			
ν_{14} (a$^{''}$)	0.0566	5.83239		-0.02290			
ν_{15} (a$^{''}$)	0.0626	5.82989		-0.05941		0.00048	

TABLE S15: The frequencies of the reference state of the isomer-II and the intra-state coupling parameters of all vibrational modes of the $\widetilde{D}^2A^{'}$ state of isomer-II are given in this table. The parameters are given in eV unit.

Vibrational mode	Anionic frequency	E_0	κ ($\frac{\kappa^2}{2\omega^2}$)	γ	δ	ϵ	ζ
ν_1 (a$^{'}$)	0.0417	5.84476	-0.14781 (6.2821)	-0.00634			
ν_2 (a$^{'}$)	0.0573	5.85743	-0.06260 (0.5968)	0.00096			
ν_3 (a$^{'}$)	0.0651	5.86409	-0.00041 (0.0000)	-0.00742	-0.00003	0.00012	
ν_4 (a$^{'}$)	0.0786	5.86578	-0.08176 (0.5410)	0.00272	0.00173		
ν_5 (a$^{'}$)	0.0950	5.85595	-0.11115 (0.6838)	-0.01503	0.00160	0.00021	
ν_6 (a$^{'}$)	0.1087	5.85741	0.06000 (0.1523)	0.00513	-0.00195	-0.00047	
ν_7 (a$^{'}$)	0.1180	5.86787	0.02627 (0.0248)	-0.01614	0.00023		
ν_8 (a$^{'}$)	0.1461	5.88159	0.07971 (0.1488)	0.01086			
ν_9 (a$^{'}$)	0.1572	5.86506	0.01704 (0.0059)	-0.01452	0.00031	0.00014	
ν_{10} (a$^{'}$)	0.1728	5.78806	0.06173 (0.0638)	0.01800	-0.00255	-0.00036	
ν_{11} (a$^{'}$)	0.1866	5.85423	-0.05829 (0.0488)	-0.00388			
ν_{12} (a$^{''}$)	0.0217	5.84773		0.01936			
ν_{13} (a$^{''}$)	0.0323	5.85627		-0.00161		-0.00009	
ν_{14} (a$^{''}$)	0.0566	5.85580		-0.01902			
ν_{15} (a$^{''}$)	0.0626	5.85598		-0.01701			

TABLE S16: The inter-state coupling between $\widetilde{X}^2A_1$-$\widetilde{A}^2B_2$ and $\widetilde{A}^2B_2$-$\widetilde{B}^2A_2$ states of isomer-I and the same between $\widetilde{A}^2A^{'}$-$\widetilde{B}^2A^{''}$ states of isomer-II are given in this table. The frequency of the coupling vibrational modes are also given in the table. All units are given in eV.

Vibrational mode	Anionic frequency	λ ($\frac{\lambda^2}{2\omega^2}$)	β
		$\tilde{X}^2A_1$-$\tilde{A}^2B_2$	
ν_{10}	0.1010	0.1651 (1.3360)	-0.0016
		$\tilde{A}^2B_2$-$\tilde{B}^2A_2$	
ν_7	0.0226	0.1204 (14.1908)	0.0015
ν_8	0.0570	0.0665 (0.6805)	-0.0009
		Electronic states of isomer-II	
		$\tilde{A}^2A^{'}$-$\tilde{B}^2A^{''}$	
ν_{14}	0.0566	0.0340 (0.1804)	
ν_{15}	0.0626	0.0437 (0.2437)	

TABLE S17: The inter-state coupling between $\widetilde{A}^2B_2$-$\widetilde{C}^2B_1$ and $\widetilde{B}^2A_2$-$\widetilde{C}^2B_1$ electronic states of the isomer-I. The data are presented in eV.

$\widetilde{A}^2B_2$-$\widetilde{C}^2B_1$			$\widetilde{B}^2A_2$-$\widetilde{C}^2B_1$		
Vibrational mode	Anionic Frequency	λ ($\frac{\lambda^2}{2\omega^2}$)	Vibrational mode	Anionic Frequency	λ ($\frac{\lambda^2}{2\omega^2}$)
ν_{14}	0.0325	0.0634 (1.9027)	ν_9	0.0358	0.1031 (4.1468)
			ν_{10}	0.1010	0.2117 (2.1966)
			ν_{12}	0.1478	0.2178 (1.0857)

TABLE S18: Normal modes combination, size of the primitive basis and single partition function (SPF) for the coupled and uncoupled full dimension and reduced dimension nuclear dynamics (time-dependent and time-independent) of C_2B_5 using MCTDH [2] approach

Combination of normal modes	Primitive basis	SPF	Figure
ν_1	16	[10, 10, 10, 10, 10]	Fig. 4 (a,b)
ν_3, ν_4, ν_6	12, 10, 10	[8, 8, 8, 8, 8]	Fig. S1
ν_2, ν_5	6, 6	[4, 4, 4, 4, 4]	Fig. S5 (a,b), black spectra
ν_1, ν_9, ν_{10}	16, 16, 14	[10, 10, 10, 10]	Fig. 5 (a-d)
ν_3, ν_4, ν_6, ν_{12}, ν_{14}	12, 10, 10, 10, 10	[8, 8, 8, 8]	Fig. 6 (C_{2v})
ν_2, ν_5, ν_7, ν_8, ν_{11}, ν_{13}, ν_{15}	6, 6, 4, 8, 4, 4, 6	[4, 4, 4, 4]	Fig. S5 (a,b) [red spectra]
ν_1, ν_9, ν_{10}	16, 16, 14	[10, 10, 10, 10, 10]	
ν_3, ν_4, ν_6, ν_{12}, ν_{14}	12, 10, 10, 10, 10	[8, 8, 8, 8, 8]	Fig. S4
ν_2, ν_5, ν_7, ν_8, ν_{11}, ν_{13}, ν_{15}	6, 6, 4, 8, 4, 4, 6	[4, 4, 4, 4, 4]	
ν_1	11	[8, 8, 8, 8, 8]	Fig. 4 (b, c)
ν_4	12	[9, 9, 9, 9, 9]	Fig. S2
ν_2, ν_3, ν_5, ν_6	8, 8, 8, 9	[5, 5, 5, 5, 5]	Fig. S3, green spectra
ν_1, ν_4, ν_6	18, 16, 12	[10, 10, 10, 10, 10]	Fig. S3, red spectra
ν_2, ν_3, ν_5	10, 10, 10	[8, 8, 8, 8, 8]	Fig. S5 (c-f), black spectra
ν_7, ν_8, ν_{11}	8, 8, 8	[6, 6, 6, 6, 6]	
ν_9, ν_{10}	6, 6	[4, 4, 4, 4, 4]	
ν_1, ν_4, ν_6	18, 16, 12	[10, 10, 10, 10, 10]	Fig. 5 (e-f)
ν_2, ν_3, ν_5, ν_{14}, ν_{15}	10, 10, 10, 10, 10	[8, 8, 8, 8, 8]	Fig. 6 (C_s), blue spectra
ν_7, ν_8, ν_{11}	8, 8, 8	[6, 6, 6, 6, 6]	Fig. S5 (c-f), black spectra
ν_9, ν_{10}, ν_{12}, ν_{13}	6, 6, 4, 4	[4, 4, 4, 4, 4]	

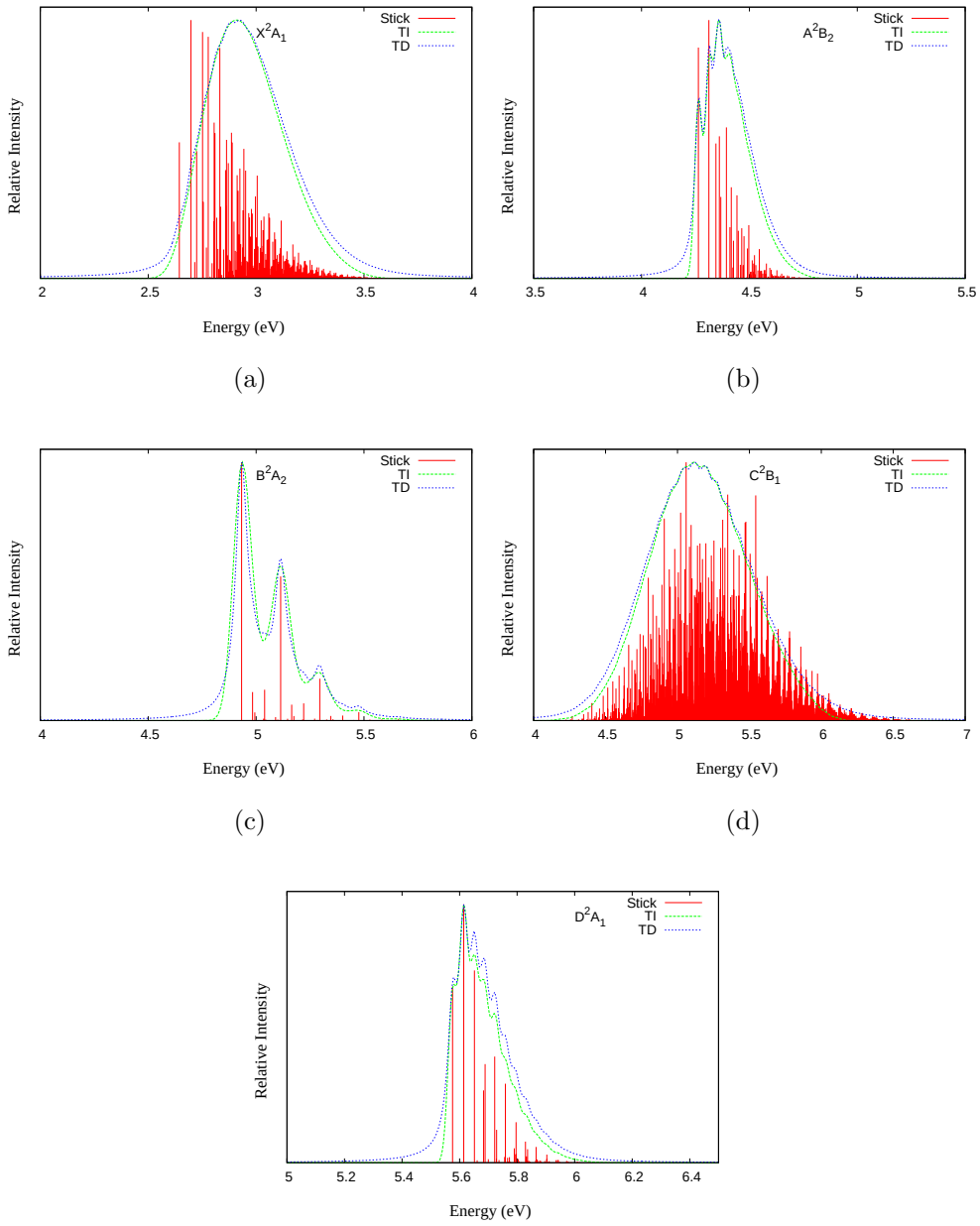

FIG. S1: The uncoupled time-dependent and time-independent spectra of the first five electronic states ($\widetilde{X}$ in panel a, $\widetilde{A}$ in panel b, $\widetilde{B}$ in panel c, $\widetilde{C}$ in panel d and $\widetilde{D}$ in panel e) of isomer-I are shown here. The vibronic energies obtained from the time-independent calculation are shown in red stick lines, while the spectrum envelope obtained from the convolution of these energies is shown in green dashed line and the spectrum envelope obtained from the time-dependent calculation is shown in blue dotted line in each panel.

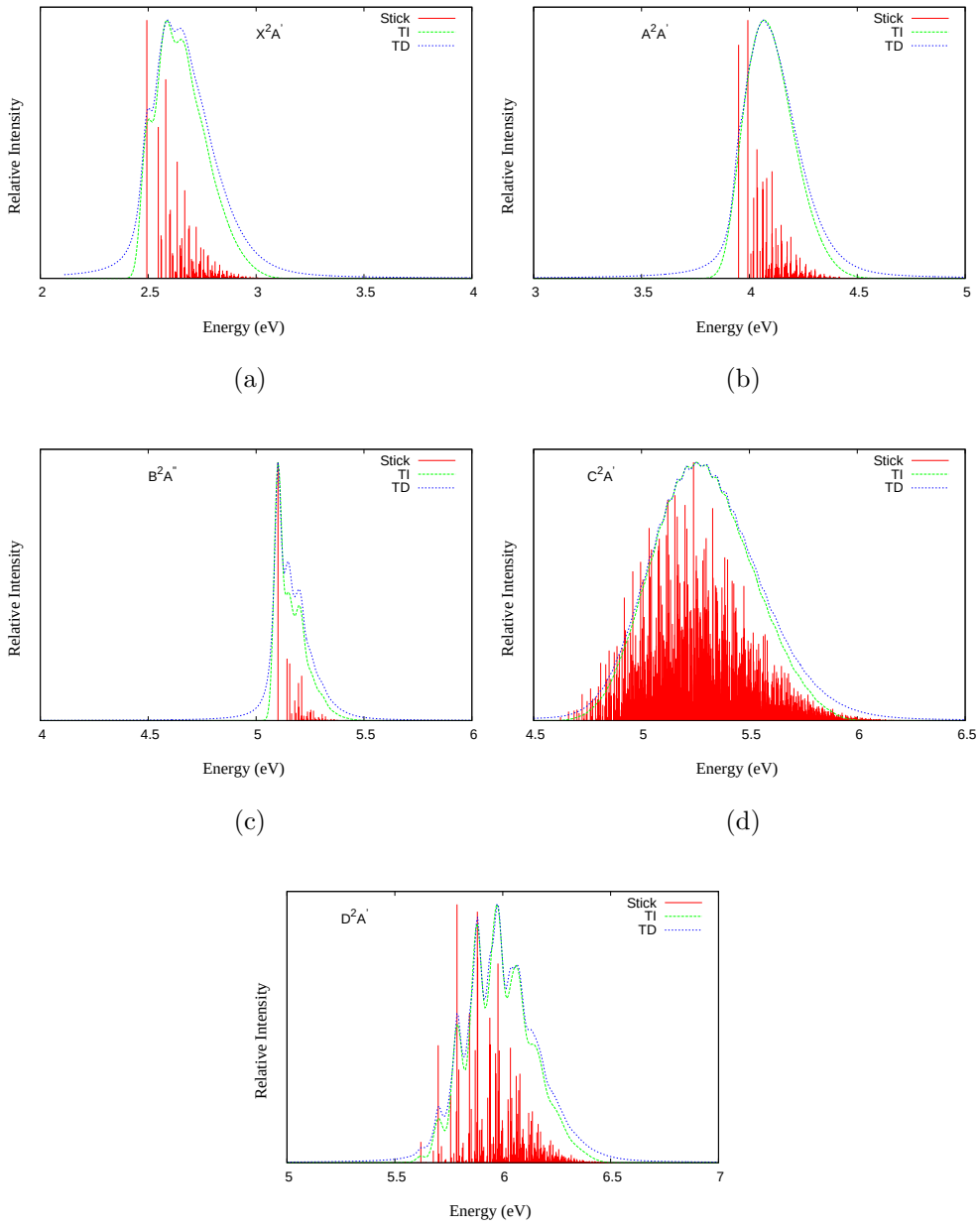

FIG. S2: The uncoupled time-dependent and time-independent spectra of the first five electronic states ($\widetilde{X}$ in panel a, $\widetilde{A}$ in panel b, $\widetilde{B}$ in panel c, $\widetilde{C}$ in panel d and $\widetilde{D}$ in panel e) of isomer-II are shown here. All calculations are performed including lowest six frequency totally symmetric vibrational modes (ν_1-ν_6). The vibronic energies obtained from time-independent calculation are shown in red stick lines, while the spectrum envelope obtained from the convolution of these energies is shown in green dashed line and the spectrum envelope obtained from the time-dependent calculation is shown in blue dotted line in each panel.

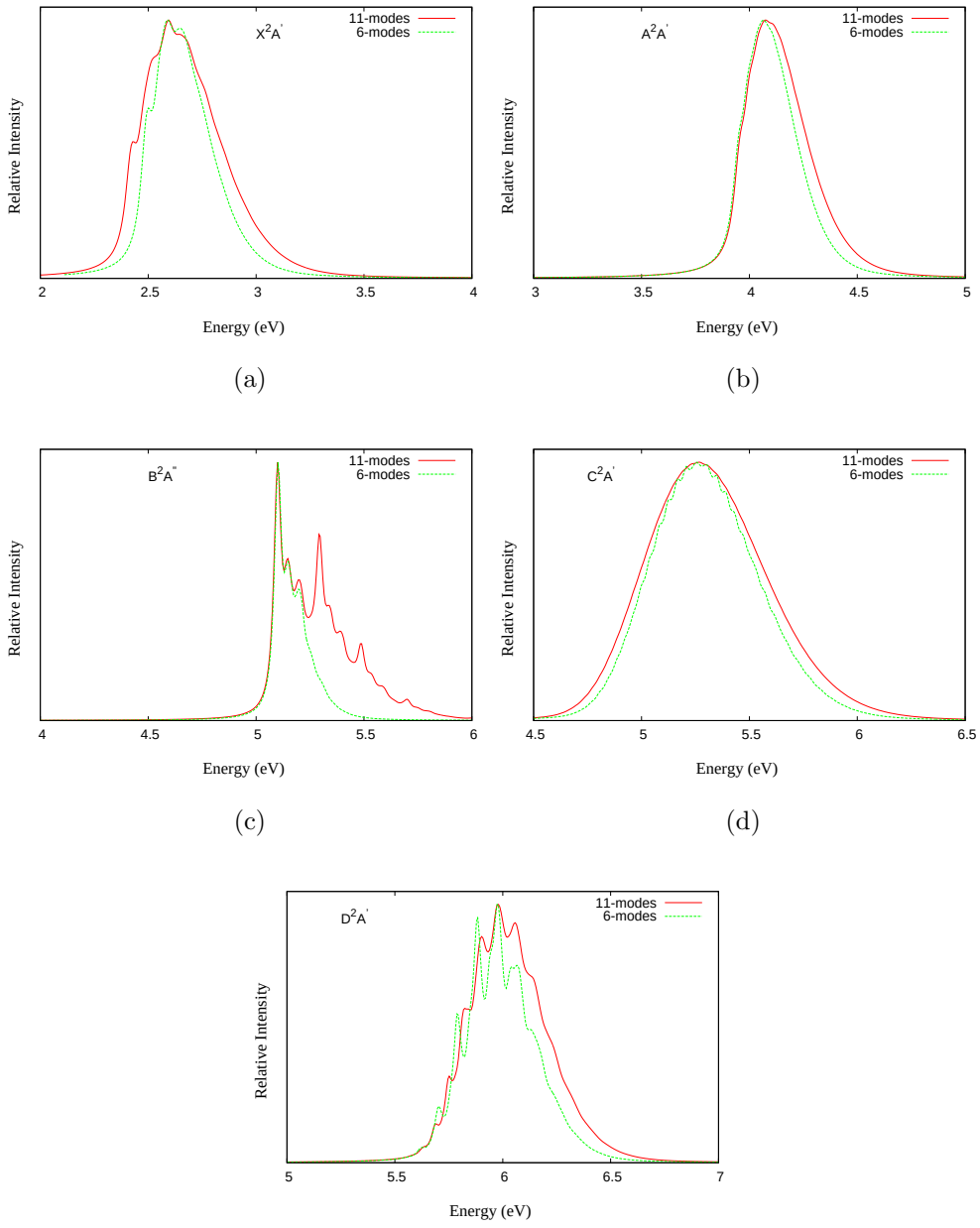

FIG. S3: The comparison between 6-modes and 11-modes uncoupled time-dependent calculations of the first five electronic states ($\widetilde{X}$ in panel a, $\widetilde{A}$ in panel b, $\widetilde{B}$ in panel c, $\widetilde{C}$ in panel d and $\widetilde{D}$ in panel e) of isomer-II is shown here.

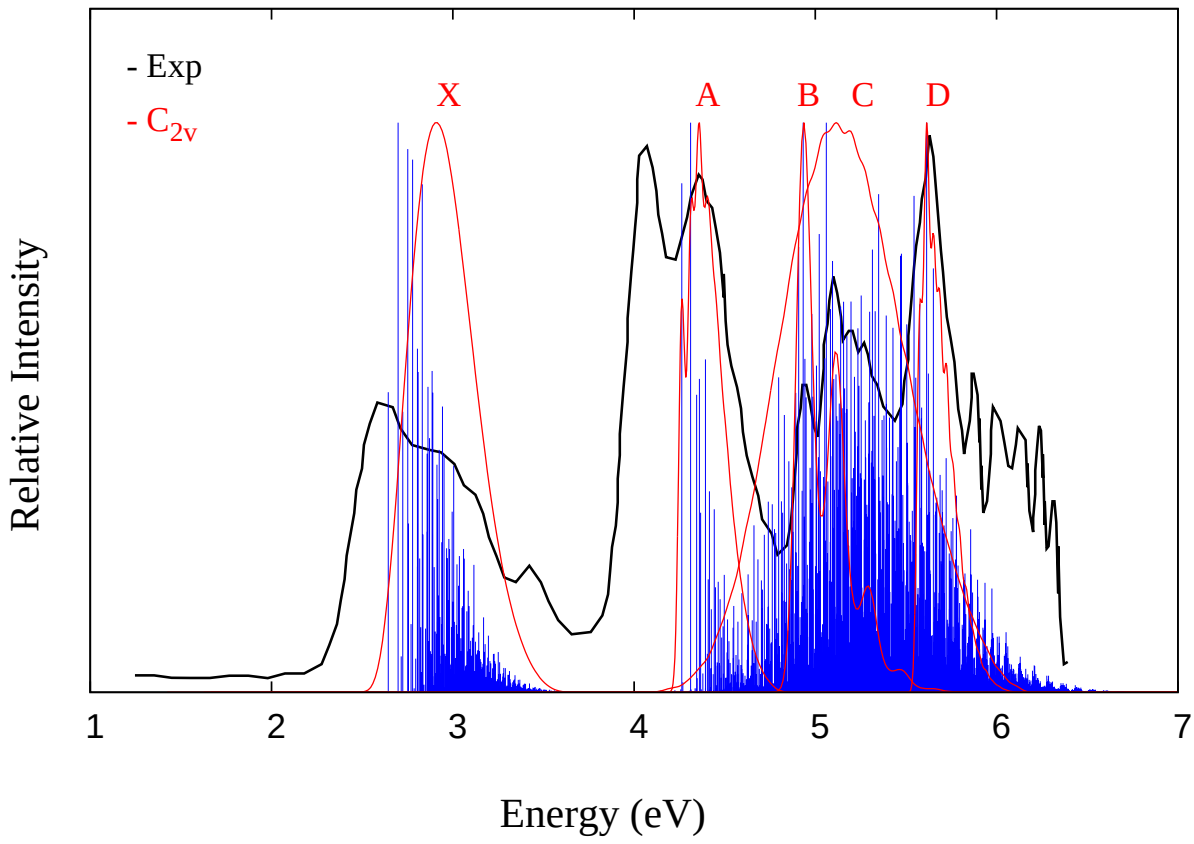

FIG. S4: Overall comparison of the five uncoupled state's spectra of isomer-I obtained from time-independent nuclear dynamics simulations with the available experimental recording [1].

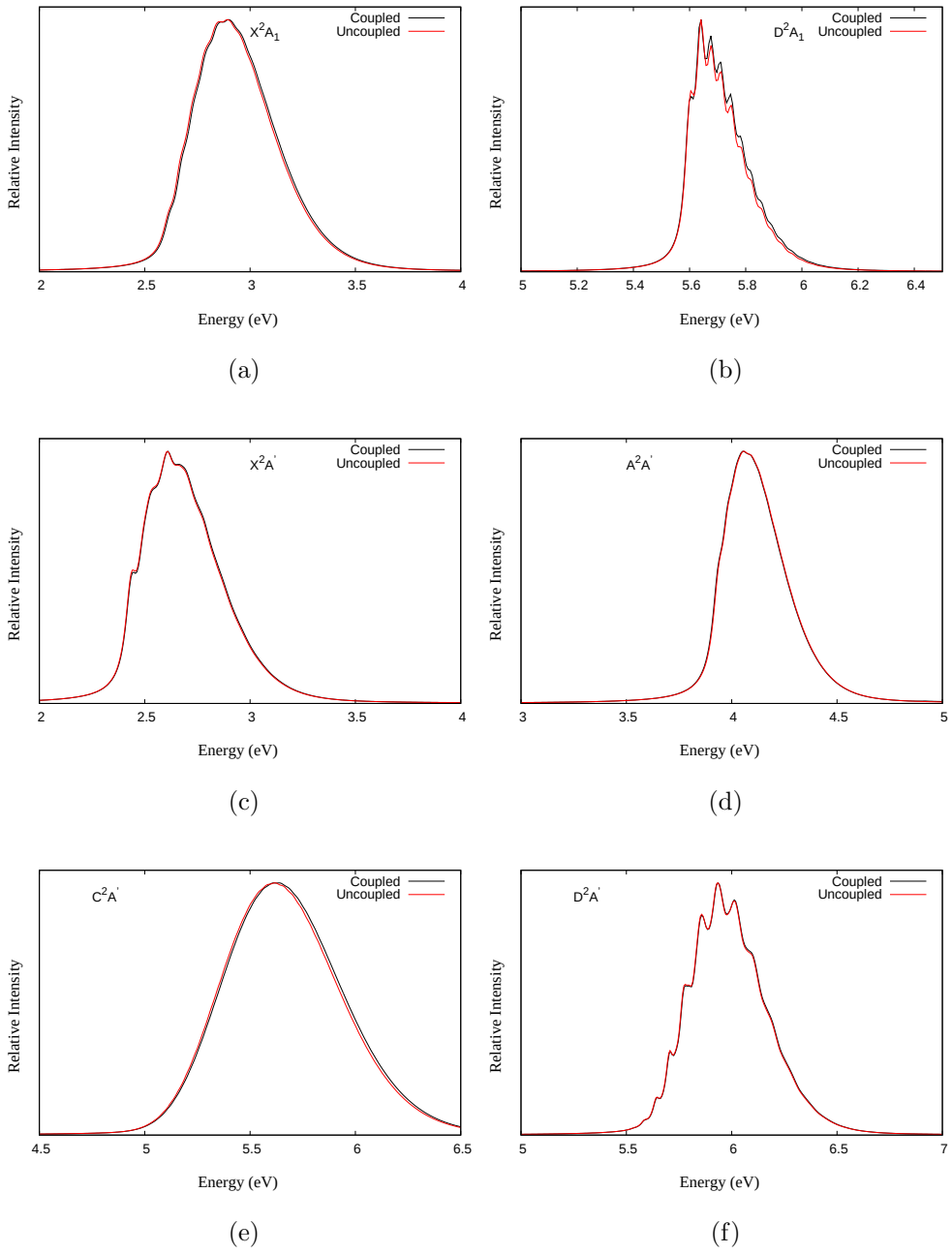

FIG. S5: The comparison between the coupled and uncoupled spectrum obtained from time-dependent calculations of $\widetilde{X}$ and $\widetilde{D}$ states of isomer-I are shown in panel a and b, while the same of $\widetilde{X}$, $\widetilde{A}$, $\widetilde{C}$ and $\widetilde{D}$ states of isomer-II are shown in panels c, d, e and f, respectively.

[1] B. B. Averkiev, D. Y. Zubarev, L. -M. Wang, W. Huang, L. S. Wang and A. I. Boldyrev, *J. Am. Chem. Soc.*,2008, **130**, 9248–9250.

[2] G. A. Worth, M. H. Beck, A. Jäckle and H. -D. Meyer, The mctdh package, Version 8.4, 2017, University of Heidelberg, Germany. See:http://mctdh.uni-hd.de.