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TD DFT insights into unusual properties of excited sandwich complexes: Structural transformations and vibronic interactions in Rydberg-state bis(η^6-benzene)chromium

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Supplementary Information

Table S1. B3LYP / BPW91 frequencies of the a_{1g} and e_{2g} vibrations in the ground neutral ($^1A_{1g}$), Rydberg ($^1B_{2u}$) and cationic ($^2A_{1g}$) states of the $(\eta^6\text{-}C_6D_6)_2Cr$ molecule. The experimental Rydberg-state frequencies obtained from the REMPI spectrum[1] are given in parentheses where available. See the main text for the vibration notations.

D_{6h} symmetry	D_{2h} symmetry	Vibration number	Neutral ($^1A_{1g}$)	R4p$_\gamma$ ($^1B_{2u}$)	Cation ($^2A_{1g}$)
a_{1g}	a_g	2s	2365 / 2305	2379 / 2347	2389 / 2343
a_{1g}	a_g	1s	940 / 921	945 / 920 (915)	941 / 919
a_{1g}	a_g	11as	609 / 595	615 / 589 (593)	613 / 594
a_{1g}	a_g	21	244 / 248	248 / 257 (248)	243 / 251
e_{2g}	a_g b_{1g}	7s	2338 / 2279	2340 / 2303 2195 / 2099	2366 / 2319 2365 / 2320
e_{2g}	a_g b_{1g}	8s	1489 / 1459	1485 / 1449 1492 / 1457	1491 / 1454
e_{2g}	a_g b_{1g}	9s	853 / 826	854 / 836 (864) 108 / 23	862 / 839
e_{2g}	a_g b_{1g}	17as	735 / 702	752 / 718(731) 749 / 714	751 / 715
e_{2g}	a_g b_{1g}	6s	604 / 584	583 / 575 580 / 556	584 / 569
e_{2g}	a_g b_{1g}	16as	408 / 394	410 / 396 411 / 385	402 / 392

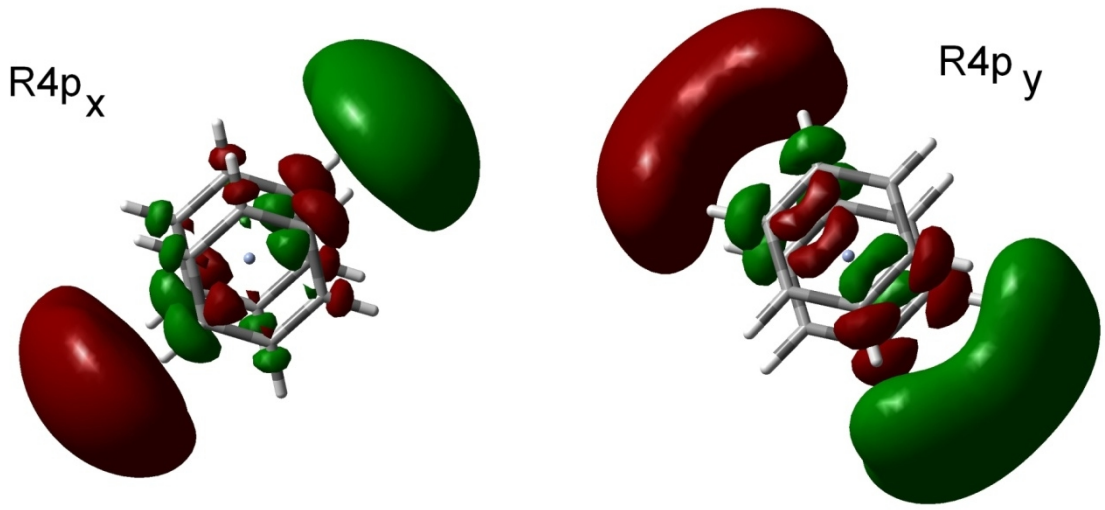

Figure S1. BPW91 isosurfaces (isovalue 0.02) of the Rydberg $4p_x$(left) and $4p_y$(right) orbitals of (η^6-$C_6H_6)_2Cr$.

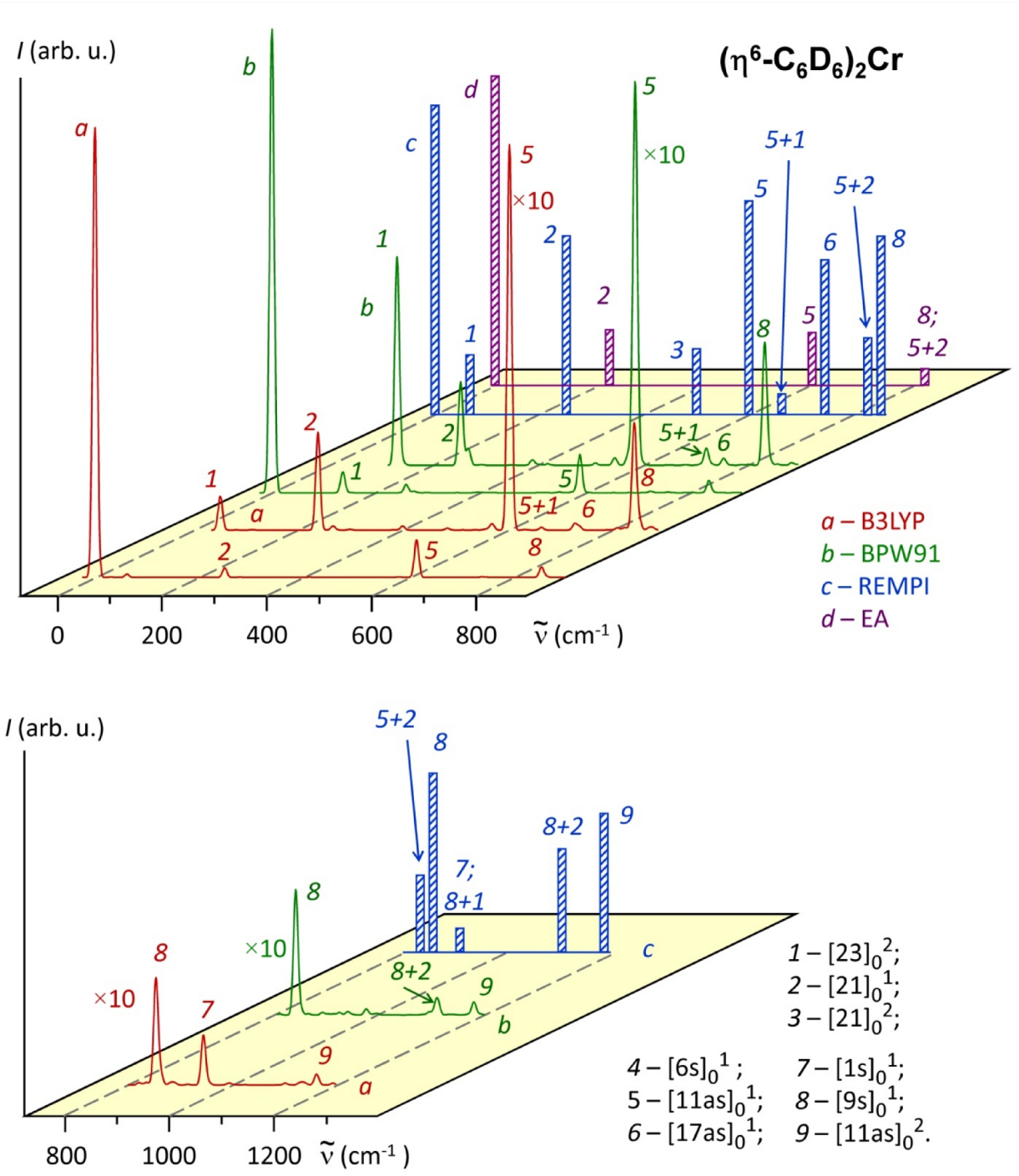

Figure S2. B3LYP (a) and B3PW91 (b) simulation of the R4$p_{x,y}$vibronic structures in the REMPI (c) and EA (d) spectrum of **1-D** in the low-energy (top) and high-energy (bottom) regions. The experimental EA[2] and REMPI[1] peak positions and relative intensities are shown by bars. See the main text for the vibration notations.

REFERENCES

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2 S. Y. Ketkov, J. C. Green and C. P. Mehnert, *J. Chem. Soc., Faraday Trans.* 1997, **93**, 2461−2466.