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CORRECTION

View Article Online
View Journal | View Issue

Cite this: *Phys. Chem. Chem. Phys.*, 2020, **22**, 3744

Correction: Dyson orbitals within the fc-CVS-EOM-CCSD framework: theory and application to X-ray photoelectron spectroscopy of ground and excited states

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DOI: 10.1039/d0cp90012e

rsc.li/pccp

Correction for 'Dyson Orbitals within the fc-CVS-EOM-CCSD framework: theory and application to X-ray photoelectron spectroscopy of ground and excited states' by M. L. Vidal *et al.*, *Phys. Chem. Chem. Phys.*, 2020, DOI: 10.1039/C9CP03695D

An error was detected, and it is hereby corrected, in the computation of the photoelectron spectra obtained by ionizing core electrons of the two lowest excited states of uracil. A re-examination of the Hartree–Fock molecular orbitals in the 6-311(2+,+)G** (uncontracted) basis (which was used in the calculations) has revealed that the SCF procedure did not converge to the desired lowest triplet states of $n\pi^*$ and $\pi\pi^*$ characters, but instead found nRy and πRy solutions. While the character of the hole orbital in these states is the same as in the S_1 and S_2 states, the character of the particle orbital is different. Thus, the XPS reported in ref. 1 do not correspond to the XPS of the S_1 and S_2 excited states. This unfortunate problem occurred because of using a non-standard basis set (uncontracted), which affected the default guess in the SCF procedure. Because of the multiple diffuse functions present in the basis, the SCF calculation of the lowest triplet inadvertently converged to a Rydberg state instead of the valence state. This problem can be easily corrected by using molecular orbitals from the ground-state calculation together with the correct user-defined orbital occupation and the MOM algorithm.

The results of the calculations of the spectra with the correct orbital occupations are reported below. Fig. 1–3 show the amended spectra at the carbon, nitrogen, and oxygen K-edges, respectively. They replace Fig. 5–7 in the original article. Tables 1 and 2 summarize the raw data (ionization energies and squared Dyson orbital norms) for the S_1 and S_2 excited states, and amend the results in Tables 5 and 6 in the original article.

Below we present the amended discussion of the computed spectra. Importantly, the main conclusion of ref. 1 remains valid: The XPS spectroscopy on the oxygen edge can be used to distinguish different electronic states in uracil.

At all three edges, the XPS spectra of the two excited states are now found significantly closer to that of the ground state. In most cases, the binding energies of the core electrons are slightly red-shifted relative to the corresponding S_0 values, indicating a destabilization of the core electrons in the excited states.

At the C K-edge, see Fig. 1, the ordering of the A and B bands is reversed in the S_2 state, indicating the stabilization (higher binding energy) of the 1s electron of the C atom at position A and destabilization of the 1s electron of the C atom at position B.

At the N K-edge (*cf.* Fig. 2), the ordering of the A and B bands changes in the S_1 state, primarily due to a larger destabilization of the 1s core electron of the N atom at position B than for the one at position A.

The significant overlap of the C and N edge spectra corresponding to the two excited states makes them less attractive probes since no specific spectral signature region emerges.

At the oxygen K-edge, see Fig. 3, substantial differences between the spectra of the three states (ground state, S_1 and S_2) are found. In line with the localized nature of the $n\pi^*$ state (see Table 3 in ref. 1), the 1s electron of the oxygen in the A position is strongly stabilized in the S_1 state, *versus* a very modest destabilization of the one in B position, with a separation between the two IEs of 4–5 eV. This confirms our previous conclusion[1] that the oxygen K-edge region would be the most interesting edge for probing the excited-state dynamics of the S_1 state by UV-pump/XPS-probe spectroscopy.

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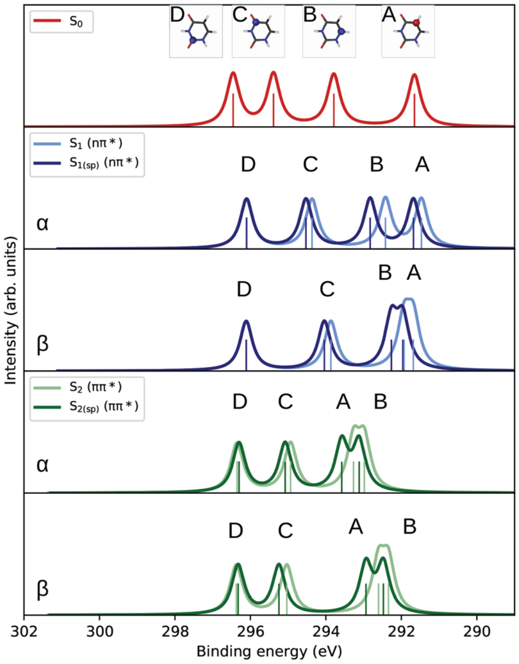

Fig. 1 Uracil. C K-edge fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted) X-ray photoelectron spectra of the ground state (S_0), first excited state (S_1, nπ*), and second excited state (S_2, ππ*) corresponding to the ejection of either an α or a β electron, obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV).

Table 1 Uracil. Ionization energies (IE, eV) and squared norms of Dyson orbitals for the first excited state (S_1). The results are reported at the Franck–Condon geometry (no label) and at state-specific zero-gradient, stationary point (label sp) geometry

	S_1				$S_{1(sp)}$			
	IE		$\lVert\phi^{\text{Dyson}}\rVert^2$		IE		$\lVert\phi^{\text{Dyson}}\rVert^2$	
K-edge	α	β	α	β	α	β	α	β
Carbon	291.47	291.68	0.876	0.882	291.68	291.96	0.878	0.883
	292.42	291.93	0.884	0.883	292.83	292.26	0.881	0.882
	294.37	293.87	0.879	0.877	294.53	294.04	0.877	0.875
	296.10	296.11	0.885	0.885	296.10	296.11	0.885	0.885
Nitrogen	407.15	407.08	0.880	0.881	407.34	407.28	0.879	0.880
	407.63	407.48	0.877	0.879	407.59	407.48	0.877	0.879
Oxygen	538.88	538.86	0.880	0.880	538.82	538.81	0.881	0.880
	544.00	542.82	0.878	0.890	544.04	542.75	0.876	0.886

Table 2 Uracil. Ionization energies (IE, eV) and squared norms of the second excited state (S_2). The results are reported at the Franck–Condon geometry (no label) and at state-specific zero-gradient, stationary point (label sp) geometry

	S_2				$S_{2(sp)}$			
	IE		$\lVert\phi^{\text{Dyson}}\rVert^2$		IE		$\lVert\phi^{\text{Dyson}}\rVert^2$	
K-edge	α	β	α	β	α	β	α	β
Carbon	292.98	292.34	0.883	0.886	293.12	292.48	0.878	0.881
	293.27	292.60	0.879	0.883	293.58	292.94	0.870	0.875
	294.94	295.04	0.879	0.880	295.08	295.24	0.872	0.875
	296.35	296.37	0.883	0.883	296.30	296.32	0.882	0.881
Nitrogen	407.28	407.27	0.880	0.881	407.45	407.44	0.878	0.879
	408.13	407.99	0.870	0.874	407.82	407.66	0.870	0.873
Oxygen	539.32	539.27	0.877	0.878	539.11	539.11	0.878	0.877
	539.57	539.29	0.882	0.885	539.64	539.64	0.888	0.888

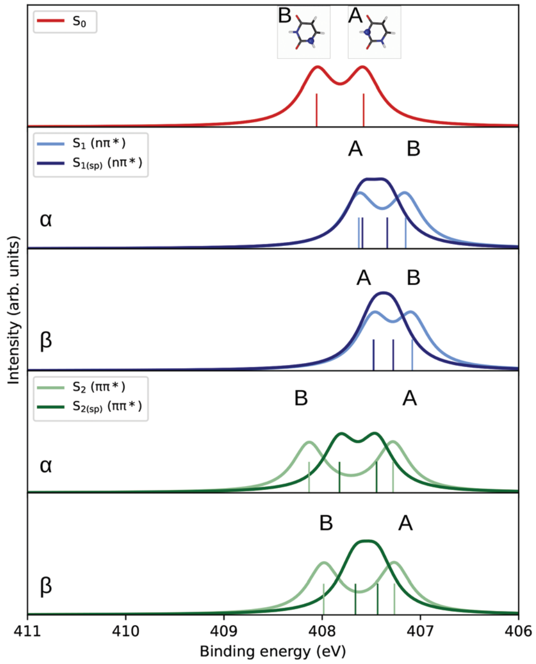

Fig. 2 Uracil. N K-edge fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted) X-ray photoelectron spectra of the ground state (S_0), first excited state (S_1, nπ*), and second excited state (S_2, ππ*) corresponding to the ejection of either an α or a β electron, obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV).

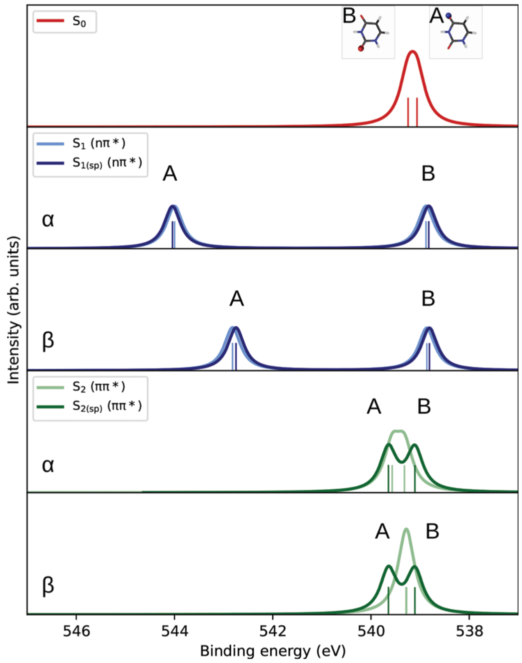

Fig. 3 Uracil. O K-edge fc-CVS-EOM-CCSD/6-311(2+,+)G** (uncontracted) X-ray photoelectron spectra of the ground state (S_0), first excited state (S_1), and second excited state (S_2) corresponding to the ejection of either an α or a β electron, obtained by convolution of the computed ionization energies and Dyson norms with a Lorentzian function (FWHM = 0.4 eV).

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers

Conflicts of interest

The authors declare the following competing financial interest(s): A. I. K. is a part owner and a board member of Q-Chem, Inc.

Acknowledgements

We are indebted to Dr Shota Tsuru for bringing our attention to the erroneous orbital guess in the MOM calculations using the 6-311(2+,+)G** (uncontracted) basis set. M. L. V. and S. C. acknowledge support from DTU Chemistry (start-up PhD grant). S. C. acknowledges support from the Independent Research Fund Denmark – DFF-RP2 grant no. 7014-00258B and from the H2020-MSCA-ITN-2017 training network ''COSINE – COmputational Spectroscopy In Natural sciences and Engineering''. A. I. K. acknowledges support by the U.S. National Science Foundation (No. CHE-1566428) and by the Simons Foundation.

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