Chemical State Analysis of Phosphorus Performed by X-ray Emission Spectroscopy

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The results of the Mulliken analysis yielding atomic character for each of the separate molecular orbitals used to build the model Kβ emission spectra presented in the paper (Figures 3-5). Tabulated values were used also to calculate the average atomic character of the main spectral components presented in the paper (Tables 2 and 3).

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Table 1: Atomic orbital contributions to the molecular orbitals in PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{1-}$ and H_3PO_4 used to build the model spectra. The $1t_1$ and $4a_1$ orbitals are omitted since they do not participate in the transition.

MO		AO orbital population [%]						AO orbital population [%]					
		P3s	P3p	P3d	O2s	O2p	H1s	P3s	P3p	P3d	O2s	O2p	H1s
		PO_4^{3-}						HPO_4^{2-}					
1	$3t_2$	-	7	2	87	4	-	1	4	-	85	10	-
2	$3t_2$	-	7	2	87	4	-	-	9	1	85	4	-
3	$3t_2$	-	7	2	87	4	-	-	9	2	85	4	-
4	$5a_1$	26	-	-	26	47	-	10	9	1	10	53	17
5	$4t_2$	-	21	-	7	72	-	16	7	-	21	52	4
6	$4t_2$	-	21	-	7	72	-	-	20	-	10	70	-
7	$4t_2$	-	21	-	7	72	-	-	20	-	10	70	-
8	1e	-	-	4	-	96	-	-	-	2	-	97	1
9	1e	-	-	4	-	96	-	-	-	2	-	97	1
10	$5t_2$	-	2	5	-	93	-	-	18	2	-	75	5
11	$5t_2$	-	2	5	-	93	-	-	6	6	-	88	0
12	$5t_2$	-	2	5	-	93	-	-	6	6	-	88	0
		$H_2PO_4^{1-}$						H_3PO_4					
1		-	4	1	87	7	1	-	5	1	87	6	1
2		5	5	2	79	7	1	-	5	1	87	5	1
3		-	10	2	83	4	-	3	7	1	81	6	1
4		13	7	-	6	58	15	18	3	-	6	59	13
5		-	10	1	1	68	18	-	12	2	-	67	18
6		14	2	-	23	53	6	-	12	2	-	67	18
7		-	16	-	11	62	8	11	8	-	21	54	4
8		-	18	-	10	70	-	-	15	-	12	65	5
9		1	11	1	9	76	-	-	15	-	12	65	5
10		-	-	3	-	94	2	-	10	2	8	78	1
11		-	5	3	-	90	-	-	4	4	1	90	-
12		-	13	5	-	81	-	-	4	4	1	90	-

Table 2: Atomic orbital contributions to the molecular orbitals used to build the K_3PO_4 model spectra. Besides atomic character calculated energies and intensities corresponding to electronic transition to 1s atomic orbital are also given. An overall shift of absolute calculated energies by -3.61 eV used to match experimental energies is already applied in the tabulated energies.

Spectroscopic label	Energy [eV]	Intensity %	AO orbital population [%]						
			P 3s	P 3p	P 3d	O 2s	O 2p	K 3s	K 3p
	2123.810	0.198	0	4	1	83	2	0	9
$K\beta'$	2124.243	0.404	0	8	2	77	4	0	9
	2124.983	0.403	0	8	2	77	3	0	9
$K\beta_x$	2135.956	0.028	27	1	0	26	44	0	0
	2138.254	1.000	0	24	0	6	68	0	0
$K\beta_{1,3}$	2138.142	0.998	0	24	0	11	62	0	0
	2137.653	0.997	0	24	0	12	63	0	0
$K\beta''$	2140.478	0.031	0	1	3	0	90	4	1
	2139.154	0.032	0	1	3	0	90	4	0

Table 3: Atomic orbital contributions to the molecular orbitals used to build the Na_2HPO_4 model spectra. An overall shift of absolute calculated energies by -4.35 eV is already applied.

Spectroscopic label	Energy [eV]	Intensity %	AO orbital population [%] P 3s	P 3p	P 3d	O 2s	O 2p	Na2s/2p	H 1s
	2123.406	0.179	4	3	1	82	6	1	1
$K\beta'$	2121.037	0.473	0	8	1	84	4	1	0
	2123.793	0.434	0	7	1	86	4	0	0
$K\beta_x$	2133.264	0.274	15	6	0	10	55	0	13
	2136.485	0.316	13	6	0	19	54	0	6
	2137.596	1.000	0	23	0	9	65	1	1
$K\beta_{1,3}$	2138.045	0.949	0	22	0	12	63	1	0
	2138.709	0.578	0	13	1	9	71	0	3
	2139.798	0.043	0	1	4	0	90	4	0
$K\beta''$	2139.936	0.032	0	8	4	0	83	3	0
	2140.427	0.033	0	7	4	0	84	2	0

Table 4: Atomic orbital contributions to the molecular orbitals used to build the NaH_2PO_4 model spectra. An overall shift of absolute calculated energies by -4.38 eV is already applied.

Spectroscopic label	Energy [eV]	Intensity %	AO orbital population [%] P 3s	P 3p	P 3d	O 2s	O 2p	H 1s
	2122.114	0.194	0	3	1	88	4	3
$K\beta'$	2123.599	0.316	5	5	0	79	7	1
	2123.632	0.851	0	8	1	84	5	0
	2132.904	0.388	16	6	0	9	57	11
$K\beta_x$	2134.686	0.688	0	11	1	1	70	15
	2136.530	0.200	9	7	0	17	60	6
	2137.602	1.000	2	18	0	9	67	2
$K\beta_{1,3}$	2138.073	0.880	0	16	0	11	68	2
	2139.168	0.816	0	11	1	9	76	2
$K\beta''$	2139.638	0.331	0	5	1	4	89	0

Table 5: Atomic orbital contributions to the molecular orbitals used to build the KH_2PO_4 model spectra. An overall shift of absolute calculated energies by -3.77 eV is already applied.

Spectroscopic label	Energy [eV]	Intensity %	AO orbital population [%] P 3s	P 3p	P 3d	O 2s	O 2p	H 1s
	2122.637	0.206	0	3	1	87	3	3
$K\beta'$	2124.128	0.326	4	5	0	79	7	1
	2122.626	0.879	0	8	1	82	6	0
	2133.733	0.402	16	6	0	9	56	11
$K\beta_x$	2135.323	0.748	0	11	1	1	68	16
	2137.139	0.197	9	6	0	18	59	6
	2138.189	1.000	2	18	0	9	67	1
$K\beta_{1,3}$	2138.631	0.962	0	17	0	11	67	2
	2139.797	0.998	0	11	1	9	74	2
	2140.176	0.214	0	3	2	3	90	1
$K\beta''$	2140.302	0.047	0	7	2	0	88	2
	2141.750	0.046	0	2	2	0	93	1

Table 6: Atomic orbital contributions to the molecular orbitals used to build the HPO_3^{2-} model spectra. An overall shift of absolute calculated energies by -3.89 eV is already applied.

Spectroscopic label	Energy [eV]	Intensity %	AO orbital population [%]					
			P $3s$	P $3p$	P $3d$	O $2s$	O $2p$	H $1s$
$K\beta'$	2124.644	0.430	0	9	2	85	4	0
	2123.886	0.428	0	9	2	85	4	0
$K\beta_x$	2134.500	0.240	30	7	0	20	22	19
$K\beta_{1,3}$	2137.394	0.983	3	30	0	5	44	16
	2138.261	1.000	0	20	0	10	69	0
	2137.903	0.998	0	20	0	10	69	0

Table 7: Atomic orbital contributions to the molecular orbitals used to build the $H_2PO_2^{1-}$ model spectra. An overall shift of absolute calculated energies by -3.36 eV is already applied.

Spectroscopic label	Energy [eV]	Intensity %	AO orbital population [%]					
			P $3s$	P $3p$	P $3d$	O $2s$	O $2p$	H $1s$
$K\beta'$	2124.557	0.393	0	12	0	81	4	0
$K\beta_x$	2133.455	0.249	40	10	0	15	6	27
$K\beta_{1,3}$	2137.125	1.000	0	44	0	0	18	37
	2138.096	0.696	3	26	0	10	52	8
	2138.722	0.742	0	18	0	14	67	0