**Structural and electronic effects of cation binding (Li+, Na+, K+, Mg2+ & Ca2+) to π system of ƞ6-benzene-Cr(CO)3 complex: A theoretical study**

A. KALPANA1, L. AKILANDESWARI\*2

*1,2Department of Chemistry, Sri Sarada College for Women, Salem 636 016, TamilNadu, India.*

Supplementary Material

SM TABLE I. Computed λmax (maximum absorption wavelength), f (oscillator strength), TDM (transition dipole moments),

Root mean square value (μ0n) (RMS) between the ground and nth excited state of all the system under study.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Systems | MB | | | | | | | MBC | | | | | | |
| State  transition | λ (nm) | *f* | Transition dipolemoment | | | RMS  (μ0n)  (e-bohr) | State  transition | λ (nm) | *f* | Transition dipolemoment | | | RMS  (μ0n)  (e-bohr) |
| x | y | z | x | y | z |
| BC | S0→S3 | 168.03 | 0.5587 | -0.1278 | -0.4628 | 0 | 0.480 | S0→S2 | 361.16 | 0.0004 | -0.0011 | -0.0122 | 0.0661 | 0.067 |
| **S0→S4** | **168.03** | **0.5588** | **-0.4629** | **0.1278** | **0** | **0.480** | S0→S3 | 361.10 | 0.0004 | -0.0006 | 0.0657 | 0.0121 | 0.067 |
| S0→S8 | 155.08 | 0.0056 | 0 | 0 | -0.0087 | 0.009 | S0→S4 | 346.01 | 0.0002 | 0.0323 | 0.0405 | -0.0043 | 0.052 |
|  |  |  |  |  |  |  | S0→S5 | 345.91 | 0.0010 | -0.0093 | 0.0202 | -0.1022 | 0.105 |
|  |  |  |  |  |  |  | S0→S6 | 345.80 | 0.0009 | -0.0117 | 0.0954 | 0.0238 | 0.099 |
|  |  |  |  |  |  |  | S0→S7 | 344.98 | 0.0005 | 0.0720 | 0.0005 | -0.0060 | 0.072 |
|  |  |  |  |  |  |  | **S0→S8** | **328.93** | **0.0016** | **-0.0002** | **-0.1242** | **-0.0418** | **0.131** |
|  |  |  |  |  |  |  | S0→S9 | 328.89 | 0.0016 | 0.0008 | -0.0419 | 0.1247 | 0.132 |
|  |  |  |  |  |  |  | S0→S10 | 308.11 | 0.0001 | 0.0006 | -0.0353 | -0.0010 | 0.035 |
| Li+-BC | S0→S2 | 193.2 | 0.0202 | 0.0085 | 0.0635 | 0 | 0.064 | S0→S4 | 390.76 | 0.0006 | -0.0051 | -0.0323 | 0.0820 | 0.088 |
| S0→S3 | 193.19 | 0.0202 | -0.0636 | 0.0084 | 0 | 0.064 | S0→S5 | 390.42 | 0.0006 | 0.0013 | -0.0824 | -0.0336 | 0.089 |
| **S0→S6** | **165.65** | **0.5223** | **-0.1315** | **0.4292** | **0** | **0.449** | **S0→S6** | **352.21** | **0.0025** | **0.1700** | **0.0058** | **0.0026** | **0.170** |
| S0→S7 | 165.65 | 0.5222 | -0.4292 | -0.1315 | 0 | 0.449 | S0→S7 | 349.04 | 0.0013 | 0.0925 | -0.0814 | 0.0041 | 0.123 |
| S0→S10 | 163.62 | 0.0066 | 0 | 0.0001 | -0.0277 | 0.028 | S0→S8 | 348.72 | 0.0012 | -0.0476 | -0.0692 | -0.0820 | 0.117 |
|  |  |  |  |  |  |  | S0→S9 | 348.49 | 0.0013 | 0.0531 | 0.0593 | -0.0911 | 0.121 |
|  |  |  |  |  |  |  | S0→S10 | 322.44 | 0.0006 | 0.0060 | 0.0061 | -0.0785 | 0.079 |
| Na+-BC | S0→S1 | 230.59 | 0.0111 | -0.0067 | 0.0494 | 0.0001 | 0.050 | S0→S2 | 398.04 | 0.0006 | 0.0000 | -0.0337 | 0.0837 | 0.090 |
| S0→S2 | 230.57 | 0.0111 | 0.0495 | 0.0069 | 0.0001 | 0.050 | S0→S3 | 397.86 | 0.0006 | 0.0018 | 0.0831 | 0.0338 | 0.090 |
| **S0→S5** | **168.36** | **0.5276** | **-0.0938** | **0.444** | **0.0009** | **0.454** | S0→S4 | 391.39 | 0.0001 | -0.0007 | -0.0035 | 0.0404 | 0.041 |
| S0→S6 | 168.35 | 0.5276 | 0.4441 | 0.0938 | 0.001 | 0.454 | S0→S5 | 391.27 | 0.0001 | 0.0007 | 0.0414 | 0.0036 | 0.042 |
|  |  |  |  |  |  |  | S0→S8 | 367.94 | 0.0012 | -0.1217 | -0.0008 | -0.0002 | 0.122 |
|  |  |  |  |  |  |  | **S0→S9** | **351.84** | **0.0015** | **0.0012** | **-0.1334** | **0.0118** | **0.134** |
|  |  |  |  |  |  |  | S0→S10 | 351.64 | 0.0015 | 0.0001 | -0.0119 | -0.1333 | 0.134 |
| K+-BC | S0→S1 | 230.94 | 0.0085 | 0 | 0.0002 | -0.0395 | 0.040 | S0→S4 | 379.73 | 0.0007 | 0.0019 | 0.0929 | 0.0145 | 0.094 |
| S0→S2 | 230.93 | 0.0085 | 0 | -0.0395 | -0.0002 | 0.040 | S0→S5 | 379.42 | 0.0007 | -0.0026 | -0.0143 | 0.0924 | 0.094 |
| S0→S5 | 172.58 | 0.0001 | -0.0055 | 0 | 0.0001 | 0.006 | S0→S6 | 377.77 | 0.0001 | -0.0001 | 0.0292 | -0.0173 | 0.034 |
| S0→S7 | 171.21 | 0.1136 | 0.1767 | -0.0001 | 0 | 0.177 | S0→S7 | 377.69 | 0.0001 | -0.0002 | -0.0152 | -0.0304 | 0.034 |
| S0→S9 | 169.78 | 0.3383 | 0 | -0.2698 | 0.2307 | 0.355 | S0→S9 | 341.11 | 0.0001 | -0.0332 | -0.0051 | -0.0049 | 0.034 |
| **S0→S10** | **169.76** | **0.3436** | **-0.0001** | **0.233** | **0.2718** | **0.358** | **S0→S10** | **339.76** | **0.0013** | **-0.0026** | **-0.0183** | **0.1175** | **0.119** |
| Mg2+-BC | S0→S1 | 334.30 | 0.0014 | 0.0098 | 0.0108 | 0 | 0.015 | S0→S1 | 1096.59 | 0.0002 | 0.0018 | 0.0651 | 0.0407 | 0.077 |
| S0→S2 | 334.28 | 0.0014 | -0.0107 | 0.0098 | -0.0001 | 0.015 | S0→S2 | 1095.48 | 0.0002 | 0.0018 | 0.0401 | -0.0655 | 0.077 |
| **S0→S8** | **174.03** | **0.0109** | **0** | **0** | **-0.0519** | **0.052** | **S0→S3** | **792.33** | **0.0484** | **-1.1238** | **-0.0011** | **0.0001** | **1.124** |
|  |  |  |  |  |  |  | S0→S5 | 402.55 | 0.0001 | 0.0020 | -0.0285 | -0.0024 | 0.029 |
|  |  |  |  |  |  |  | S0→S6 | 402.43 | 0.0001 | -0.0014 | 0.0018 | -0.0282 | 0.028 |
|  |  |  |  |  |  |  | S0→S7 | 395.43 | 0.0001 | -0.0007 | 0.0356 | 0.0053 | 0.036 |
|  |  |  |  |  |  |  | S0→S8 | 395.14 | 0.0001 | 0.0001 | -0.0057 | 0.0363 | 0.037 |
|  |  |  |  |  |  |  | S0→S9 | 374.08 | 0.0016 | 0.0000 | 0.1391 | -0.0113 | 0.140 |
|  |  |  |  |  |  |  | S0→S10 | 373.93 | 0.0016 | 0.0010 | 0.0112 | 0.1395 | 0.140 |
| Ca2+-BC | S0→S1 | 296.74 | 0.0027 | 0 | 0 | 0.0157 | 0.016 | S0→S1 | 744.07 | 0.0003 | 0.0002 | 0.0394 | -0.0834 | 0.092 |
| S0→S2 | 296.72 | 0.0027 | 0 | 0.0157 | 0 | 0.016 | S0→S2 | 743.49 | 0.0003 | 0.0013 | 0.0835 | 0.0395 | 0.092 |
| **S0→S10** | **173.55** | **0.0069** | **0.0335** | **-0.0001** | **0** | **0.034** | **S0→S3** | **667.06** | **0.0174** | **-0.6181** | **0.0001** | **-0.0001** | **0.618** |
|  |  |  |  |  |  |  | S0→S5 | 430.26 | 0.0001 | 0.0008 | -0.0075 | -0.0359 | 0.037 |
|  |  |  |  |  |  |  | S0→S6 | 430.18 | 0.0001 | -0.0001 | 0.0359 | -0.0077 | 0.037 |
|  |  |  |  |  |  |  | S0→S9 | 374.44 | 0.0009 | 0.0003 | -0.0892 | 0.0523 | 0.103 |
|  |  |  |  |  |  |  | S0→S10 | 374.36 | 0.0009 | 0.0003 | -0.0518 | -0.0892 | 0.103 |

Data corresponding to the maximum absorption wavelength are in bold letters.

SM TABLE II . NTO pictures and MO transitions corresponding to λmax of MB systems under study.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Systems | λmax  &  *f* | NTO | | | MO transition | | |
| % contribution | Hole | Particle |
| B | 168.035  (0.559) | 50% |  |  | HOMO-1 → LUMO  HOMO → LUMO+1  HOMO-1 → LUMO+1  HOMO → LUMO | 0.69  -0.69  -0.16  -0.16 | (47%)  (47%)  (2%)  (2%) |
| 50% |  |  |
| Li+-B | 165.649  (0.522) | 49% |  |  | HOMO-1 → LUMO  HOMO → LUMO+1  HOMO-1 → LUMO+1  HOMO → LUMO | 0.62  -0.62  0.33  0.33 | (38%)  (38%)  (11%)  (11%) |
| 49% |  |  |
| Na+-B | 168.357  (0.528) | 49% |  |  | HOMO-1 → LUMO+2  HOMO → LUMO+1 | 0.70  -0.70 | (49%)  (49%) |
| 49% |  |  |
| K+-B | 169.766  (0.344) | 63% |  |  | HOMO-1 → LUMO+3  HOMO → LUMO+1  HOMO → LUMO+5  HOMO-1→LUMO+5  HOMO-1→LUMO+1 | 0.57  0.57  0.46  0.28  0.15 | (32%)  (32%)  (21%)  (8%)  (2%) |
| 34% |  |  |
| Mg2+-B | 174.029  (0.011) | 53% |  |  | HOMO-2 → LUMO+1  HOMO-3 → LUMO+2 | 0.73  0.67 | (53%)  (45%) |
| 45% |  |  |
| Ca2+-B | 173.551  (0.007) | 49% |  |  | HOMO-3 → LUMO+2  HOMO-2 → LUMO+1 | 0.70  0.70 | (49%)  (48%) |
|  | 48% |  |  |

SM TABLE III. NTO pictures and MO transitions corresponding to λmax of MBC systems under study.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Systems | λmax  &  *f* | NTO | | | MO transition | | |
| % contribution | Hole | Particle |
| BC | 328.925  (0.002) | 71% |  |  | HOMO-2 →LUMO+1  HOMO-2 → LUMO+2  HOMO-1 → LUMO+3  HOMO → LUMO+2  HOMO-2 → LUMO+13  HOMO-1 → LUMO+12 | 0.71  -0.37  0.28  -0.27  -0.18  0.15 | (51%)  (14%)  (8%)  (7%)  (3%)  (2%) |
| 10% |  |  |
| Li+-BC | 352.210  (0.003) | 49% |  |  | HOMO → LUMO+5  HOMO → LUMO+4  HOMO-1 → LUMO+4 HOMO-1 → LUMO+5  HOMO → LUMO+12  HOMO-1 → LUMO+11 | 0.45  -0.45  -0.44  -0.41  -0.22  -0.20 | (21%)  (20%)  (19%)  (17%)  (5%)  (4%) |
| 43% |  |  |
| Na+-BC | 351.840  (0.002) | 77% |  |  | HOMO-2 → LUMO+3  HOMO-2 → LUMO+11  HOMO-2 → LUMO+1  HOMO-2 → LUMO+6  HOMO → LUMO+4  HOMO-1 → LUMO+3 | 0.66  -0.31  -0.27  0.27  -0.23  0.23 | (43%)  (10%)  (7%)  (7%)  (5%)  (5%) |
| K+-BC | 339.759  (0.001) | 70% |  |  | HOMO-3 → LUMO+2  HOMO-3 → LUMO+1  HOMO-3→LUMO+5  HOMO-3→LUMO+14  HOMO-2→LUMO+3  HOMO-2→LUMO+2 | 0.56  0.39  0.39  0.21  -0.20  0.17 | (31%)  (15%)  (15%)  (4%)  (4%)  (3%) |
| Mg2+-BC | 792.337  (0.048) | 98% |  |  | HOMO-2 → LUMO | 0.99 | (98%) |
| Ca2+-BC | 667.052  (0.017) | 99% |  |  | HOMO-2 → LUMO | 1.00 | (99%) |