

The electronic properties of three popular high spin complexes [TM(acac)₃, TM= Cr, Mn, and Fe] revisited: an experimental and theoretical study.

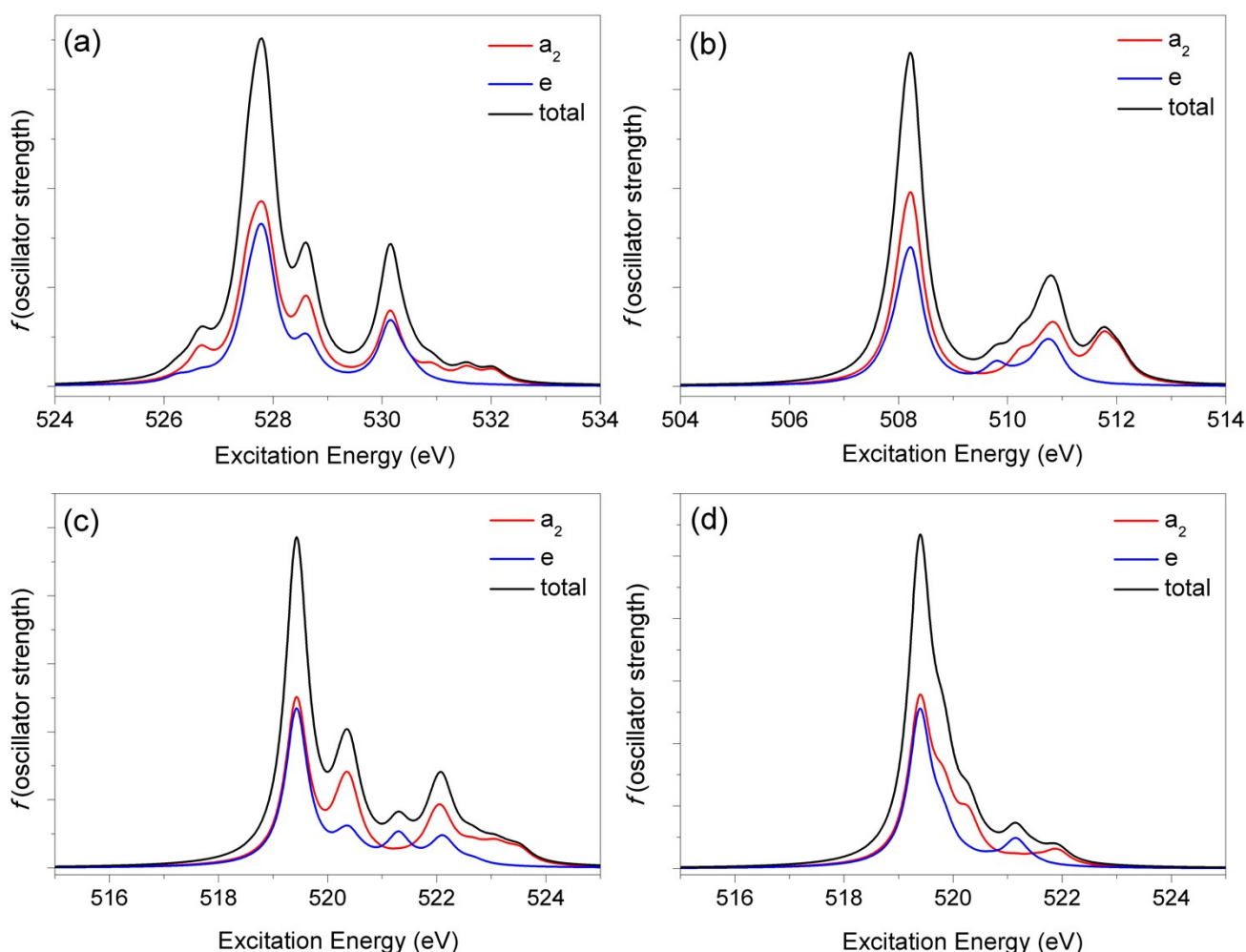
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Figure S1. Spin-unrestricted scalar relativistic ZORA TD-DFT 1s⁰ excitation spectra of Cr(acac)₃ evaluated with diverse exchange-correlations functionals: (a) LB94,¹ (b) SAOP,² (c) PBE0³ and (d) M06.⁴ Simulated spectra have not been shifted and have a Gaussian broadening of 0.25 eV.



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Figure S2. Spin \uparrow and spin \downarrow COOPs between TM^{III} e_g -like 3d AOs and the e linear combination of the $(\text{acac})_3^{3-}$ -based n (solid lines) and n_+ (dotted lines) FMOs. Bonding (antibonding) combinations correspond to positive (negative) peaks in the COOP plots. Vertical bars represent the HOMO energies.

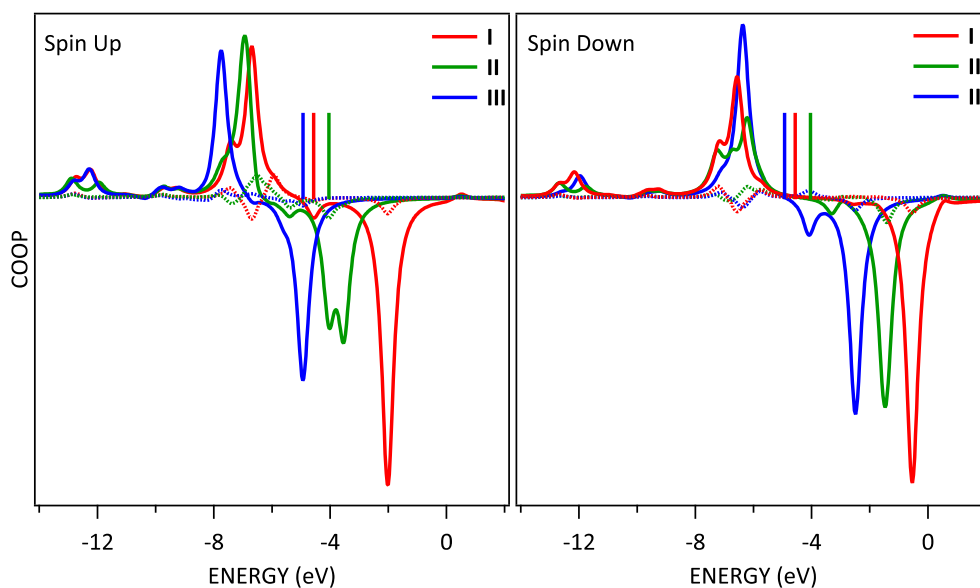


Figure S3. Superimposed licorice representation of I (Cr^{III} ion in yellow), II (Mn^{III} ion in burgundy), and III (Fe^{III} ion in olive green) BP86 optimized structures. Hydrogen atoms of the acac fragments are not displayed for the sake of clarity.

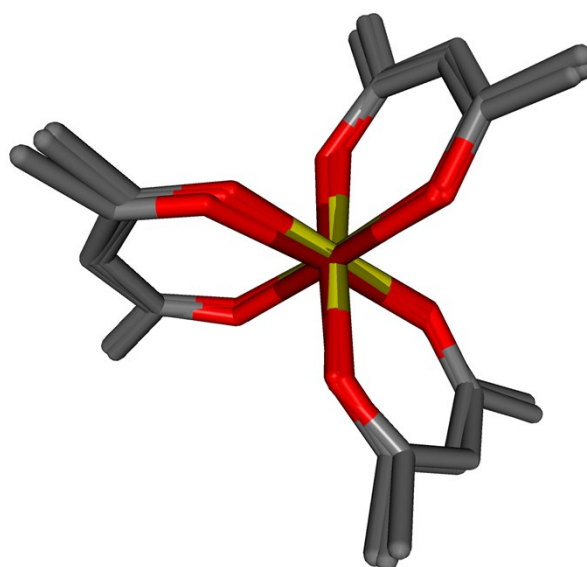


Table S1. Nalewajski–Mrozek [ref. 1] TM–O bond multiplicity index (INM), Hirshfeld [ref. 2] (Q_{Hir}^{TM}) and Voronoi [ref. 3] (Q_{Vor}^{TM}) charges of TM and O atomic species, and bonding energies (BEs in kcal/mol) of I, II and III decomposed according to the ZTS scheme [ref. 4] and taking I as a reference.

	I	II	III
INM	0.47	0.25 / 0.46 ^a	0.38
$Q_{Hir}^{TM}/Q_{Vor}^{TM}$	0.58 / 0.55	0.37 / 0.26	0.43 / 0.35
Q_{Hir}^O/Q_{Vor}^O	-0.21 / -0.22	-0.21 / -0.20 ^b -0.17 / -0.16 ^c	-0.19 / -0.19
BE	0	27	61
ΔE_{ster}	0	-17	-115
ΔE_{int}	0	44	176

^aThe former (latter) value refers to the (Mn–O)^l ((Mn–O)^s) bonds. ^bValues relative to the O atoms involved in the two (Mn–O)^l bonds. ^cValues relative to the O atoms involved in the four (Mn–O)^s.

- 1 (a) R. F. Nalewajski and J. Mrozek, *Int. J. Quantum Chem.*, 1994, **51**, 187; (b) R. F. Nalewajski, J. Mrozek, S. J. Formosinho and A. J. C. Varandas, *Int. J. Quantum Chem.*, 1994, **52**, 1153; (c) R. F. Nalewajski and J. Mrozek, *Int. J. Quantum Chem.*, 1996, **57**, 377; R. F. Nalewajski, J. Mrozek and G. Mazur, *Can. J. Chem.*, 1996, **74**, 1121; (d) R. F. Nalewajski, J. Mrozek and A. Michalak, *Int. J. Quantum Chem.*, 1997, **61**, 589; (e) R. F. Nalewajski, J. Mrozek and A. Michalak, *Pol. J. Chem.*, 1998, **72**, 1779.
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Table S2. Experimental and theoretical ionization energies (IEs in eV) of the HOMO in **I**, **II** and **III**. Theoretical IEs have been evaluated by carrying out spin-unrestricted non-relativistic Slater transition state (^sTS) calculations for the 30e(**⊗**), the 94a(**⊗**) and the 31e(**⊗**) MOs in **I**, **II** and **III**, respectively

	I	II	III
Exp.	7.46, ^{1,4} 7.5, ² 7.50 ³	7.32 ¹	~6.3 ^a
^s TS	6.84	6.34	6.95

^aEstimated from the spectrum of Fe(hfa)₃⁵ by applying a 2 eV red shift.⁶

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- 2 V. I. Vovna, I. B. Lvov, Y. V. Ivanov, S. N. Slabzhennikov, A. I. Streltsov and A. Yu. Ustinov, *J. Electron. Spectrosc.*, 1998, **96**, 141.
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- 6 The M(hfa)₃ PE spectra (M = Al, Cr, Fe) are very similar to the M(acac)₃ ones, with the M(hfa)₃ spectral patterns uniformly blue-shifted by ~ 2 eV with respect to the M(acac)₃ ones. A rough estimate of the HOMO ^{III}IEs can be then obtained by referring to the Fe(hfa)₃ spectrum and applying a red-shift of 2 eV

Table S3. Selected optimized geometrical parameters for **I** – **III**. Bond lengths and bond angles are in Å and deg, respectively. Beside X-ray values (in parentheses) [refs. 1,2], theoretical B3LYP literature values [refs. 1, 3]. (in bold) are also reported for comparison.^a

	M–O	C–O	C–C	O–M–O ^b	M–O–C
I	1.977 / 1.977	1.273 / 1.272	1.405/ 1.403	91.5/ 89.7	126.4/ 128.0
	(1.953)	(1.260)	(1.385)	(91.1)	(126.7)
II	1.928/1.941/2.163	1.273 ^c	1.406 ^c	89.5 ^c	126.6 ^c
	1934/1.951/2.147	1.276^c	1.405^c	89.2^c	127.7^c
	(1.932/1.937/2.110)	(1.268) ^c	(1.384) ^c	(89.2) ^c	(127.0) ^c
III	2.014/ 2.011	1.272/ 1.275	1.405 / 1.405	87.5/ 87.4	129.3/ 129.8
	(1.992)	(1.262)	(1.382)	(87.4)	(129.1)

^aLiterature values pertaining to **I** and **III** are those reported in ref. 1, while those pertaining to **II** are taken from refs. 2 (X-ray) and 3 (B3LYP). ^bIt refers to the angle within the pseudoaromatic ring. ^cMean value.

- 1 I. Diaz-Acosta, J. Baker, W. Cordes and P. Pulay, *J. Phys. Chem. A*, 2001, **105**, 238.
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Table S4. DFT-BP86 Optimized Cartesian Coordinates of Cr(acac)₃ (I)

Cr	0.000000	0.000000	0.000000
O	1.406389	0.782165	1.155070
O	1.406389	-0.782165	-1.155070
O	-0.025820	1.609051	-1.155070
O	-1.380570	-0.826886	-1.155070
O	-1.380570	0.826886	1.155070
O	-0.025820	-1.609051	1.155070
C	3.021118	2.285131	2.030360
C	1.958547	1.934150	1.010059
C	1.651744	2.860904	0.000000
C	0.695750	2.663227	-1.010059
C	0.468423	3.758931	-2.030360
C	-3.303487	0.000000	0.000000
C	-2.654297	0.729076	1.010059
C	-3.489541	1.473799	2.030360
C	-2.654297	-0.729076	-1.010059
C	-3.489541	-1.473799	-2.030360
C	1.958547	-1.934150	-1.010059
C	3.021118	-2.285131	-2.030360
C	0.695750	-2.663227	1.010059
C	1.651744	-2.860904	0.000000
C	0.468423	-3.758931	2.030360
H	2.196839	3.805037	0.000000
H	-4.393679	0.000000	0.000000
H	3.145990	1.456830	2.735622
H	-0.311344	3.452922	-2.735622
H	-2.834647	1.996093	2.735622
H	3.145990	-1.456830	-2.735622
H	-0.311344	-3.452922	2.735622
H	-2.834647	-1.996093	-2.735622
H	2.196839	-3.805037	0.000000
H	3.979854	2.489098	1.531867
H	2.739023	3.193785	2.581707
H	0.165695	4.691203	-1.531867
H	1.396387	3.968956	-2.581707
H	-4.145549	2.202105	1.531867
H	-4.135410	0.775171	2.581707
H	-4.145549	-2.202105	-1.531867
H	-4.135410	-0.775171	-2.581707
H	2.739023	-3.193785	-2.581707
H	3.979854	-2.489098	-1.531867
H	1.396387	-3.968956	2.581707
H	0.165695	-4.691203	1.531867

Table S5. DFT-BP86 Optimized Cartesian Coordinates of Mn(acac)₃ (II)

Mn	0.000000	0.000000	0.000000
O	-1.591196	0.748706	1.302678
O	-1.383557	-0.781855	-1.114218
O	1.536360	-0.891954	-1.287511
O	0.126169	-1.588377	1.118618
O	1.372494	0.831906	1.122860
O	-0.061738	1.593876	-1.144417
C	-3.770555	1.285283	2.081121
C	-2.832043	0.684808	1.050477
C	-3.390434	0.075671	-0.106923
C	-2.667371	-0.601293	-1.089721
C	-3.392444	-1.226067	-2.261080
C	3.244253	-2.365189	-2.027708
C	2.182320	-1.951313	-1.025114
C	1.976053	-2.760592	0.125228
C	0.995637	-2.549203	1.096379
C	0.864239	-3.512875	2.255143
C	3.003492	2.307932	1.972109
C	1.953613	1.966006	0.942814
C	1.679322	2.856707	-0.107004
C	0.697878	2.630743	-1.084457
C	0.459976	3.652849	-2.169824
H	-3.736797	0.664992	2.989304
H	-3.415865	2.286105	2.361114
H	-4.807995	1.340880	1.729871
H	-4.472210	0.115115	-0.227457
H	-3.223075	-2.312605	-2.259274
H	-4.469591	-1.026106	-2.232253
H	-2.971090	-0.835869	-3.198481
H	4.029708	-1.595922	-2.058522
H	3.698295	-3.335319	-1.793184
H	2.792880	-2.402836	-3.029106
H	2.614159	-3.634603	0.248965
H	0.919542	-2.953312	3.199491
H	-0.125672	-3.991076	2.221479
H	1.641132	-4.285600	2.239659
H	3.826307	1.581349	1.902994
H	3.401078	3.319943	1.837492
H	2.570395	2.210106	2.977127
H	2.248739	3.782634	-0.156122
H	0.514882	3.156976	-3.148911
H	-0.557464	4.058495	-2.069891
H	1.183546	4.474538	-2.130741

Table S6. DFT-BP86 Optimized Cartesian Coordinates of Fe(acac)₃ (III)

Fe	0.000000	0.000000	0.000000
O	1.398218	0.909215	1.178940
O	1.398218	-0.909215	-1.178940
O	0.088294	1.665500	-1.178940
O	-1.486512	-0.756285	-1.178940
O	-1.486512	0.756285	1.178940
O	0.088294	-1.665500	1.178940
C	2.987580	2.422400	2.101023
C	1.966491	2.049776	1.043193
C	1.707287	2.957107	0.000000
C	0.791913	2.727919	-1.043193
C	0.604070	3.798520	-2.101023
C	-3.414573	0.000000	0.000000
C	-2.758404	0.678143	1.043193
C	-3.591650	1.376120	2.101023
C	-2.758404	-0.678143	-1.043193
C	-3.591650	-1.376120	-2.101023
C	1.966491	-2.049776	-1.043193
C	2.987580	-2.422400	-2.101023
C	0.791913	-2.727919	1.043193
C	1.707287	-2.957107	0.000000
C	0.604070	-3.798520	2.101023
H	2.252526	3.901489	0.000000
H	-4.505052	0.000000	0.000000
H	3.101086	1.598413	2.813286
H	-0.166277	3.484826	-2.813286
H	-2.934809	1.886413	2.813286
H	3.101086	-1.598413	-2.813286
H	-0.166277	-3.484826	2.813286
H	-2.934809	-1.886413	-2.813286
H	2.252526	-3.901489	0.000000
H	3.959615	2.643886	1.636917
H	2.668208	3.326890	2.639155
H	0.309865	4.751070	-1.636917
H	1.547067	3.974181	-2.639155
H	-4.269480	2.107184	1.636917
H	-4.215276	0.647291	2.639155
H	-4.269480	-2.107184	-1.636917
H	-4.215276	-0.647291	-2.639155
H	2.668208	-3.326890	-2.639155
H	3.959615	-2.643886	-1.636917
H	1.547067	-3.974181	2.639155
H	0.309865	-4.751070	1.636917

Table S7. *EEs* (eV) and oscillator strengths *f* for the 1s O excitation spectrum of **I** from spin-unrestricted SR ZORA TDDFT calculations.^{a,b}

Sym	EE	isos	fsos	<i>f</i> (x10 ³)	Peak
e	519.4	3e [↓] +3e [↑] +2a ₂ [↑] +3e [↑]	18a ₁ ⁽²²⁾ +19a ₁ ⁽¹⁹⁾ +31e ⁽¹⁷⁾ +31e ⁽¹⁷⁾	35.9	A
a ₂	519.4	3e [↑] +2a ₂ [↓] +2a ₂ [↑] +3e [↓]	31e ⁽³⁵⁾ +18a ₁ ⁽²³⁾ +19a ₁ ⁽¹⁹⁾ +30e ⁽¹⁸⁾	37.9	A
a ₂	520.3	2a ₂ [↓] +3e [↓]	18a ₁ ⁽⁴⁸⁾ +30e ⁽⁴³⁾	6.4	S
e	520.4	2a ₂ [↑] +2e [↑]	32e ⁽⁴⁶⁾ +32e ⁽³⁸⁾	5.3	S
a ₂	520.4	2e [↑] +3e [↑]	32e ⁽⁷²⁾ +32e ⁽²¹⁾	14.2	S
e	521.3	2e [↓] +2a ₂ [↓]	32e ⁽³⁴⁾ +32e ⁽³²⁾	5.3	B
a ₂	522.0	2a ₂ [↓] +2a ₂ [↓] +2a ₂ [↓]	22a ₁ ⁽⁵⁰⁾ +20a ₁ ⁽¹⁵⁾ +21a ₁ ⁽¹⁵⁾	5.4	B
a ₂	522.1	2e [↓] +3e [↓] +2e [↓]	37e ⁽³¹⁾ +37e ⁽²⁵⁾ +38e ⁽¹¹⁾	7.6	B

^a Only excitations up to *EE* 523 eV and contributions > 10% are reported. *EEs* herein reported have been shifted in Fig. 9 by 12.2 eV. ^b Only transitions having $f \times 10^3 > 5$ are reported.

Table S8. *EEs* (eV) and oscillator strengths *f* for the 1s O excitation spectrum of **II** from spin-unrestricted SR ZORA TDDFT calculations.^{a,b}

Sym	EE	isos	Fsos	<i>f</i> (x10 ³)	Peak
a	518.4	9a [↑]	95a ⁽⁹⁸⁾	4.6	A
a	518.5	8a [↑]	95a ⁽⁹⁸⁾	4.6	A
a	518.5	11a [↑]	95a ⁽⁷⁸⁾	4.5	A
a	518.8	7a [↑]	95a ⁽⁹⁸⁾	4.7	A
a	518.8	6a [↑]	95a ⁽⁹⁸⁾	4.5	A
a	518.9	10a [↑] +10a [↓] +10a [↓]	97a ⁽⁶⁰⁾ +92a ⁽¹²⁾ +91a ⁽¹⁰⁾	18.6	A
a	519.0	11a [↑] +11a [↑]	98a ⁽⁵⁷⁾ +95a ⁽¹²⁾	14.7	A
a	519.4	7a [↑] +7a [↓]	96a ⁽⁵⁶⁾ +91a ⁽³⁵⁾	16.0	S
a	519.4	6a [↑] +6a [↓]	96a ⁽⁵⁶⁾ +91a ⁽³⁵⁾	16.6	S
a	519.6	9a [↑] +9a [↓] +9a [↓]	98a ⁽⁴⁷⁾ +91a ⁽²⁴⁾ +92a ⁽¹³⁾	10.7	S
a	519.6	8a [↑] +8a [↓] +8a [↓]	97a ⁽⁴⁶⁾ +91a ⁽²³⁾ +92a ⁽¹⁸⁾	10.5	S
a	519.9	9a [↓] +9a [↓]	91a ⁽⁴³⁾ +93a ⁽³⁹⁾	3.8	S
a	519.9	8a [↓] +8a [↓]	91a ⁽⁴⁸⁾ +93a ⁽²⁸⁾	3.4	S
a	520.1	8a [↓] +8a [↓] +8a [↓] +8a [↓]	92a ⁽⁵⁰⁾ +93a ⁽¹⁹⁾ +95a ⁽¹³⁾ +94a ⁽¹²⁾	3.5	S
a	520.6	8a [↓] +8a [↓]	94a ⁽⁷⁰⁾ +93a ⁽¹¹⁾	3.2	B
a	521.2	9a [↓] +9a [↓] +9a [↓]	101a ⁽⁴⁷⁾ +103a ⁽²⁹⁾ +104a ⁽¹²⁾	3.5	B

^a Only excitations up to *EE* 523 eV and contributions > 10% are reported. *EEs* herein reported have been shifted in Fig. 10 by 12.6 eV. ^b Only transitions having $f \times 10^3 > 3$ and contributions to the TCRFS/SRFS $\geq 1\%$ are reported.

Table S9. *EEs* (eV) and oscillator strengths *f* for the 1s O excitation spectrum of **III** from spin-unrestricted SR ZORA TDDFT calculations.^{a,b}

Sym	EE	isos	fsos	<i>f</i> (x10 ³)	Peak
e	518.45	3e [↓] +2e [↓]	18a ₁ ⁽⁴⁴⁾ +18a ₁ ⁽³⁷⁾	3.8	S
a ₂	518.56	3e [↓] +2e [↓] +2a ₂ [↓]	30e ⁽⁴⁸⁾ +30e ⁽²⁴⁾ +18a ₁ ⁽¹³⁾	6.4	S
e	519.14	2e [↑] +2a ₂ [↑] +3e [↑]	32e ⁽¹⁸⁾ +32e ⁽¹⁷⁾ +19a ₁ ⁽¹⁷⁾	5.5	A
a ₂	519.14	2e [↑] +2a ₂ [↑] +3e [↑]	32e ⁽²³⁾ +19a ₁ ⁽²²⁾ +32e ⁽¹⁷⁾	5.6	A
e	519.58	3e [↓] +2a ₂ [↓] +2a ₂ [↑]	19a ₁ ⁽¹⁹⁾ +32e ⁽¹⁸⁾ +32e ⁽¹³⁾	33.4	A
a ₂	519.58	3e [↓] +2a ₂ [↓]	32e ⁽³³⁾ +19a ₁ ⁽²⁰⁾	34.9	A
e	519.74	2a ₂ [↓] +3e [↓]	31e ⁽⁴³⁾ +31e ⁽³⁶⁾	4.9	A
a ₂	519.74	3e [↓] +2e [↓]	31e ⁽⁵⁰⁾ +31e ⁽³⁷⁾	11.0	A

^a Only excitations up to *EE* 523 eV and contributions > 10% are reported. *EEs* herein reported have been shifted in Fig. 11 by 12.2 eV. ^bOnly transitions having $f \times 10^3 > 3$ are reported. All excitations associated to states hidden under the B peak have $f \times 10^3 < 2$.