SUPPORTING INFORMATION

Another Look at Photoelectron Spectra of the Anion $Cr_2O_2^-$: Multireference Characters and Energetic Degeneracy

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Table S1: Relative energies of selected states calculated with the RASPT2/ANO-RCC-VDZ method. Four isomers a, b, c, and d are drawn in Figure 2.

isomer	sym	state	relative energy (eV)
a - anion	C_{2v}	$^2A_1$	1.34
		$^2B_2$	1.88
		$^4A_1$	1.35
		$^4B_2$	1.89
		$^6A_1$	1.34
		$^6B_2$	1.90
		$^8A_1$	1.32
		$^8B_2$	1.90
		$^{10}A_1$	1.25
		$^{10}B_2$	1.86
		$^{12}A_2$	3.96
		$^{12}B_2$	4.41
b - anion	C_{2v}	$^2A_2$	2.50
		$^2B_1$	2.33
		$^4B_1$	2.76
		$^4B_2$	1.92
		$^6A_2$	2.25
		$^6B_2$	0.78
		$^8A_1$	0.68
		$^8A_2$	4.91
		$^8B_1$	0.61
		$^8B_2$	1.71

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isomer	sym	state	relative energy (eV)
		$^{10}A_1$	1.57
		$^{10}A_2$	0.03
		$^{10}B_1$	1.33
		$^{10}B_2$	0.38
		$^{12}A_1$	5.34
		$^{12}A_2$	5.89
c - anion	D_{2h}	$^{2}B_{1g}$	1.34
		$^{2}A_{u}$	1.07
		$^{4}B_{2u}$	0.80
		$^{4}B_{1g}$	1.00
		$^{6}B_{3g}$	0.78
		$^{6}A_{u}$	0.96
		$^{8}B_{2u}$	0.68
		$^{8}B_{1g}$	0.94
		$^{10}B_{2g}$	0.00
		$^{10}B_{3g}$	0.38
		$^{12}A_{g}$	3.46
		$^{12}B_{2g}$	3.07
d - anion	D_{2h}	$^{2}B_{1g}$	1.34
		$^{2}A_{u}$	1.07
		$^{4}A_{g}$	1.28
		$^{4}A_{u}$	1.50
		$^{6}B_{3g}$	0.78

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isomer	sym	state	relative energy (eV)
		$^{6}A_{u}$	0.96
		$^{8}B_{3u}$	0.41
		$^{8}B_{2u}$	0.68
		$^{10}A_{g}$	0.04
		$^{10}B_{2g}$	0.00
		$^{12}B_{3u}$	3.52
		$^{12}B_{1u}$	3.41
a - neutral	C_{2v}	$^{1}A_{1}$	2.63
		$^{1}B_{2}$	3.35
		$^{3}A_{1}$	2.66
		$^{3}B_{2}$	3.37
		$^{5}A_{1}$	2.69
		$^{5}B_{2}$	3.38
		$^{7}A_{1}$	2.73
		$^{7}B_{2}$	3.38
		$^{9}A_{1}$	2.74
		$^{9}A_{2}$	3.29
		$^{11}A_{2}$	5.72
		$^{11}B_{2}$	5.29
b - neutral	C_{2v}	$^{1}A_{1}$	2.63
		$^{1}B_{2}$	3.06
		$^{3}B_{1}$	2.66
		$^{3}B_{2}$	2.69

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isomer	sym	state	relative energy (eV)
		$^5A_1$	1.86
		$^5A_2$	2.61
		$^7B_1$	2.73
		$^7B_2$	2.74
		$^9A_1$	1.38
		$^9A_2$	5.27
		$^{11}A_2$	7.19
		$^{11}B_2$	7.46
c - neutral	D_{2h}	^1A_g	2.63
		$^1B_{3u}$	2.18
		$^3B_{2u}$	2.85
		$^3B_{1u}$	2.66
		^5A_g	2.69
		$^5B_{1g}$	4.65
		$^7B_{1u}$	2.73
		$^7B_{3g}$	2.70
		$^9B_{1g}$	1.95
		$^9B_{2g}$	1.38
		$^{11}B_{1u}$	4.68
		$^{11}B_{2g}$	4.57
d - neutral	D_{2h}	^1A_g	1.64
		$^1B_{3u}$	2.18
		$^3B_{1g}$	3.23

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isomer	sym	state	relative energy (eV)
		$^{3}B_{1u}$	2.66
		$^{5}B_{2u}$	2.16
		$^{5}B_{2g}$	1.86
		$^{7}B_{3u}$	1.67
		$^{7}B_{3g}$	1.99
		$^{9}B_{2g}$	1.38
		$^{9}B_{3g}$	1.92
		$^{11}A_{g}$	5.49
		$^{11}B_{2g}$	4.58

Table S2: Equilibrium geometries and harmonic vibrational frequencies of states involved in the first two bands X' and X

state		equilibrium coordinate (Bohrs)			harmonic vibrational frequency (cm^{-1})
$^{10}A_g$	Cr	0.000000000	0.000000000	2.476415988	153, 248, 332, 367, 605, 658
	Cr	0.000000000	0.000000000	-2.476415988	
	O	0.000000000	2.459680575	0.000000000	
	O	0.000000000	-2.459680575	0.000000000	
$^{9}A_g$	Cr	0.000000000	0.000000000	2.444400250	143, 336, 484, 570, 636, 684
	Cr	0.000000000	0.000000000	-2.444400250	
	O	0.000000000	2.445303539	0.000000000	
	O	0.000000000	-2.445303539	0.000000000	
$^{10}B_{2g}$	Cr	0.000000000	0.000000000	2.368792314	105, 275, 355, 417, 589, 665
	Cr	0.000000000	0.000000000	-2.368792314	
	O	0.000000000	2.561225001	0.000000000	
	O	0.000000000	-2.561225001	0.000000000	
$^{9}B_{2g}$	Cr	0.000000000	0.000000000	2.332430206	153, 253, 277, 359, 624, 686
	Cr	0.000000000	0.000000000	-2.332430206	
	O	0.000000000	2.561381848	0.000000000	
	O	0.000000000	-2.561381848	0.000000000	

To ensure that the TPSS functional is appropriate for use of Franck-Condon simulation, optimal geometrical parameters of four states involved in the first two bands X and X' were calculated at this level and compared to those optimized at the RASPT2. As can be seen in Table S3, the TPSS results are negligibly different from the RASPT2 ones.

Table S3: Comparison of geometrical parameters between the RASPT2 and TPSS methods

parameter	$^{10}A_g$		$^{10}B_{2g}$		$^{9}A_g$		$^{9}B_{2g}$	
	RASPT2	TPSS	RASPT2	TPSS	RASPT2	TPSS	RASPT2	TPSS
r_{Cr-O} (Å)	1.842	1.847	1.833	1.846	1.824	1.830	1.825	1.833
r_{Cr-Cr}(Å)	2.573	2.621	2.447	2.507	2.566	2.587	2.454	2.469
r_{O-O} (Å)	2.637	2.603	2.731	2.711	2.592	2.588	2.702	2.711
∠OCrO	91.42	89.61	96.27	94.47	90.59	90.02	95.51	95.36