

## ELECTRONIC SUPPORTING INFORMATION

### A THEORETICAL STUDY OF THE PHOTOCHEMISTRY OF INDIGO IN ITS NEUTRAL AND DIANIONIC (LEUCOINDIGO) FORMS.

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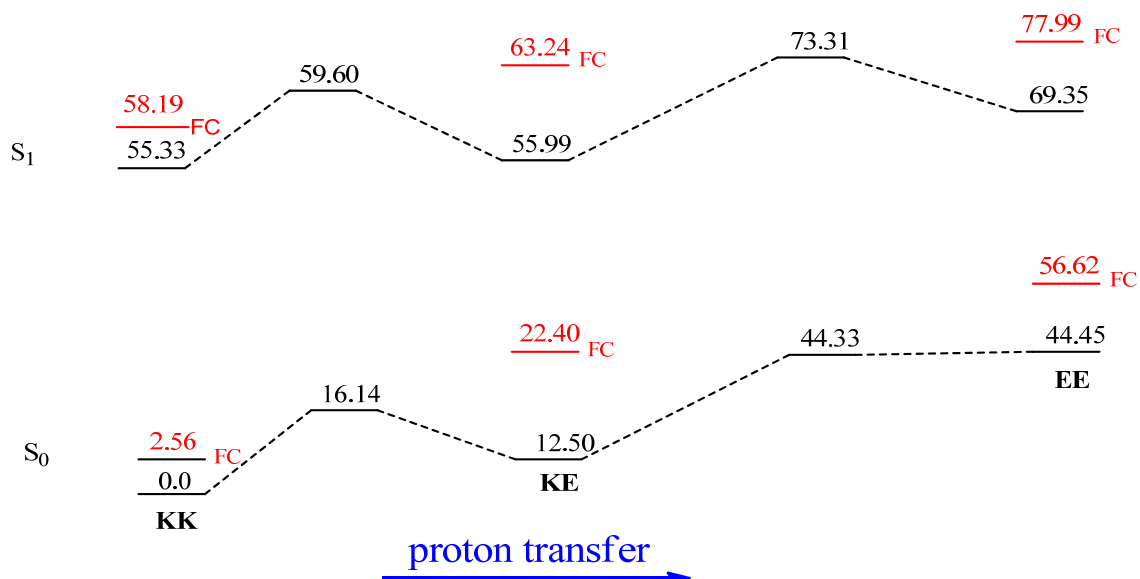
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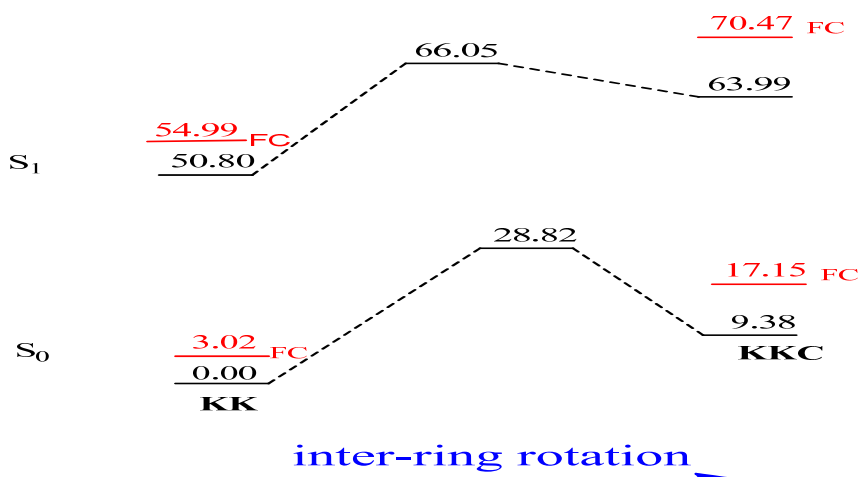
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#### SUMMARY OF DATA:

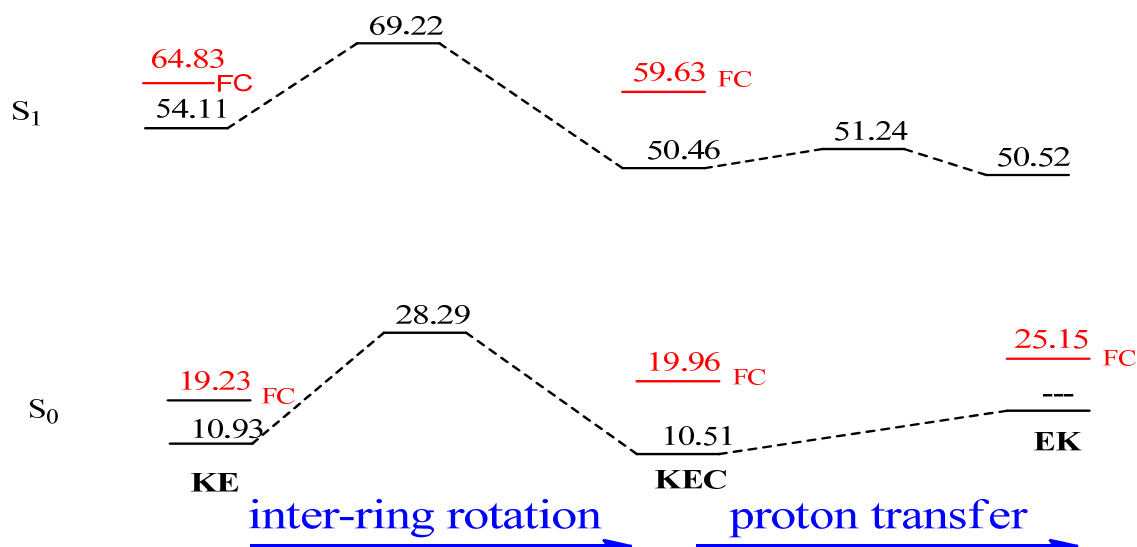
- Figures of the results obtained for indigo in continuous phase (DMF) ..... 2
- Figures of the results obtained for leucoindigo in continuous phase (Water) ... 3
- Cartesian geometries of all the stationary points and Conical Intersections located in this paper (gas phase results only) ..... 6



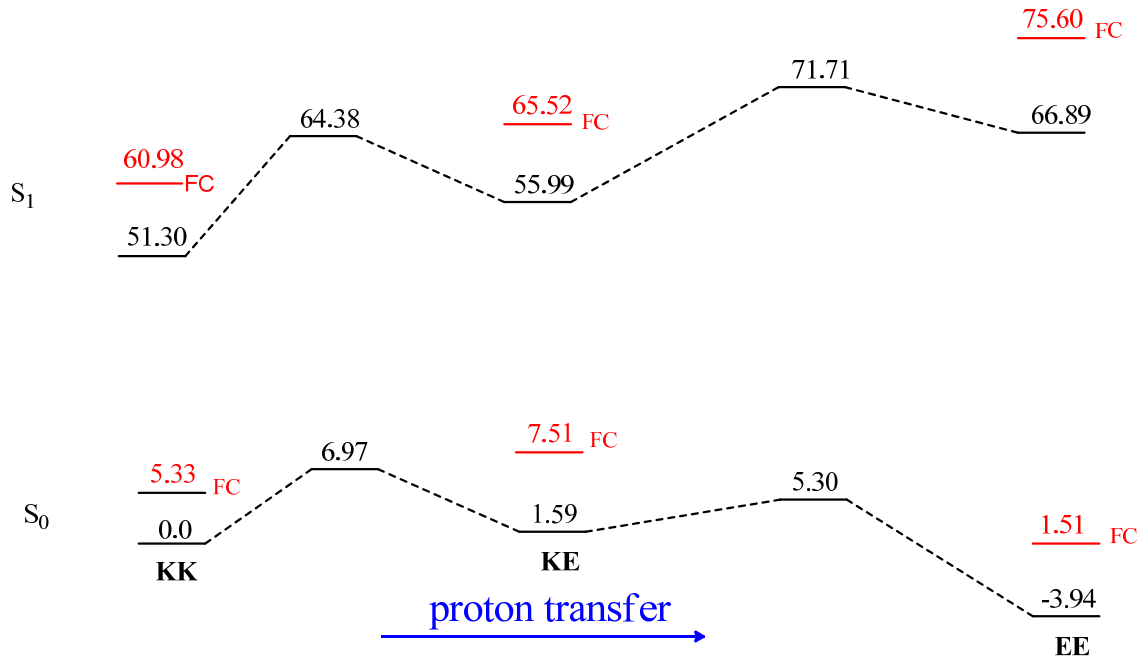
**Figure 1S.** Energies corresponding to the proton transfer reactions in the ground ( $S_0$ ) and first singlet excited ( $S_1$ ) electronic states of neutral indigo in DMF. Energies relative to the KK minimum in  $S_0$  are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).



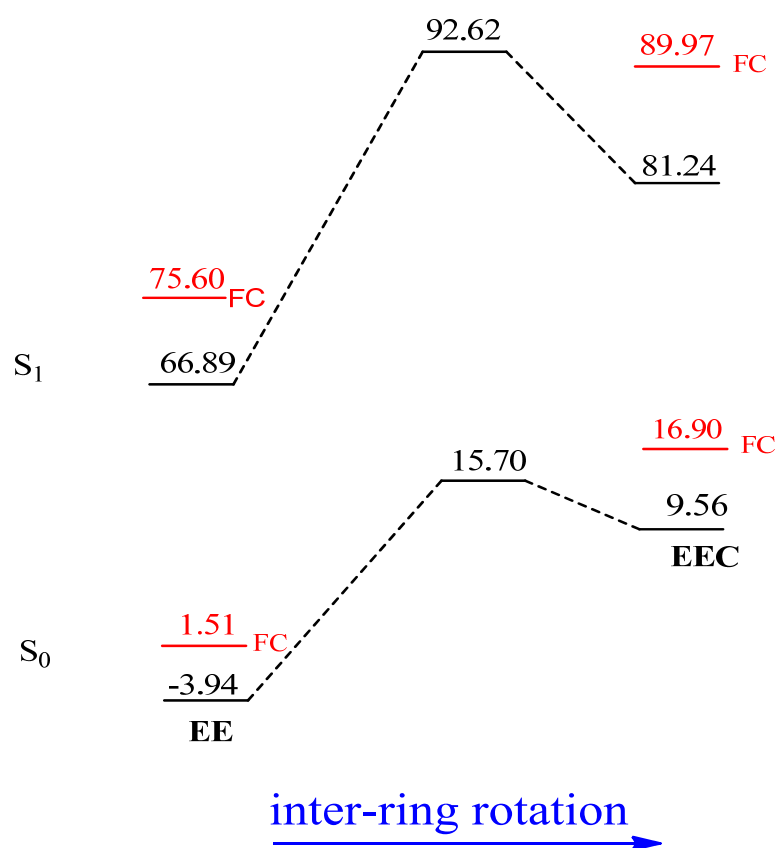
**Figure 2S.** Energies corresponding to the internal rotation along the C-C inter-ring bond of the KK tautomer in the ground ( $S_0$ ) and first singlet excited ( $S_1$ ) electronic states of neutral indigo in DMF. Energies relative to the KK minimum in  $S_0$  are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).



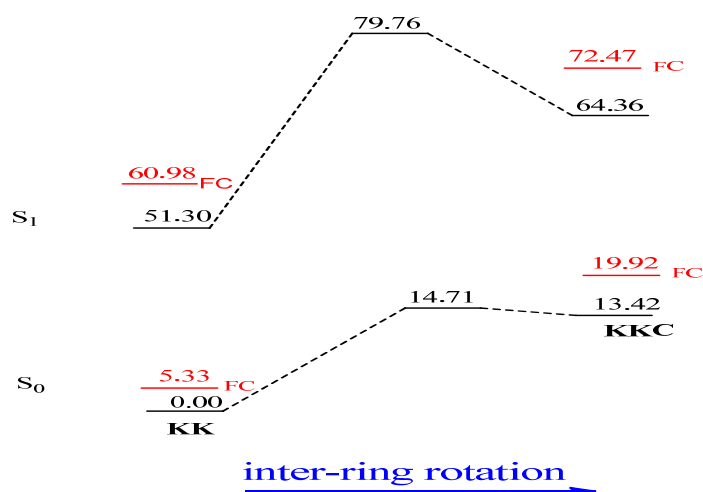
**Figure 3S.** Energies corresponding to the internal rotation along the C-C inter-ring bond of the KE tautomer and the following proton transfer reaction along the O-H...O direction in the ground ( $S_0$ ) and first singlet excited ( $S_1$ ) electronic states of neutral indigo in DMF. Energies relative to the KK minimum in  $S_0$  are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).



**Figure 4S.** Energies corresponding to the proton transfer reactions in the ground ( $S_0$ ) and first singlet excited ( $S_1$ ) electronic states of leucoindigo in water. Energies relative to the KK minimum in  $S_0$  are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).

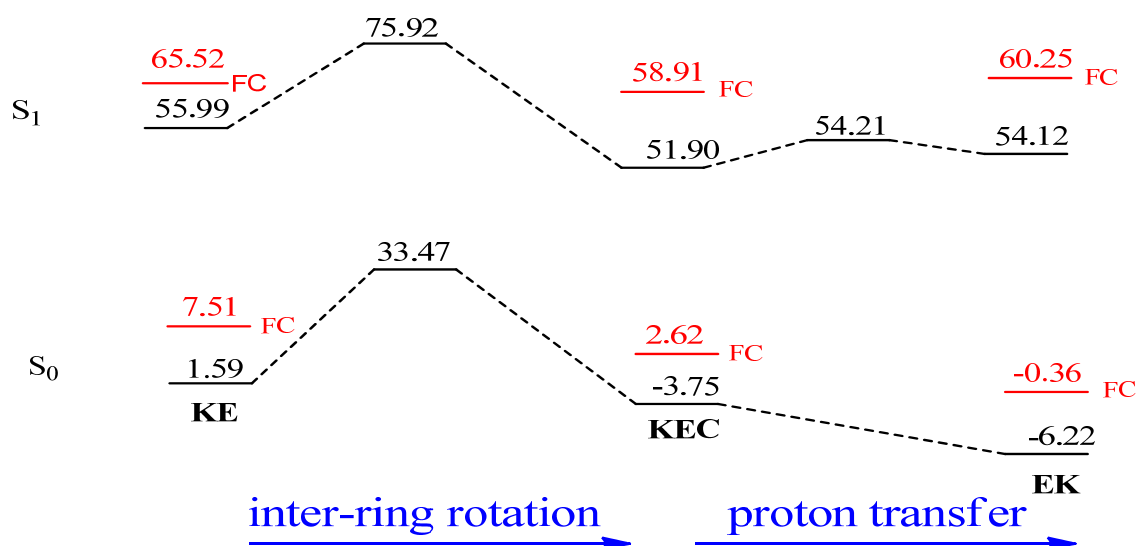


**Figure 5S.** Energies corresponding to the internal rotation along the C-C inter-ring bond of the EE tautomer in the ground ( $S_0$ ) and first singlet excited ( $S_1$ ) electronic states of leucoindigo in water. Energies relative to the KK minimum in  $S_0$  are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).



**Figure 6S.** Energies corresponding to the internal rotation along the C-C inter-ring bond of the KK tautomer in the ground ( $S_0$ ) and first singlet excited ( $S_1$ ) electronic states of leucoindigo in water. Energies relative to the KK minimum in  $S_0$  are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).

structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).



**Figure 7S.** Energies corresponding to the internal rotation along the C-C inter-ring bond of the KE tautomer and the following proton transfer reaction along the O-H...O direction in the ground (S<sub>0</sub>) and first singlet excited (S<sub>1</sub>) electronic states of leucoindigo in water. Energies relative to the KK minimum in S<sub>0</sub> are reported in kcal/mol. Red lines and values indicate the energies of the Franck-Condon (FC) structures obtained by calculating the energy in a given electronic state using the optimized geometry of the other state (see main text for details).

## CARTESIAN GEOMETRIES OF THE STATIONARY AND CONICAL INTERSECTION POINTS FOR THE INDIGO IN GAS PHASE:

### GROUND STATE

#### KK

6	2.231085	0.105215	-3.397079
6	2.246045	0.063659	-1.990811
6	3.443779	0.071848	-1.287107
6	4.632282	0.121953	-2.000168
6	4.607099	0.162981	-3.399254
6	3.418602	0.155570	-4.119117
7	0.926586	0.087634	-3.859501
6	0.055304	0.034299	-2.791605
6	0.852730	0.016001	-1.535840
1	3.430958	0.039212	-0.202705
1	5.583014	0.129537	-1.479463
1	5.545888	0.201946	-3.942860
1	3.418815	0.187884	-5.203027
6	-3.481743	-0.029939	-3.659570
6	-3.466856	-0.070616	-2.253280
6	-4.654376	-0.122055	-1.531325
6	-5.842796	-0.131400	-2.251297
6	-5.867901	-0.091135	-3.650408
6	-4.679392	-0.039927	-4.363383
6	-2.088414	0.018753	-4.114449
6	-1.291088	0.002672	-2.858581
7	-2.162420	-0.050513	-1.790726
1	-4.654646	-0.153710	-0.447395
1	-6.781583	-0.171298	-1.707755
1	-6.818570	-0.100213	-4.171203
1	-4.666506	-0.007934	-5.447806
8	-1.616329	0.063672	-5.243978
8	0.380795	-0.029220	-0.406361
1	0.599097	0.106350	-4.814541
1	-1.834843	-0.071475	-0.835751

#### KE

6	2.231085	0.105215	-3.397079
6	2.246045	0.063659	-1.990811
6	3.443779	0.071848	-1.287107
6	4.632282	0.121953	-2.000168
6	4.607099	0.162981	-3.399254
6	3.418602	0.155570	-4.119117
7	0.926586	0.087634	-3.859501
6	0.055304	0.034299	-2.791605
6	0.852730	0.016001	-1.535840
1	3.430958	0.039212	-0.202705
1	5.583014	0.129537	-1.479463
1	5.545888	0.201946	-3.942860
1	3.418815	0.187884	-5.203027
6	-3.481743	-0.029939	-3.659570
6	-3.466856	-0.070616	-2.253280
6	-4.654376	-0.122055	-1.531325
6	-5.842796	-0.131400	-2.251297
6	-5.867901	-0.091135	-3.650408
6	-4.679392	-0.039927	-4.363383
6	-2.088414	0.018753	-4.114449
6	-1.291088	0.002672	-2.858581

7	-2.162420	-0.050513	-1.790726
1	-4.654646	-0.153710	-0.447395
1	-6.781583	-0.171298	-1.707755
1	-6.818570	-0.100213	-4.171203
1	-4.666506	-0.007934	-5.447806
8	-1.616329	0.063672	-5.243978
8	0.380795	-0.029220	-0.406361
1	0.599097	0.106350	-4.814541
1	-1.834843	-0.071475	-0.835751

### EE

6	2.123418	0.096786	-3.419356
6	2.174556	0.049519	-1.973102
6	3.407270	0.056935	-1.277956
6	4.563151	0.110126	-2.004996
6	4.514183	0.156627	-3.427610
6	3.336979	0.151004	-4.134492
7	0.862721	0.082155	-3.924157
6	0.072586	0.025821	-2.824257
6	0.840348	0.003006	-1.578701
1	3.419961	0.020926	-0.193750
1	5.526458	0.117486	-1.508220
1	5.452376	0.198286	-3.973060
1	3.323981	0.186981	-5.217632
6	-3.393347	-0.032062	-3.673413
6	-3.342391	-0.079269	-2.227141
6	-4.556048	-0.133760	-1.512245
6	-5.733152	-0.139695	-2.219351
6	-5.781913	-0.093213	-3.641926
6	-4.625902	-0.039749	-4.368785
6	-2.059070	0.014624	-4.067598
6	-1.291501	-0.008141	-2.821921
7	-2.081759	-0.064413	-1.722124
1	-4.543305	-0.169693	-0.429102
1	-6.671400	-0.181578	-1.674011
1	-6.745118	-0.100766	-4.138901
1	-4.638455	-0.003682	-5.452989
8	-1.493646	0.068151	-5.243740
1	-0.496580	0.087917	-5.097273
8	0.275095	-0.050458	-0.402455
1	-0.721850	-0.070117	-0.548876

### KKC

6	2.008489	0.083310	-1.516889
6	2.390356	0.007308	-2.855678
6	3.728364	0.012162	-3.221408
6	4.685723	0.110078	-2.220160
6	4.293002	0.202401	-0.881671
6	2.953418	0.188161	-0.505657
7	0.613831	0.013176	-1.406676
6	0.044277	0.020511	-2.689254
6	1.170571	-0.045926	-3.689224
1	3.999204	-0.050395	-4.270112
1	5.740329	0.118839	-2.471681
1	5.052911	0.283653	-0.110946
1	2.663599	0.252176	0.537829
6	-3.510617	0.056293	-3.650152



6	-3.496124	-0.108354	-2.265726
6	-4.674091	-0.269434	-1.549539
6	-5.866179	-0.248083	-2.266856
6	-5.891357	-0.067075	-3.652825
6	-4.703988	0.086340	-4.356557
6	-2.114201	0.152146	-4.125907
6	-1.292259	0.012268	-2.869827
7	-2.181049	-0.057424	-1.786013
1	-4.670293	-0.402463	-0.472857
1	-6.802271	-0.371845	-1.731604
1	-6.841647	-0.050664	-4.174567
1	-4.688091	0.218085	-5.433330
8	-1.727161	0.330690	-5.258943
8	1.098818	-0.148396	-4.893300
1	0.147499	0.520240	-0.666824
1	-1.922852	-0.614732	-0.983079

### KEC

6	0.027025	-0.006634	-0.029312
6	0.006727	-0.006794	1.369873
6	1.207710	0.002080	2.116414
6	2.448033	0.011291	1.463784
6	2.465199	0.011427	0.086107
6	1.260844	0.002500	-0.647939
6	0.839339	-0.000684	3.495795
6	-0.556744	-0.011068	3.549767
7	-1.039588	-0.014469	2.243192
6	-1.464108	-0.017990	4.636316
7	-2.757239	-0.027675	4.498084
6	-3.308574	-0.032087	5.803098
6	-2.333497	-0.024919	6.812348
6	-1.050805	-0.014987	6.111188
6	-2.661856	-0.027738	8.156056
6	-4.014172	-0.038018	8.493889
6	-4.984665	-0.045112	7.492511
6	-4.650315	-0.042287	6.135573
8	0.084905	-0.006603	6.560452
8	1.726577	0.005914	4.483981
1	3.365253	0.018099	2.042338
1	3.410289	0.018444	-0.445476
1	1.306050	0.002836	-1.732330
1	-0.892419	-0.013435	-0.604683
1	-5.411046	-0.047872	5.363609
1	-6.032748	-0.053093	7.775233
1	-4.314861	-0.040512	9.535487
1	-1.886591	-0.022036	8.915365
1	-2.025012	-0.022365	2.037019
1	1.257533	0.002350	5.352071

### FIRST SINGLET EXCITED ELECTRONIC STATE

#### KK

6	2.230119	0.104340	-3.382678
6	2.232463	0.062456	-1.967363
6	3.435944	0.071862	-1.281320
6	4.622137	0.122857	-2.012007
6	4.604235	0.163883	-3.410478

6	3.406573	0.155291	-4.119424
7	0.921419	0.084994	-3.821284
6	0.066007	0.032079	-2.751803
6	0.834348	0.014421	-1.513359
1	3.441461	0.039852	-0.197088
1	5.574030	0.130980	-1.492122
1	5.541400	0.203203	-3.955094
1	3.392320	0.187080	-5.203584
6	-3.468155	-0.029046	-3.683054
6	-3.465826	-0.070535	-2.267729
6	-4.642276	-0.121713	-1.530994
6	-5.839918	-0.131025	-2.239966
6	-5.857804	-0.090449	-3.638451
6	-4.671615	-0.039188	-4.369125
6	-2.070050	0.019426	-4.137041
6	-1.301726	0.002318	-2.898576
7	-2.157144	-0.050503	-1.829096
1	-4.628036	-0.153172	-0.446825
1	-6.777080	-0.170567	-1.695360
1	-6.809681	-0.099125	-4.158355
1	-4.677119	-0.007513	-5.453367
8	-1.592354	0.064818	-5.281372
8	0.356671	-0.031500	-0.369041
1	0.553098	0.103670	-4.770668
1	-1.788822	-0.069444	-0.879719

### KE

6	2.236482	0.106006	-3.429720
6	2.188514	0.051807	-2.008414
6	3.377244	0.053993	-1.259872
6	4.577226	0.109423	-1.931903
6	4.610629	0.162818	-3.341504
6	3.458616	0.162077	-4.103981
7	0.960105	0.091835	-3.917237
6	0.077988	0.029918	-2.855441
6	0.815711	0.003976	-1.656441
1	3.336563	0.012602	-0.176956
1	5.509882	0.112424	-1.378941
1	5.572344	0.205848	-3.842605
1	3.498705	0.203458	-5.186847
6	-3.446112	-0.027234	-3.717135
6	-3.358041	-0.078899	-2.275575
6	-4.531527	-0.138145	-1.487668
6	-5.743677	-0.144681	-2.135562
6	-5.820636	-0.093767	-3.549666
6	-4.680333	-0.035164	-4.343073
6	-2.068422	0.026041	-4.206517
6	-1.305205	-0.000639	-2.975657
7	-2.089755	-0.063041	-1.839486
1	-4.454635	-0.176613	-0.406853
1	-6.662541	-0.189480	-1.561158
1	-6.799164	-0.101070	-4.018596
1	-4.747439	0.003579	-5.424855
8	-1.607922	0.080901	-5.364502
8	0.304561	-0.054415	-0.434587
1	-0.678688	-0.075331	-0.536736
1	0.623804	0.119082	-4.872041

### EE

6	2.183478	0.098069	-3.413564
6	2.190073	0.050237	-1.982313
6	3.391175	0.055900	-1.255411
6	4.577362	0.109080	-1.956219
6	4.569723	0.156109	-3.364250
6	3.393399	0.151354	-4.100028
7	0.903187	0.083859	-3.945158
6	0.098937	0.028338	-2.887782
6	0.829652	0.004228	-1.626292
1	3.377784	0.019190	-0.171153
1	5.523552	0.114994	-1.426970
1	5.518433	0.197489	-3.890531
1	3.404581	0.187964	-5.183434
6	-3.425842	-0.032466	-3.692449
6	-3.365850	-0.079287	-2.250845
6	-4.555836	-0.134544	-1.487204
6	-5.761392	-0.142199	-2.154978
6	-5.803602	-0.096102	-3.561207
6	-4.642090	-0.041040	-4.340318
6	-2.042102	0.016329	-4.117861
6	-1.301014	-0.003650	-2.973769
7	-2.110303	-0.063012	-1.802238
1	-4.498769	-0.169395	-0.404984
1	-6.690501	-0.184012	-1.598114
1	-6.768477	-0.103503	-4.057400
1	-4.702385	-0.006257	-5.422401
8	-1.577726	0.069845	-5.365361
1	-0.593258	0.092032	-5.292048
8	0.289160	-0.049538	-0.428767
1	-0.693700	-0.070262	-0.546090

### KKC

6	2.063421	0.089272	-1.434832
6	2.282158	0.044998	-2.822257
6	3.575965	0.058171	-3.339717
6	4.637351	0.136139	-2.453157
6	4.409056	0.197930	-1.071883
6	3.125629	0.172788	-0.542790
7	0.698927	0.017458	-1.177759
6	0.019502	0.023247	-2.399187
6	0.973805	0.010466	-3.461559
1	3.734046	0.017323	-4.411610
1	5.654987	0.152974	-2.827344
1	5.255903	0.262745	-0.396531
1	2.959978	0.210797	0.528802
6	-3.414803	0.015603	-3.591761
6	-3.570765	-0.119087	-2.201693
6	-4.830456	-0.250236	-1.629874
6	-5.927777	-0.230448	-2.480314
6	-5.782813	-0.078585	-3.865875
6	-4.525318	0.046684	-4.432992
6	-1.984239	0.079592	-3.858364
6	-1.345127	-0.009235	-2.584339
7	-2.323666	-0.075617	-1.588551
1	-4.954056	-0.358041	-0.557356
1	-6.922599	-0.330953	-2.058794
1	-6.664912	-0.062697	-4.496376

1	-4.394362	0.157277	-5.503614
8	-1.428165	0.207452	-4.985965
8	0.737181	-0.040300	-4.701915
1	0.299792	0.460609	-0.363811
1	-2.150431	-0.573279	-0.728014

### KEC

6	0.036325	-0.006576	-0.020099
6	-0.002616	-0.006999	1.376062
6	1.192089	0.001874	2.135717
6	2.440788	0.011269	1.499638
6	2.476775	0.011681	0.122116
6	1.280397	0.002799	-0.623022
6	0.815219	-0.001047	3.513494
6	-0.614037	-0.011800	3.542517
7	-1.070283	-0.015096	2.229932
6	-1.441041	-0.018083	4.652471
7	-2.836965	-0.028413	4.509759
6	-3.315488	-0.032171	5.749602
6	-2.274668	-0.024497	6.755768
6	-1.027617	-0.015010	6.028783
6	-2.592670	-0.027085	8.105040
6	-3.935446	-0.037225	8.459097
6	-4.967996	-0.044842	7.483368
6	-4.680442	-0.042491	6.141883
8	0.161832	-0.006104	6.487919
8	1.618412	0.004863	4.526856
1	3.348566	0.018014	2.092958
1	3.427505	0.018856	-0.398817
1	1.337262	0.003335	-1.706952
1	-0.874494	-0.013341	-0.608742
1	-5.455920	-0.048203	5.384391
1	-6.000563	-0.052640	7.815088
1	-4.211568	-0.039450	9.508342
1	-1.810512	-0.021314	8.856126
1	-2.049720	-0.022308	1.997390
1	1.048118	0.000566	5.453126

### EK

6	-0.017362	0.000116	-0.042857
6	-0.055288	0.000204	1.371557
6	1.169497	0.000081	2.126093
6	2.396233	-0.000110	1.489982
6	2.406054	-0.000186	0.094686
6	1.213914	-0.000074	-0.661049
6	0.762808	0.000251	3.509927
6	-0.630845	0.000333	3.489204
7	-1.132156	0.000367	2.154437
6	-1.519929	0.000474	4.558150
6	-1.197191	0.000613	5.980143
6	-2.484269	0.000760	6.659245
6	-3.486684	0.000715	5.670955
7	-2.886936	0.000537	4.424449
6	-2.821566	0.000930	8.010007
6	-4.162846	0.001052	8.357568
6	-5.151132	0.001004	7.363466
6	-4.834197	0.000836	6.011060

8	-0.051214	0.000624	6.483530
8	1.591929	0.000281	4.528938
1	-2.038734	0.000965	8.760895
1	-4.454987	0.001186	9.401672
1	-6.196061	0.001104	7.656739
1	-5.609820	0.000803	5.252860
1	-0.944119	0.000198	-0.605402
1	1.276903	-0.000141	-1.743513
1	3.357078	-0.000331	-0.427440
1	3.320837	-0.000184	2.056457
1	-3.344539	0.000550	3.527396
1	1.047769	0.000404	5.391453

### CONICAL INTERSECTIONS

#### CI<sub>SPT</sub>

7	0.062481	0.006967	0.051181
6	0.073497	0.008173	1.303003
6	1.461427	0.002917	1.886754
6	2.409904	-0.002499	0.797411
6	1.593443	0.000056	-0.313461
6	-1.077020	0.014305	2.231576
6	-0.829267	0.014543	3.536436
6	0.546360	0.008998	4.074269
6	1.645025	0.003546	3.273363
8	3.691543	-0.008440	0.829475
6	1.923126	-0.003107	-1.634071
7	3.231789	-0.010042	-2.102589
6	3.222914	-0.011762	-3.463111
6	1.879792	-0.005404	-3.910004
6	1.067312	-0.000001	-2.757026
6	1.583531	-0.005436	-5.283681
6	2.622944	-0.011854	-6.174743
6	3.961041	-0.018211	-5.715174
6	4.280257	-0.018246	-4.378356
8	-0.266344	0.007118	-2.760367
1	0.562962	-0.000616	-5.611613
1	2.432653	-0.012127	-7.229365
1	4.753144	-0.023092	-6.439043
1	5.298951	-0.023011	-4.046278
1	-2.066429	0.018202	1.821901
1	-1.634599	0.018705	4.244272
1	0.658058	0.009555	5.140709
1	2.638210	-0.000263	3.674555
1	-0.647854	0.009664	-1.874717
1	4.002115	-0.012715	-1.469492

#### CI<sub>IRI</sub>

6	2.272492	0.641852	-3.244661
6	2.263967	-0.270651	-2.182286
6	3.442955	-0.672242	-1.582670
6	4.630230	-0.135448	-2.071303
6	4.616496	0.768398	-3.125074
6	3.426242	1.179149	-3.739041
7	0.912628	0.854032	-3.651288
6	0.067387	0.165264	-2.943099
6	0.886759	-0.593398	-1.968907

1	3.437790	-1.372632	-0.772297
1	5.563681	-0.422584	-1.633076
1	5.544491	1.165606	-3.484497
1	3.433665	1.874659	-4.552677
6	-3.457719	-0.535572	-3.404247
6	-3.413484	0.588920	-2.555313
6	-4.609466	1.158146	-2.078877
6	-5.798472	0.593335	-2.462059
6	-5.840700	-0.533970	-3.313965
6	-4.678164	-1.097152	-3.784119
6	-2.075296	-0.887737	-3.719188
6	-1.372017	0.094165	-3.026476
7	-2.125803	0.995676	-2.296209
1	-4.574705	2.015180	-1.434256
1	-6.723133	1.013221	-2.110777
1	-6.792661	-0.946293	-3.591067
1	-4.695865	-1.952618	-4.432422
8	-1.593323	-1.859492	-4.406357
8	0.376397	-1.405123	-1.117286
1	-0.583541	-1.510277	-1.160869
1	0.613449	1.444898	-4.395167

### CI<sub>IR2</sub>

7	-0.264993	-0.186155	0.000804
6	-0.104497	0.038528	1.373641
6	1.209950	-0.209278	1.761528
6	1.970680	-0.609557	0.565045
6	1.010921	-0.737867	-0.458641
6	-1.064933	0.417854	2.306138
6	-0.659657	0.581225	3.619535
6	0.666420	0.366421	4.009844
6	1.608819	-0.030492	3.076902
8	3.222529	-0.713584	0.440084
6	1.495211	-0.308457	-1.735214
7	1.606843	-1.046640	-2.780381
6	2.200865	-0.407698	-3.927778
6	2.492644	0.904060	-3.583625
6	2.063545	1.093890	-2.183822
6	3.079147	1.748411	-4.496465
6	3.364385	1.240124	-5.766901
6	3.063592	-0.073213	-6.088591
6	2.466461	-0.935264	-5.159507
8	2.076254	2.071116	-1.493542
1	3.312498	2.761765	-4.237182
1	3.823478	1.872366	-6.499887
1	3.292860	-0.443048	-7.068055
1	2.239323	-1.951467	-5.412109
1	-2.081883	0.599399	2.014678
1	-1.379235	0.888360	4.355219
1	0.946587	0.509230	5.035578
1	2.630192	-0.207487	3.352894
1	-1.089947	-0.682239	-0.257559
1	1.343458	-2.008398	-2.733719

## CARTESIAN GEOMETRIES OF THE STATIONARY AND CONICAL INTERSECTION POINTS FOR LEUCOINDIGO IN GAS PHASE:

### GROUND STATE

#### KK

6	2.215598	0.105254	-3.421701
6	2.198735	0.062518	-1.981173
6	3.420539	0.072662	-1.300943
6	4.616717	0.122792	-2.006145
6	4.615881	0.164087	-3.413572
6	3.417940	0.155552	-4.125929
7	0.926305	0.086019	-3.843589
6	0.083414	0.032606	-2.729760
6	0.815394	0.015064	-1.527304
1	3.410076	0.040474	-0.213280
1	5.565820	0.130433	-1.470916
1	5.560349	0.203153	-3.954379
1	3.417930	0.187468	-5.214307
6	-3.434137	-0.029039	-3.669172
6	-3.451561	-0.070982	-2.228610
6	-4.654013	-0.121744	-1.524709
6	-5.851766	-0.131612	-2.237409
6	-5.852118	-0.091063	-3.644860
6	-4.655799	-0.040393	-4.349748
6	-2.050750	0.019027	-4.122480
6	-1.319145	0.003097	-2.919743
7	-2.162381	-0.050425	-1.806271
1	-4.654269	-0.153170	-0.436313
1	-6.796370	-0.171208	-1.696895
1	-6.801035	-0.099709	-4.180412
1	-4.645122	-0.008768	-5.437423
8	-1.587344	0.065461	-5.326926
8	0.352552	-0.031623	-0.322716
1	0.493422	0.101171	-4.765093
1	-1.730246	-0.067352	-0.884563

#### KE

6	2.206594	0.102482	-3.409686
6	2.213825	0.051933	-1.961265
6	3.461625	0.060442	-1.307998
6	4.633132	0.116087	-2.054309
6	4.607807	0.164527	-3.454553
6	3.384437	0.157628	-4.137192
7	0.899833	0.083491	-3.814071
6	0.077985	0.024348	-2.704033
6	0.864074	0.003974	-1.558323
1	3.500766	0.023413	-0.222250
1	5.593243	0.122192	-1.538832
1	5.538770	0.207603	-4.015799
1	3.352635	0.194839	-5.224119
6	-3.391584	-0.029562	-3.660614
6	-3.383675	-0.079857	-2.204988
6	-4.629889	-0.134359	-1.533502
6	-5.806648	-0.138664	-2.259304
6	-5.806717	-0.089561	-3.674946
6	-4.598384	-0.035574	-4.358571
6	-2.001344	0.019581	-4.073630

6	-1.323754	-0.006622	-2.826482
7	-2.144978	-0.066507	-1.694747
1	-4.646553	-0.172542	-0.444521
1	-6.760006	-0.180917	-1.729712
1	-6.751790	-0.094431	-4.217280
1	-4.576462	0.002763	-5.448044
8	-1.472965	0.073756	-5.251341
8	0.337191	-0.053629	-0.288472
1	-0.640782	-0.072461	-0.448948
1	0.417895	0.102933	-4.721998

### EE

6	2.171762	0.097876	-3.421710
6	2.199215	0.050192	-1.966677
6	3.431926	0.058729	-1.294315
6	4.612769	0.112445	-2.019320
6	4.589434	0.158761	-3.430290
6	3.386887	0.151635	-4.122955
7	0.907044	0.082199	-3.902555
6	0.111866	0.024840	-2.779387
6	0.839007	0.003700	-1.594508
1	3.456636	0.023168	-0.206056
1	5.569738	0.119107	-1.497846
1	5.529294	0.200628	-3.980500
1	3.368565	0.187366	-5.211311
6	-3.418028	-0.032807	-3.679923
6	-3.390593	-0.080886	-2.224914
6	-4.605735	-0.134594	-1.523683
6	-5.808276	-0.141317	-2.216348
6	-5.831597	-0.094605	-3.627319
6	-4.650745	-0.040910	-4.352295
6	-2.057814	0.013426	-4.052096
6	-1.330702	-0.008231	-2.867192
7	-2.125886	-0.065426	-1.744040
1	-4.587408	-0.170579	-0.435335
1	-6.748151	-0.183143	-1.666161
1	-6.788568	-0.100948	-4.148791
1	-4.675433	-0.005069	-5.440547
8	-1.513743	0.069256	-5.315446
1	-0.540311	0.087584	-5.145127
8	0.294945	-0.051969	-0.331119
1	-0.678447	-0.070675	-0.501374

### EEC

6	2.17176200	0.09787600	-3.42171000
6	2.19921500	0.05019200	-1.96667700
6	3.43192600	0.05872900	-1.29431500
6	4.61276900	0.11244500	-2.01932000
6	4.58943400	0.15876100	-3.43029000
6	3.38688700	0.15163500	-4.12295500
7	0.90704400	0.08219900	-3.90255500
6	0.11186600	0.02484000	-2.77938700
6	0.83900700	0.00370000	-1.59450800
1	3.45663600	0.02316800	-0.20605600
1	5.56973800	0.11910700	-1.49784600
1	5.52929400	0.20062800	-3.98050000
1	3.36856500	0.18736600	-5.21131100



6	-3.50008221	-0.08133602	-2.31355796
6	-3.29870021	-0.02780864	-3.75463241
6	-4.42105510	-0.02757982	-4.59813641
6	-5.69773525	-0.07777960	-4.05637757
6	-5.88976213	-0.12962510	-2.65852108
6	-4.80428726	-0.13147551	-1.79560412
6	-2.19433107	-0.06651499	-1.77911747
6	-1.33070200	-0.00823100	-2.86719200
7	-1.98565177	0.01588298	-4.07860382
1	-4.27259810	0.01238038	-5.67632742
1	-6.56490899	-0.07729563	-4.71655151
1	-6.90217215	-0.16849495	-2.25692196
1	-4.95904661	-0.17158195	-0.71827988
8	-1.80543554	-0.10113750	-0.45898679
1	-2.66268337	-0.13915861	0.03151793
8	0.29494500	-0.05196900	-0.33111900
1	-0.67844700	-0.07067500	-0.50137400

### KKC

6	1.933629	0.248320	-1.566784
6	2.396602	-0.110620	-2.857375
6	3.767799	-0.259691	-3.064681
6	4.657218	-0.015656	-2.023141
6	4.185360	0.373175	-0.757855
6	2.814720	0.500488	-0.520507
7	0.562295	0.242326	-1.605228
6	0.127501	0.021039	-2.964207
6	1.257184	-0.273797	-3.778699
1	4.108377	-0.550604	-4.055831
1	5.729964	-0.119197	-2.184143
1	4.891057	0.573794	0.046808
1	2.444930	0.788074	0.463472
6	-3.517203	0.174123	-3.645908
6	-3.409310	-0.270499	-2.304462
6	-4.533729	-0.581360	-1.547063
6	-5.793690	-0.427314	-2.130130
6	-5.917106	0.045599	-3.447669
6	-4.785841	0.347970	-4.198825
6	-2.175994	0.385960	-4.220381
6	-1.299722	0.029979	-3.156457
7	-2.076823	-0.273897	-1.978064
1	-4.435141	-0.934387	-0.520751
1	-6.685463	-0.672815	-1.555494
1	-6.909816	0.168473	-3.879938
1	-4.854390	0.704523	-5.224092
8	-1.971918	0.828663	-5.387337
8	1.373126	-0.639232	-4.983868
1	0.032732	0.898133	-1.047605
1	-1.708136	-0.968523	-1.343218

### KEC

6	0.025349	-0.006422	-0.009051
6	0.006967	-0.007475	1.378411
6	1.219942	0.001318	2.152711
6	2.443938	0.011096	1.461851
6	2.454479	0.012197	0.073323
6	1.259620	0.003574	-0.665164
6	0.857816	-0.002359	3.529327

6	-0.535872	-0.013027	3.573813
7	-1.024926	-0.016338	2.271092
6	-1.439248	-0.019492	4.679740
7	-2.816524	-0.030172	4.473279
6	-3.322158	-0.033029	5.715541
6	-2.287936	-0.024286	6.739907
6	-1.040140	-0.015192	6.034518
6	-2.637364	-0.025821	8.094018
6	-3.973008	-0.035725	8.469729
6	-4.985924	-0.044303	7.478323
6	-4.674126	-0.043035	6.130227
8	0.182428	-0.005023	6.524953
8	1.696030	0.003070	4.578119
1	3.372198	0.017803	2.026872
1	3.406471	0.019887	-0.456326
1	1.291864	0.004648	-1.752699
1	-0.905523	-0.013217	-0.573583
1	-5.461439	-0.049684	5.376157
1	-6.032536	-0.052049	7.787195
1	-4.249789	-0.036970	9.523966
1	-1.848668	-0.019143	8.846292
1	-2.021096	-0.022156	2.120208
1	1.060422	-0.000114	5.487056

### EKA

6	-0.001961	-0.006791	-0.015848
6	0.006096	-0.006992	1.378638
6	1.236382	0.002228	2.116326
6	2.440413	0.011455	1.407773
6	2.432334	0.011653	0.018324
6	1.216378	0.002583	-0.690210
6	0.929453	-0.000244	3.536739
6	-0.471446	-0.010918	3.587894
7	-0.998326	-0.014966	2.289315
6	-1.387015	-0.017867	4.701093
7	-2.750384	-0.028171	4.478646
6	-3.289272	-0.032189	5.715671
6	-2.271285	-0.024491	6.755175
6	-1.042415	-0.015273	6.057753
6	-2.652200	-0.027454	8.106219
6	-3.997861	-0.037635	8.444225
6	-4.990618	-0.045081	7.438529
6	-4.643372	-0.042410	6.094394
8	0.204692	-0.005793	6.611555
8	1.781848	0.006138	4.516824
1	3.373303	0.018430	1.966682
1	3.371930	0.018877	-0.532349
1	1.225318	0.002857	-1.778936
1	-0.942075	-0.013834	-0.565226
1	-5.410193	-0.048189	5.319923
1	-6.042864	-0.053040	7.724774
1	-4.295769	-0.039947	9.492976
1	-1.888599	-0.021725	8.883023
1	-1.997655	-0.021993	2.162267
1	0.876411	-0.000653	5.847638

## FIRST SINGLET EXCITED ELECTRONIC STATE

### KK

6	2.235959	0.104934	-3.397682
6	2.226239	0.063194	-1.977226
6	3.453871	0.073018	-1.277759
6	4.646008	0.123768	-2.010530
6	4.640536	0.164375	-3.405750
6	3.428209	0.155742	-4.131785
7	0.934428	0.085741	-3.833553
6	0.074076	0.032591	-2.746352
6	0.840230	0.016013	-1.533053
1	3.454100	0.041303	-0.191989
1	5.601246	0.131915	-1.484052
1	5.585511	0.203440	-3.946901
1	3.416917	0.187195	-5.218282
6	-3.461940	-0.029563	-3.673184
6	-3.471670	-0.070961	-2.252729
6	-4.663905	-0.122432	-1.518633
6	-5.876205	-0.132118	-2.244714
6	-5.881668	-0.091812	-3.639937
6	-4.689543	-0.040366	-4.372696
6	-2.075942	0.018341	-4.117327
6	-1.309806	0.002604	-2.904000
7	-2.170167	-0.050487	-1.816811
1	-4.652622	-0.153633	-0.432130
1	-6.821170	-0.171750	-1.703584
1	-6.836887	-0.100753	-4.166437
1	-4.689764	-0.008913	-5.458473
8	-1.600360	0.064593	-5.301589
8	0.364658	-0.030417	-0.348792
1	0.541200	0.102565	-4.768047
1	-1.776926	-0.068378	-0.882344

### KE

6	2.239894	0.103342	-3.408851
6	2.223846	0.052565	-1.969165
6	3.460516	0.059413	-1.281770
6	4.644425	0.114570	-2.013271
6	4.643989	0.163493	-3.411481
6	3.432354	0.158250	-4.126069
7	0.941882	0.086048	-3.839149
6	0.089157	0.026274	-2.744697
6	0.863047	0.005340	-1.589913
1	3.477751	0.021872	-0.196072
1	5.597083	0.119838	-1.483457
1	5.587106	0.206017	-3.952959
1	3.420190	0.196014	-5.212801
6	-3.433712	-0.029608	-3.685483
6	-3.409981	-0.078465	-2.259950
6	-4.595701	-0.134045	-1.520072
6	-5.829534	-0.140661	-2.227377
6	-5.854016	-0.092999	-3.620138
6	-4.673029	-0.036962	-4.376572
6	-2.058183	0.020070	-4.115777
6	-1.320294	-0.004975	-2.862516
7	-2.110967	-0.062913	-1.767559
1	-4.561010	-0.170853	-0.433972

1	-6.767706	-0.183564	-1.673211
1	-6.818003	-0.099530	-4.133599
1	-4.696385	0.000110	-5.462547
8	-1.534879	0.073363	-5.281072
8	0.326443	-0.052055	-0.330709
1	-0.649791	-0.070706	-0.494083
1	0.519789	0.108061	-4.765242

### EE

6	2.177360	0.097879	-3.411794
6	2.210972	0.050476	-1.968075
6	3.446384	0.058279	-1.276436
6	4.629520	0.112876	-2.024126
6	4.600735	0.158858	-3.421654
6	3.385695	0.152193	-4.132210
7	0.896784	0.082203	-3.901723
6	0.094851	0.025328	-2.799988
6	0.854038	0.004063	-1.595691
1	3.470603	0.022577	-0.190027
1	5.591029	0.119746	-1.509660
1	5.540670	0.200806	-3.972999
1	3.364862	0.187974	-5.218525
6	-3.429773	-0.033244	-3.678482
6	-3.396320	-0.080510	-2.234813
6	-4.604738	-0.134596	-1.514483
6	-5.819716	-0.141167	-2.225234
6	-5.848341	-0.095321	-3.622735
6	-4.665078	-0.040953	-4.370333
6	-2.072752	0.012939	-4.050684
6	-1.313657	-0.008282	-2.846255
7	-2.115745	-0.064955	-1.744702
1	-4.584035	-0.170271	-0.428166
1	-6.759728	-0.182936	-1.674002
1	-6.809796	-0.102117	-4.137303
1	-4.689142	-0.005359	-5.456746
8	-1.500445	0.068055	-5.277602
1	-0.520077	0.086288	-5.094381
8	0.281916	-0.051283	-0.368627
1	-0.698425	-0.069795	-0.551682

### EEC

6	2.180724	0.203832	-3.338645
6	2.248031	-0.084983	-1.964748
6	3.476235	-0.178068	-1.268038
6	4.657763	0.040283	-2.035577
6	4.597492	0.329312	-3.387622
6	3.360634	0.422077	-4.089176
7	0.867216	0.246251	-3.802695
6	0.058788	0.002566	-2.760104
6	0.882478	-0.217685	-1.580947
1	3.513767	-0.407702	-0.207854
1	5.631478	-0.021167	-1.546782
1	5.528266	0.490585	-3.935006
1	3.312565	0.642251	-5.150223
6	-3.613115	-0.073444	-2.323371
6	-3.367410	-0.159455	-3.746866
6	-4.467938	-0.237565	-4.618400

6	-5.761874	-0.220725	-4.105671
6	-5.991433	-0.125778	-2.720637
6	-4.927185	-0.052268	-1.826956
6	-2.321219	-0.017532	-1.785126
6	-1.391978	-0.055304	-2.853709
7	-2.048851	-0.148750	-4.050538
1	-4.288814	-0.303175	-5.689949
1	-6.612129	-0.279727	-4.785123
1	-7.014752	-0.111618	-2.345362
1	-5.109108	0.017236	-0.754849
8	-2.029850	0.146423	-0.405649
1	-1.876324	1.090713	-0.260124
8	0.495376	-0.528707	-0.333109
1	-0.487345	-0.439626	-0.284361

### KKC

6	1.955918	0.123963	-1.565552
6	2.419030	-0.020706	-2.875594
6	3.800216	-0.061303	-3.134675
6	4.683234	0.081254	-2.047756
6	4.208519	0.248825	-0.749676
6	2.824693	0.270748	-0.469963
7	0.567433	0.063187	-1.578352
6	0.106766	0.026829	-2.926472
6	1.260347	-0.097483	-3.790598
1	4.152524	-0.182551	-4.154107
1	5.759870	0.063321	-2.219514
1	4.918789	0.359568	0.069918
1	2.448715	0.380888	0.544143
6	-3.533235	0.085764	-3.675119
6	-3.432200	-0.146261	-2.301227
6	-4.558698	-0.355230	-1.486397
6	-5.819253	-0.303574	-2.120450
6	-5.934840	-0.049356	-3.484439
6	-4.796867	0.154718	-4.287429
6	-2.174383	0.210838	-4.243927
6	-1.289673	0.021663	-3.115028
7	-2.090436	-0.096749	-1.942114
1	-4.463642	-0.533148	-0.418122
1	-6.720158	-0.460317	-1.526918
1	-6.927716	-0.011218	-3.933562
1	-4.867782	0.343857	-5.353852
8	-1.918108	0.457648	-5.445273
8	1.333357	-0.264849	-5.030145
1	0.044194	0.656918	-0.945063
1	-1.748402	-0.734196	-1.232168

### KEC

6	0.024747	-0.007146	-0.028684
6	0.018803	-0.007229	1.368780
6	1.226937	0.001973	2.131928
6	2.464707	0.011391	1.447634
6	2.463492	0.011425	0.051331
6	1.273605	0.002397	-0.681355
6	0.855015	-0.000812	3.506722
6	-0.542166	-0.011472	3.571579
7	-1.018368	-0.015287	2.257415

6	-1.446302	-0.018141	4.678541
7	-2.783382	-0.028046	4.498950
6	-3.320053	-0.032081	5.774983
6	-2.301265	-0.024522	6.780851
6	-1.056075	-0.015163	6.076535
6	-2.655792	-0.027251	8.149134
6	-4.015515	-0.037407	8.487136
6	-5.009969	-0.044758	7.506816
6	-4.669753	-0.042152	6.132058
8	0.153371	-0.006204	6.540347
8	1.711218	0.005774	4.547956
1	3.393614	0.018459	2.010138
1	3.413625	0.018670	-0.483230
1	1.308956	0.002706	-1.769642
1	-0.906161	-0.014220	-0.591014
1	-5.435124	-0.047823	5.358766
1	-6.059266	-0.052586	7.802918
1	-4.305999	-0.039623	9.539415
1	-1.884347	-0.021531	8.915301
1	-2.008303	-0.022118	2.078210
1	1.130998	0.001338	5.410285

### EK

6	-0.003179	-0.006880	-0.050589
6	0.056754	-0.006555	1.376703
6	1.251618	0.002470	2.084468
6	2.502656	0.012049	1.414909
6	2.458608	0.011850	-0.010488
6	1.261033	0.002804	-0.702389
6	0.909199	-0.000290	3.512257
6	-0.529892	-0.011262	3.582406
7	-0.988450	-0.014659	2.293880
6	-1.423962	-0.018078	4.690285
7	-2.788772	-0.028317	4.493029
6	-3.310404	-0.032324	5.736779
6	-2.287837	-0.024711	6.767323
6	-1.069954	-0.015519	6.059900
6	-2.650793	-0.027530	8.125027
6	-3.992456	-0.037632	8.473754
6	-4.992975	-0.045081	7.475905
6	-4.662963	-0.042511	6.128150
8	0.173828	-0.006229	6.603619
8	1.720027	0.005799	4.498736
1	3.433647	0.019096	1.968794
1	3.391990	0.019001	-0.575218
1	1.286292	0.003095	-1.793964
1	-0.941906	-0.013957	-0.593200
1	-5.436505	-0.048270	5.361925
1	-6.041669	-0.052979	7.773055
1	-4.282261	-0.039880	9.524023
1	-1.878757	-0.021784	8.892603
1	-1.978792	-0.021971	2.111477
1	0.837124	-0.001180	5.846649

## CONICAL INTERSECTIONS

### CI<sub>DPT</sub>

7	0.155669	0.040517	0.052534
6	0.060203	0.018472	1.403704
6	1.368496	-0.035765	1.935561
6	2.325584	-0.045095	0.820972
6	1.529418	0.004003	-0.324291
6	-1.053524	0.040779	2.247844
6	-0.839189	0.008691	3.614944
6	0.454222	-0.044619	4.152662
6	1.555426	-0.066603	3.308511
8	3.607955	-0.091437	0.922336
6	1.915943	0.001162	-1.683280
7	3.156722	-0.041417	-2.158624
6	3.233404	0.103778	-3.610663
6	1.978221	0.166345	-4.074680
6	1.044791	0.125788	-2.853172
6	1.615349	0.065365	-5.420922
6	2.740300	-0.190924	-6.296824
6	4.024722	-0.220186	-5.839698
6	4.489144	-0.039084	-4.459127
8	-0.194233	0.146495	-2.838986
1	0.598367	0.092776	-5.759130
1	2.549818	-0.390654	-7.344008
1	4.794257	-0.393704	-6.589791
1	5.198296	0.809270	-4.377971
1	-2.050173	0.081729	1.846168
1	-1.686360	0.025105	4.279367
1	0.586337	-0.068430	5.219987
1	2.556148	-0.107467	3.697023
1	-0.576382	0.076797	-0.612840
1	3.942034	-0.115768	-1.555790

### CI<sub>IRI</sub>

6	2.236007	0.666488	-3.169060
6	2.302586	-0.256996	-2.138742
6	3.587716	-0.631649	-1.556636
6	4.715319	-0.051647	-2.181083
6	4.640633	0.872926	-3.195741
6	3.364358	1.379948	-3.720902
7	0.907209	0.811235	-3.526307
6	0.103107	-0.006875	-2.723580
6	0.949481	-0.652026	-1.881505
1	3.673126	-1.421859	-0.834586
1	5.699121	-0.339857	-1.824399
1	5.558923	1.280274	-3.599734
1	3.317128	1.655981	-4.771429
6	-3.547715	-0.569029	-3.448477
6	-3.488242	0.484579	-2.532537
6	-4.639924	1.108386	-2.085829
6	-5.861631	0.660470	-2.574184
6	-5.925638	-0.391449	-3.493202
6	-4.767342	-1.013322	-3.937974
6	-2.157201	-0.965474	-3.690359
6	-1.366528	-0.043583	-2.844069
7	-2.151356	0.774929	-2.182295
1	-4.577528	1.917352	-1.383437

1	-6.771416	1.128517	-2.242492
1	-6.883839	-0.718958	-3.855765
1	-4.806270	-1.821560	-4.644247
8	-1.766228	-1.883331	-4.440919
8	0.584735	-1.577051	-0.898048
1	-0.345663	-1.539972	-0.714828
1	0.571352	1.500864	-4.147161

### Cl<sub>IR2</sub>

7	-0.74092	0.02709	-0.04543
6	-0.07252	0.27854	1.12917
6	1.09075	-0.54623	1.1876
6	1.05469	-1.46718	0.1003
6	-0.10111	-1.02223	-0.88208
6	-0.44855	1.09294	2.17924
6	0.31679	1.01415	3.4107
6	1.40544	0.17891	3.49835
6	1.83723	-0.60022	2.41094
8	1.88966	-2.39111	-0.16338
6	0.73314	-0.39883	-1.87164
7	1.72482	-1.12893	-2.48346
6	2.40543	-0.40529	-3.44569
6	1.79787	0.85767	-3.54429
6	0.73066	0.92267	-2.54785
6	2.27495	1.78167	-4.45958
6	3.35578	1.43693	-5.26924
6	3.94929	0.18326	-5.16023
6	3.47512	-0.75822	-4.24174
8	-0.07316	1.8817	-2.41574
1	1.81134	2.74744	-4.5316
1	3.73701	2.14539	-5.9838
1	4.78597	-0.06799	-5.78809
1	3.93329	-1.72577	-4.15528
1	-1.31253	1.73166	2.10606
1	-0.00483	1.58389	4.26943
1	1.95247	0.12258	4.4308
1	2.69055	-1.24813	2.4912
1	-1.68497	0.28322	-0.17221
1	2.02787	-1.96768	-2.02356

For all the geometries given above the first column corresponds to the atomic number and the three following columns respectively to the  $x$ ,  $y$  and  $z$  Cartesian coordinates in Å.