ELECTRONIC SUPPLEMENTARY INFORMATION

Origin of the complex main and satellite features in Fe 2p XPS of Fe_2O_3

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I. Details of the Calculation and Plotting of XPS Intensities

How the XPS intensities and BEs are calculated and broadened in order to be able to make direct comparisons with experiment is reviewed briefly with references where further details are given. The relative XPS intensities, I_{rel}, for ionization of a particular orbital to one of the final states is given by the Sudden Approximation, SA. [1-2] where suitable sums over initial states final states are made; for details of the application to XPS see, for example, Refs. [3-5]. For the plots presented in the main text, a sum of the I_{rel} over states in a very narrow energy range, δBE=0.02 eV, is used. These intensities are normalized to a convenient value whose choice is explained when the intensities are discussed. Another concern is to sum the total intensities over a manifold of states to show the intensity in a given region or to show the magnitude of the total XPS intensity recovered with a given set of wavefunctions, WFs. For the initial states, a sum, rather than the rigorous average, is made over the Boltzmann weighted occupations of low lying excited states at room temperature. [6] Since, the normalization of the relative SA intensities is arbitrary and only the different values of I_{rel} for different shells and different final ionized states is important, summation over initial states rather than averaging over them makes no difference to these relative values.

For the plots of the theoretical XPS intensity, a Voigt convolution of a Gaussian and a Lorentzian broadening. [7] is used to broaden the calculated intensities. A dual broadening is used with different Lorentzian FWHM for the region around the lower BE(rel) XPS features and the higher BE(rel) features; this is to take into account the shorter lifetime of $2p_{1/2}$ ions than $2p_{3/2}$ ions. Starting estimates for the Lorentzian FWHM are taken from the tabulation of core excited lifetimes of Campbell and Papp.[8] and for the Gaussian FWHM from expectations for the experimental resolution. These initial estimates of the lifetimes may be modified to obtain an improved fit between the XPS predicted from our theory and experiment. The choice for the Gaussian FWHM is 1.2 eV and for the Lorentzian FWHM, it is 0.41 in the lower BE(rel) region and 1.14 eV in the higher BE(rel) region where the change is at BE(rel)=8.0 eV; further information is given in Ref. [5]. When theory and experiment are compared, there is a rigid shift to align theory and experiment and the experimental and broadened theoretical intensities are scaled so that the maxima of each have the same value; no other adjustments are made. The scaling so that the theoretical and experimental intensities are the same at the BE with maximum intensity places an emphasis on the accuracy of the calculation at this BE and may exaggerate uncertainties or errors in other regions. Thus, it should be viewed as a way to compare the theoretical and experimental intensities rather than establishing absolute accuracies of the intensities at different BEs.

II. Convergence of Cluster WFs

The calculations of the orbitals used for the core ionic states are chosen using an overlap criterion to select the orbitals to be occupied rather than an aufbau selection of the lowest energy orbitals. The selected orbitals, which are solutions at a given self-consistent field, SCF, iteration, of the Dirac-Fock operator are those which have the largest overlap with the orbitals used to construct the Fock operator. The approach, described in more detail in the review of Bagus *et al.* [3], has been used since the very early days of the calculation of orbitals and WFs of core-excited states; see, for example, Refs. [4, 9-10] For the configuration interaction, CI, WFs of the core-ionized states, as described in the main text, only determinants with a hole in the core-level as used in the expansion of the CI WFs; thus, variational collapse is not possible.

For the calculation of the orbitals, a very tight SCF convergence threshold was used. The convergence was on the gradient of the norm of the error vector [11] which was required to be less than $5x10^{-8}$. there was no difficulty to achieve this convergence.

III. Intensity Summations

In Table SI, we examine the limitations of considering only the XPS SA intensity obtained by summing only the contributions of states with I>0.0001 compared to the intensity by summing over all states. The normalization for the SA intensity is the same as used in Table II of the main text. As shown in Table SI, summing the XPS intensity over states with this threshold gives essentially 100% of the total intensity.

IV. Composition of States in the Different Regions

In this section, we supplement the information in Sec. V of the main text and provide tables with quantitative information on the properties of states in the four regions in Tables SII to SV. For each group, properties of the states in the group are shown graphically in Figs. S1 to S4. The properties and the presentation in these tables and figures follows that in the main text. In the tables, these group intensities, denoted I_{Norm}, are normalized so that I_{Norm}=1.0 for the most intense group in that region. This normalization is used to clearly show whether there is a single main peak in the region or whether the intensity is distributed over several groups with comparable intensities. However, in the tables we also give, for the most intense group, in parenthesis after I_{Norm}=1 the absolute intensity with the same normalization as in the figures, Figs. S1 to S4, and Fig. 4 in the main text. In the tables, the properties are only given for the six most intense groups in the region while for Figs. S1 to S4, they are given for all groups where states are present. For the 6 groups listed in the tables, we also give, labelled Fraction Total I, the percent of the total XPS intensity of these groups of the total XPS SA intensity in this region as given in Tables III and IV of the main text. This provides a direct measure of how much the intensity is distributed into the groups with low intensity not shown in the tables. In the following, additional information to that given in the main text is made for each of the regions; to ensure that the SI can be read without repeated reference to the main text, a small portion of the descriptions in the main text will be repeated here.

Region 1, $0 \leq BE(rel) < 6.0$ eV

For the SO WFs, almost all the intensity in this region, over 96%, is in the 6 groups in Table SII and most of the intensity is in two groups separated by 1.0 eV which is consistent with the doublet observed in the Fe 2p XPS of Fe_2O_3; see Fig. 1. For the CI14 WFs, the largest intensity is still for the first group with $0 \leq BE(rel) < 0.5$ eV but the remaining intensity is distributed over more groups than for the SO WFs. and the total XPS intensity recovered by these 6 groups is a somewhat smaller fraction, 86%, of the total intensity in this region. For the six groups with the largest intensity, see Table SII, Occ(Shake) goes from a minimum of 0.16 electrons for the most intense group at $0 \leq BE(rel) < 0.5$eV to a maximum of 0.36 electrons for the least intense group at 3.5≤BE(rel)<4.0eV. However, the XPS intensity of this latter group is small, only 13% of the intensity of the group with the largest intensity, see Fig. 4 of the main text. The groups for 4.0≤BE(rel)<6.0eV have somewhat larger values of Occ(Shake) between 0.6 and 0.7 but the intensity carried by these groups is a small fraction, 8%, of the total intensity in this region.

Region 2, 6.0≤BE(rel)<12.0 eV

Most of the intensity in this region is in five groups as shown by the bars in Fig. S2 at group energies of 9.5 and 10.5 to 12.0 eV. In these regions, the Occ(Shake) is between 0.85 and 0.87, Table SIII.

Region 3, 12.0≤BE(rel)<18.0 eV

The properties of the states in Region 3 are presented in Fig. S3 and Table SIV. For the SO WFs, the group at 15.5≤BE(rel)<16.0 eV, which has almost the maximum SA intensity, the Occ($2p_{1/2}$) is 1.3 while for the group with the highest SA intensity, at 14.0≤BE(rel)<14.5 eV, the Occ($2p_{1/2}$) is 1.6. For the CI14 WFs, 80% of the intensity is distributed almost uniformly over the six groups from 13.5≤BE(rel)<16.5eV. The involvement of configurations with 2p occupations of $(2p_{1/2})^2(2p_{3/2})^3$ is rather large as can be seen from Fig. S3 and Table SIV where the smallest Occ($2p_{1/2}$) is 1.8 and the largest Occ($2p_{3/2}$) is 3.2. These values are very far from those expected for WFs dominated by configurations with $(2p_{1/2})^1(2p_{3/2})^4$

Region 4, 18.0≤BE(rel)<26.0 eV

The characteristics of the states in this region are given in Fig. S4 and Table SV.

Table SI. Summations of SA intensities for states with individual SA intensity I>0.0001, as I_{rel}, as well as percent of the total for summations over all ionic states. These sums are given for SO and CI14 final state WFs; see text.

	SO		CI14	
	Sum for I>0.0001	% of Total I_{rel}[a]	Sum for I>0.0001	% of Total I_{rel}[a]
$I_{rel}(2p_{1/2})$	7.19	100.0	10.51	99.5%
$I_{rel}(2p_{3/2})$	14.38	100.0	21.11	99.9%
$I_{rel}(2p)$	21.58	100.0	31.63	99.8%

[a]Total I_{rel} as given in Table II of the main text for the SO and CI14 WFs

Table SII. Properties of groups of states in a BE range of 0.5 eV for the SO and the CI14 final state WFs in the first Region with 0.0≤BE(rel)<6.0 eV. The properties are the sum of the intensities and the intensity weighted average occupations of the Fe $2p_{1/2}$ and $2p_{3/2}$ shells, Occ($2p_{1/2}$) and Occ($2p_{3/2}$). In addition, for the CI14 WFs, the shake occupation, Occ(Shake), is also given. The properties of the 6 groups with the largest intensity are listed. The intensity, I_{Norm}, is normalized to 1 for the most intense group and the I_{rel} with the normalization used in Tables II to IV is given as I(Absolute) for the group with I_{Norm}=1.0. The fraction of the total I_{rel} in this range is given. See text.

BE(Groups)-eV	I_{Norm}(Absolute)	Occ($2p_{1/2}$)	Occ($2p_{3/2}$)	Occ(Shake)
		SO WFs		
$0.0 \le BE_{rel} < 0.5$	1.00(5.39)	2.00	3.00	-------
$1.0 \le BE_{rel} < 1.5$	0.70	1.98	3.02	-------
$2.0 \le BE_{rel} < 2.5$	0.38	1.98	3.02	-------
$2.5 \le BE_{rel} < 3.0$	0.16	1.99	3.01	-------
$3.0 \le BE_{rel} < 3.5$	0.04	2.00	3.00	-------
$5.5 \le BE_{rel} < 6.0$	0.07	1.99	3.01	-------
Fraction Total I	96.1%	-------	-------	-------
		CI14 WFs		
$0.0 \le BE_{rel} < 0.5$	1.00(5.43)	2.00	3.00	0.16
$0.5 \le BE_{rel} < 1.0$	0.27	1.99	3.01	0.26
$1.0 \le BE_{rel} < 1.5$	0.29	1.99	3.01	0.27
$2.0 \le BE_{rel} < 2.5$	0.28	1.99	3.01	0.27
$2.5 \le BE_{rel} < 3.0$	0.16	1.99	3.01	0.28
$3.5 \le BE_{rel} < 4.0$	0.13	1.99	3.01	0.36
Fraction Total I	86.0%	-------	-------	-------

Table SIII. Properties of groups of states in a BE range of 0.5 eV for the SO and the CI14 final state WFs in the second region with 6.0≤BE(rel)<12.0 eV. See the text and the caption to Table VI.

BE(Groups)-eV	I_{Norm}(Absolute)	Occ($2p_{1/2}$)	Occ($2p_{3/2}$)	Occ(Shake)
		SO WFs		
$6.0 \le BE_{rel} < 6.5$	0.81	1.99	3.01	-------
$6.5 \le BE_{rel} < 7.0$	0.99	1.99	3.01	-------
$7.0 \le BE_{rel} < 7.5$	1.00(0.33)	1.99	3.01	-------
$7.5 \le BE_{rel} < 8.0$	0.44	1.98	3.02	-------
$9.0 \le BE_{rel} < 9.5$	0.32	1.98	3.02	-------
$9.5 \le BE_{rel} < 10.0$	0.39	1.98	3.02	-------
Fraction Total I	80.2%	-------	-------	-------
		CI14 WFs		
$7.0 \le BE_{rel} < 7.5$	0.17	1.98	3.02	0.73
$9.0 \le BE_{rel} < 9.5$	1.00(2.27)	1.99	3.01	0.87
$10.0 \le BE_{rel} < 10.5$	0.37	1.98	3.02	0.86
$10.5 \le BE_{rel} < 11.0$	0.33	1.98	3.02	0.86
$11.0 \le BE_{rel} < 11.5$	0.28	1.97	3.03	0.86
$11.5 \le BE_{rel} < 12.0$	0.24	1.97	3.03	0.85
Fraction Total I	81.7%	-------	-------	-------

Table SIV. Properties of groups of states in a BE range of 0.5 eV for the SO and the CI14 final state WFs in the third region with 12.0≤BE(rel)<18.0 eV. See the text and the caption to Table VI.

BE(Groups)-eV	I_{Norm}(Absolute)	Occ($2p_{1/2}$)	Occ($2p_{3/2}$)	Occ(Shake)
		SO WFs		
$13.0 \leq BE_{rel} < 13.5$	0.07	1.94	3.06	-------
$13.5 \leq BE_{rel} < 14.0$	0.16	1.91	3.09	-------
$14.0 \leq BE_{rel} < 14.5$	1.00(2.21)	1.56	3.44	-------
$15.0 \leq BE_{rel} < 15.5$	0.39	1.64	3.36	-------
$15.5 \leq BE_{rel} < 16.0$	0.98	1.30	3.70	-------
$16.0 \leq BE_{rel} < 16.5$	0.06	1.52	3.48	-------
Fraction Total I	94.6%	-------	-------	-------
		CI14 WFs		
$13.5 \leq BE_{rel} < 14.0$	0.76	1.94	3.06	0.88
$14.0 \leq BE_{rel} < 14.5$	1.00(1.31)	1.93	3.07	0.88
$14.5 \leq BE_{rel} < 15.0$	0.60	1.90	3.10	0.83
$15.0 \leq BE_{rel} < 15.5$	0.62	1.82	3.13	0.81
$15.5 \leq BE_{rel} < 16.0$	0.79	1.85	3.15	0.78
$16.0 \leq BE_{rel} < 16.5$	0.75	1.81	3.19	0.75
Fraction Total I	80.1%	-------	-------	-------

Table SV. Properties of groups of states in a BE range of 0.5 eV for the SO and the CI14 final state WFs in the fourth region with 18.0≤BE(rel)<26.0 eV. See the text and the caption to Table VI.

BE(Groups)-eV	I_{Norm}(Absolute)	Occ($2p_{1/2}$)	Occ($2p_{3/2}$)	Occ(Shake)
		SO WFs		
$18.0 \le BE_{rel} < 18.5$	0.85	1.13	3.87	-------
$18.5 \le BE_{rel} < 19.0$	1.00(0.15)	1.12	3.88	-------
$19.0 \le BE_{rel} < 19.5$	0.91	1.14	3.86	-------
$19.5 \le BE_{rel} < 20.0$	0.32	1.05	3.95	-------
$20.0 \le BE_{rel} < 20.5$	0.15	1.10	3.90	-------
$21.5 \le BE_{rel} < 22.0$	0.12	1.04	3.96	-------
Fraction Total I	91.5%	-------	-------	-------
		CI14 WFs		
$18.0 \le BE_{rel} < 18.5$	0.22	1.67	3.33	0.91
$23.0 \le BE_{rel} < 23.5$	0.94	1.61	3.40	1.48
$23.5 \le BE_{rel} < 24.0$	0.32	1.64	3.36	1.53
$24.0 \le BE_{rel} < 24.5$	0.27	1.65	3.35	1.57
$24.5 \le BE_{rel} < 25.0$	1.00(0.82)	1.60	3.40	1.50
$25.0 \le BE_{rel} < 25.5$	0.41	1.64	3.36	1.55
Fraction Total I	70.1%	-------	-------	-------

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Figure Captions

Fig. S1. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 1, 0≤BE(rel)<6.0, for (a) SO WFs and (b)CI14 WFs. The properties are intensity, vertical bars, and $2p_{1/2}$, $2p_{3/2}$, and Shake occupations shown as points; see legend.

Fig. S2. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 2, 6.0≤BE(rel)<12.0, for (a) SO WFs and (b)CI14 WFs; see caption to Fig. 5.

Fig. S3. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 3, 12.0≤BE(rel)<18.0, for (a) SO WFs and (b)CI14 WFs; see caption to Fig. 5.

Fig. S4. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 4, 18.0≤BE(rel)<26.0, for (a) SO WFs and (b)CI14 WFs; see caption to Fig. 5.

Fig. S1. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 1, 0≤BE(rel)<6.0, for (a) SO WFs and (b)CI14 WFs. The properties are intensity, vertical bars, and $2p_{1/2}$, $2p_{3/2}$, and Shake occupations shown as points; see legend.

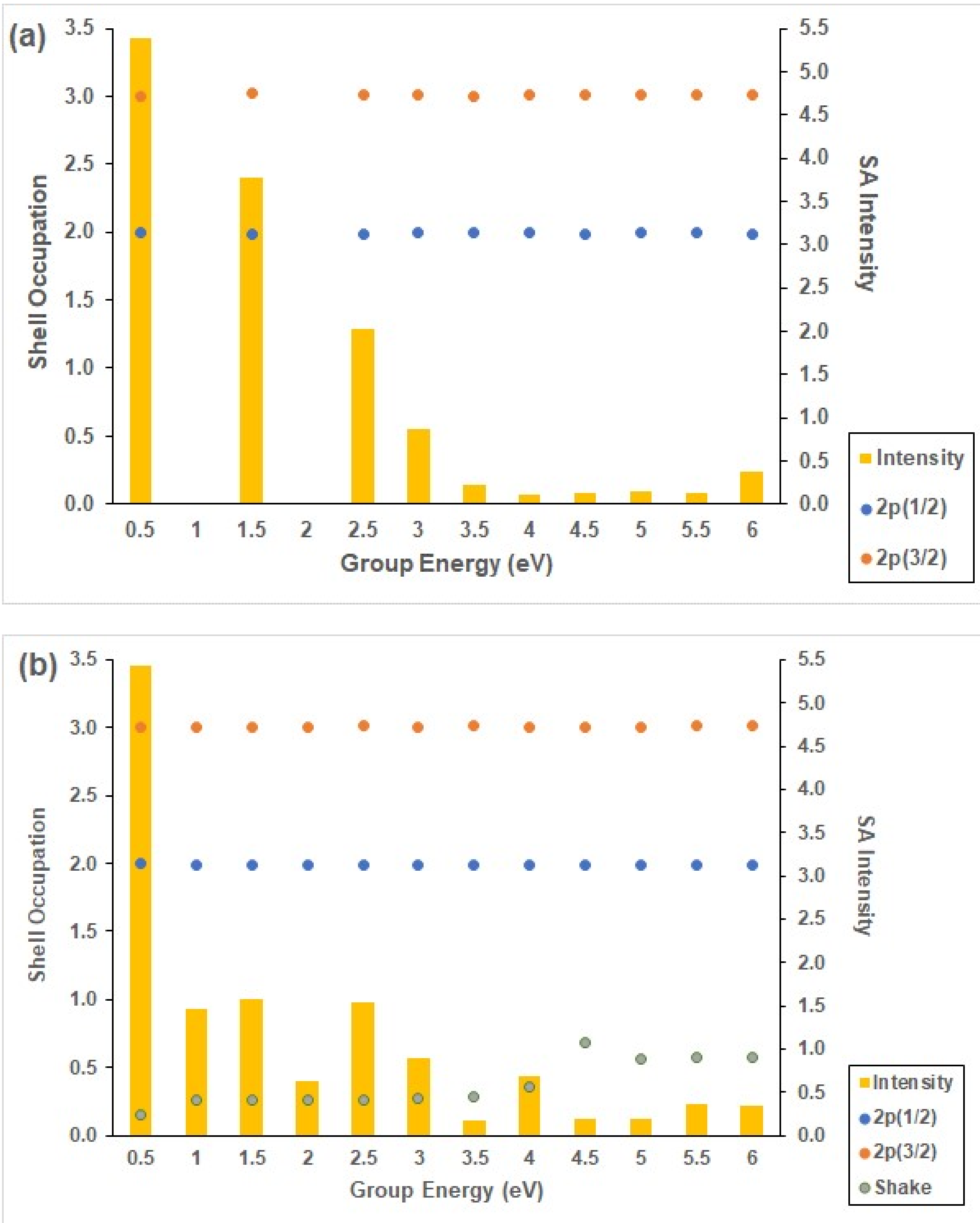
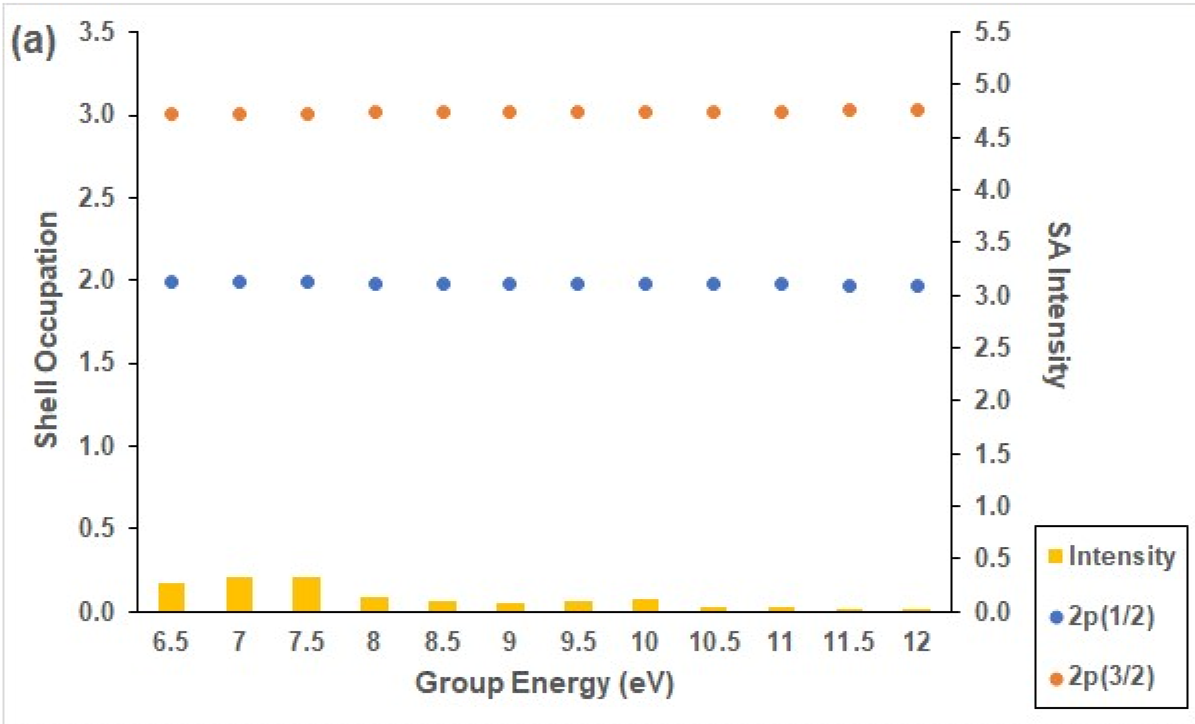


Fig. S2. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 2, 6.0≤BE(rel)<12.0, for (a) SO WFs and (b)CI14 WFs; see caption to Fig. 5.



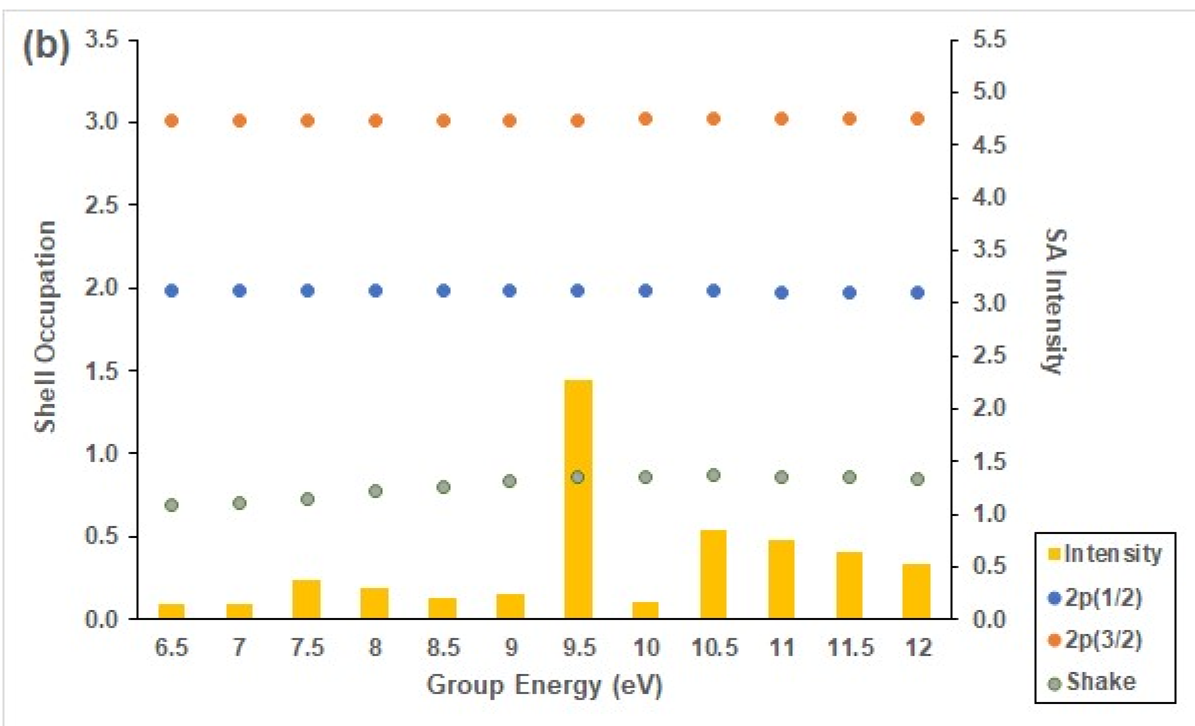


Fig. S3. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 3, 12.0≤BE(rel)<18.0, for (a) SO WFs and (b)CI14 WFs; see caption to Fig. 5.

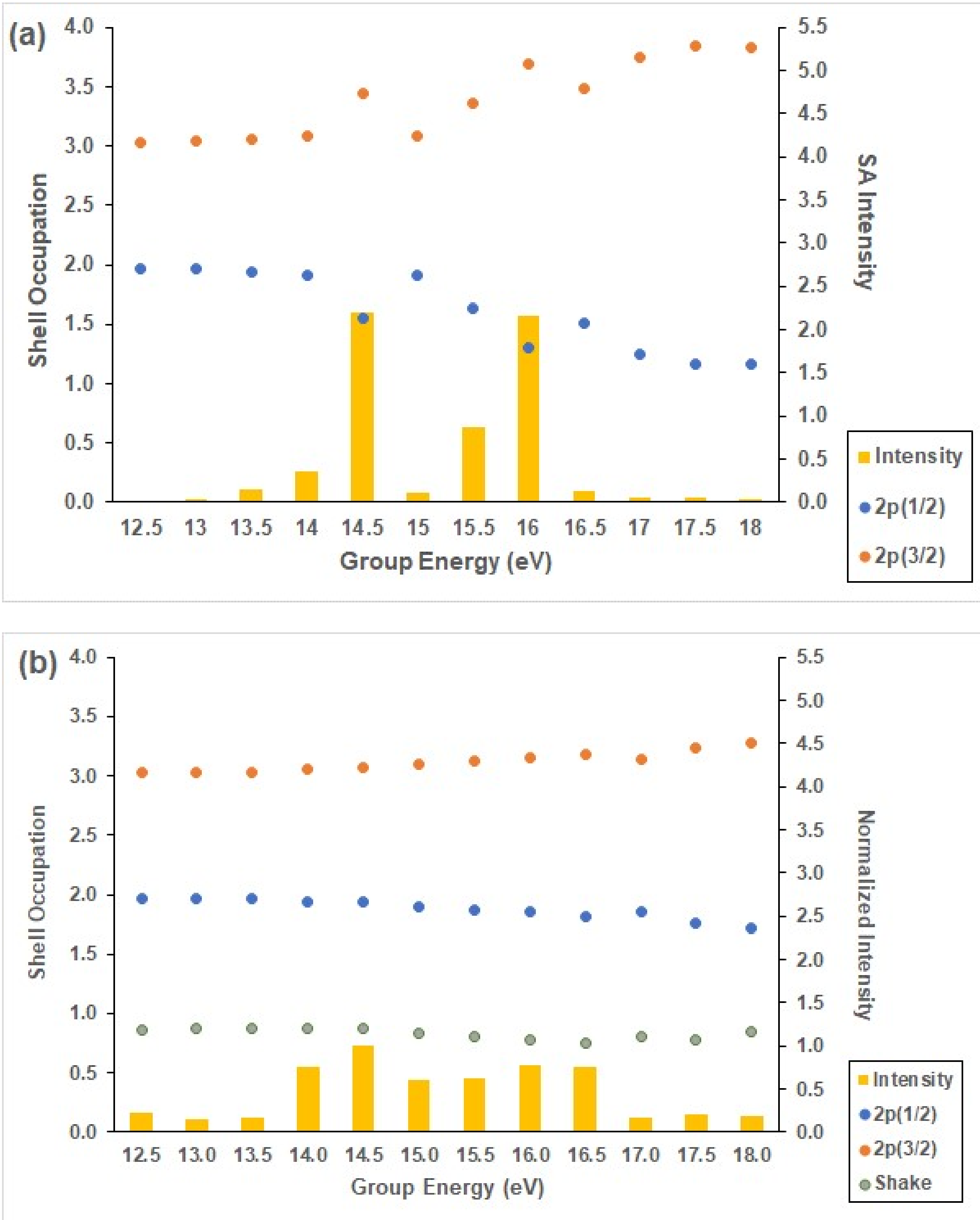


Fig. S4. Plots of the properties of groups of states in BE ranges of 0.5 eV for states in Region 4, 18.0≤BE(rel)<26.0, for (a) SO WFs and (b)CI14 WFs; see caption to Fig. 5.