Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for Publication:

Tuning the Photodynamics of Sub-nanometer Neutral Chromium Oxide Clusters Through Sequential Oxidation

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The ground state geometries of chromium oxide clusters were optimized at the density functional theory (DFT) level within the Gaussian16[1] software suite using the GGA functional uBPW91 with the standard 6-311G+ (3d) basis set. The electron density distribution of the cluster was calculated using a C squared population analysis (CSPA) for both the ground state and excited states of the cluster. The contribution of the a-th atomic orbital to the i-th molecular orbital is written in terms of the molecular orbital coefficients, normalized to the square of all atomic orbital coefficients, k, as:

$$\Phi_{ai} = \frac{c_{ai}^2}{\sum_k c_{ki}^2}$$

The difference between the atomic number and the summation of all occupied orbitals reveals the relative charge of each atom for the ground state. Several occupied virtual pairs contribute to a given TD-DFT excitation, and the contribution coefficient of each pair, C_{ai}, is output by Gaussian16. It should be noted that the maximum total electron density transferred from a photoexcitation is 1, but the linear combination of several occupied-virtual pairs that contribute to the photoexcitation can reduce this value. Thus, values less than 1 indicate conflict between orbital pairs (the individual excitations cancel one another for no net change between atomic orbitals), or excitation within the d-d orbitals occurs.

Photoexcitation involves several molecular orbitals, making transition densities an efficient representation of the location and distribution of holes and electrons. Further, the broad bandwidth of the ~30 fs laser pulse accesses excited states near 3.1 eV. Thus, we selected the excited state molecular orbitals with the largest LMCT value and highlighted by a green arrow as

presented in Figure S1-S4 for analysis. The y axis range is maintained within each cluster series for easy comparison.

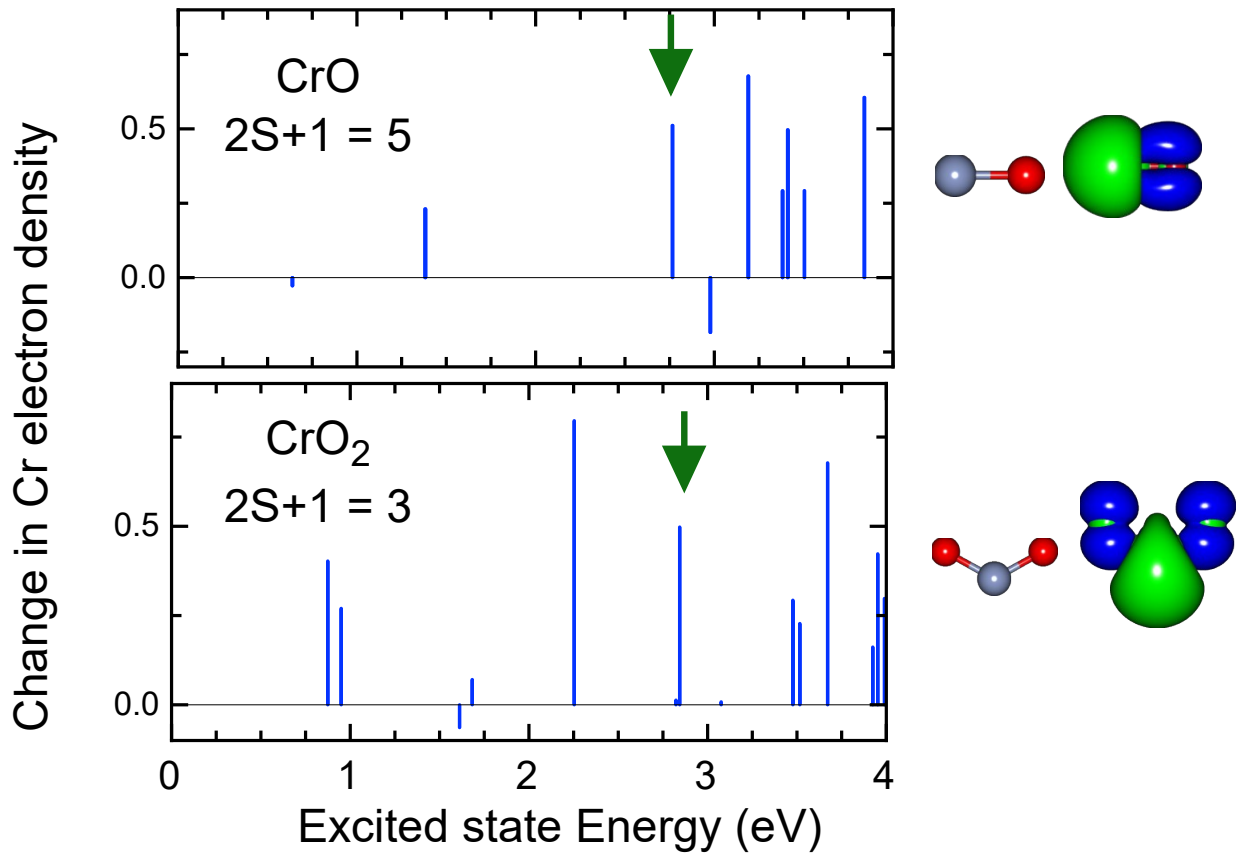

Fig. S1. The change in Cr electron density (LMCT character) of the CrO and CrO_2 clusters for all excited states < 4 eV calculated at the TD-CAM-B3LYP level using the basis set described in the main text. The selected excited state that is compared to experimental results is shown by the green arrow. The cluster's lowest energy geometry and spin configuration are shown. TD-CAM-B3LYP S0 transition densities for are presented at an isodensity of 0.002/Å^3. The electron density is green, the hole density is blue, chromium atoms are blue, and oxygen atoms are red.

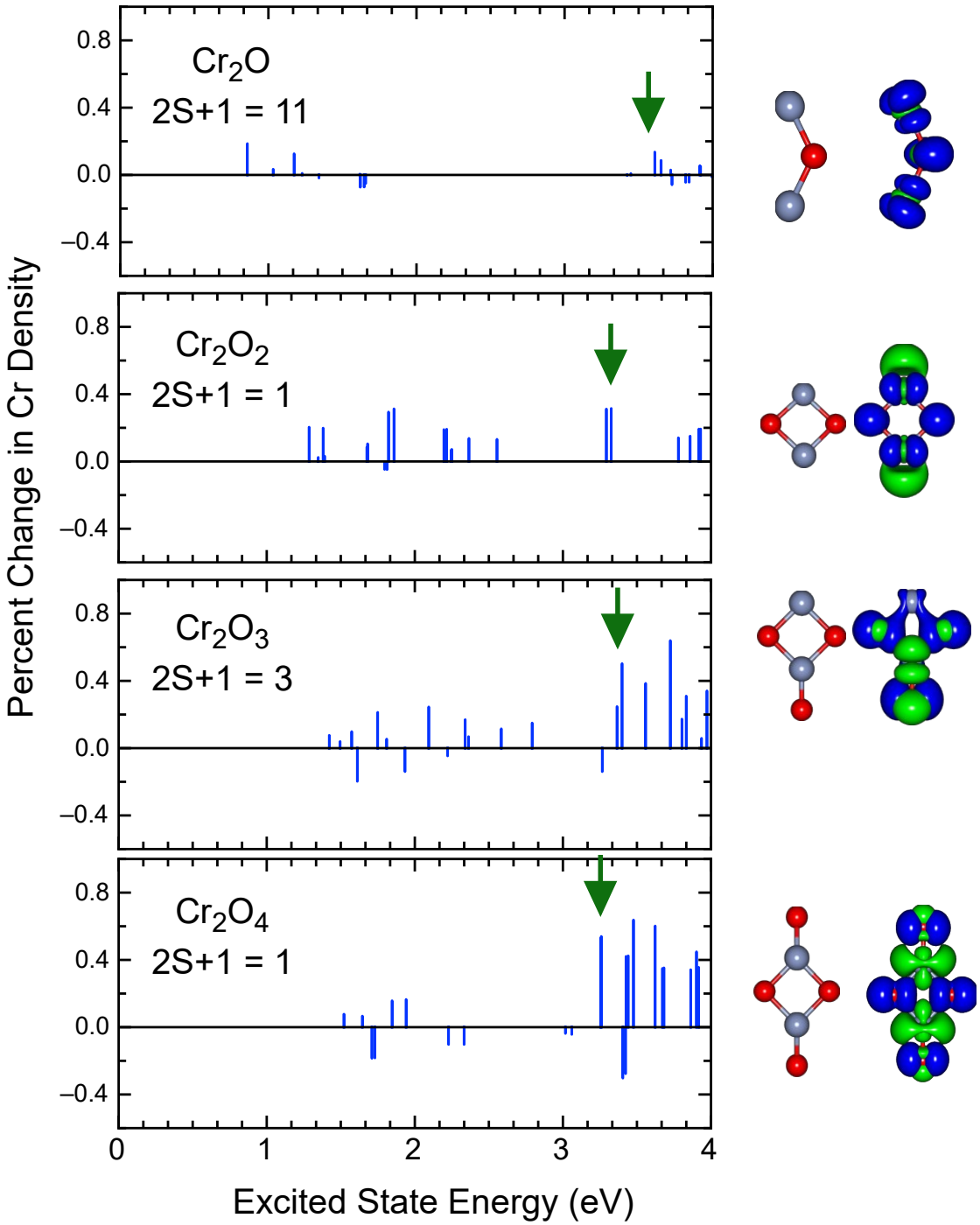

Fig. S2. Change in Cr electron density (LMCT character) of the $Cr_2O_{1\text{-}4}$ clusters, similar to Fig. S1.

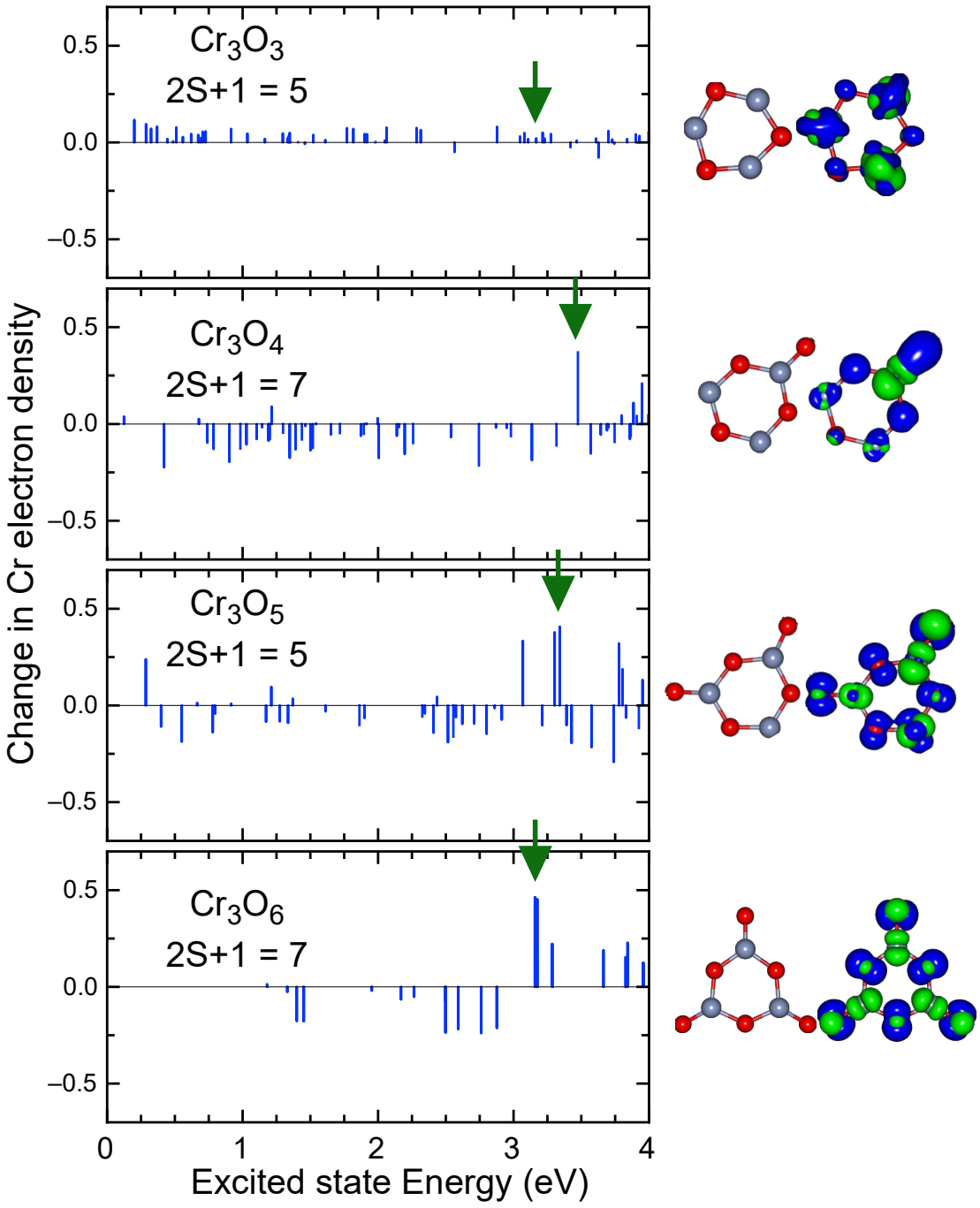

Fig. S3. Change in Cr electron density (LMCT character) for the $Cr_3O_{3\text{-}6}$ clusters, with properties listed similar to Fig. S1.

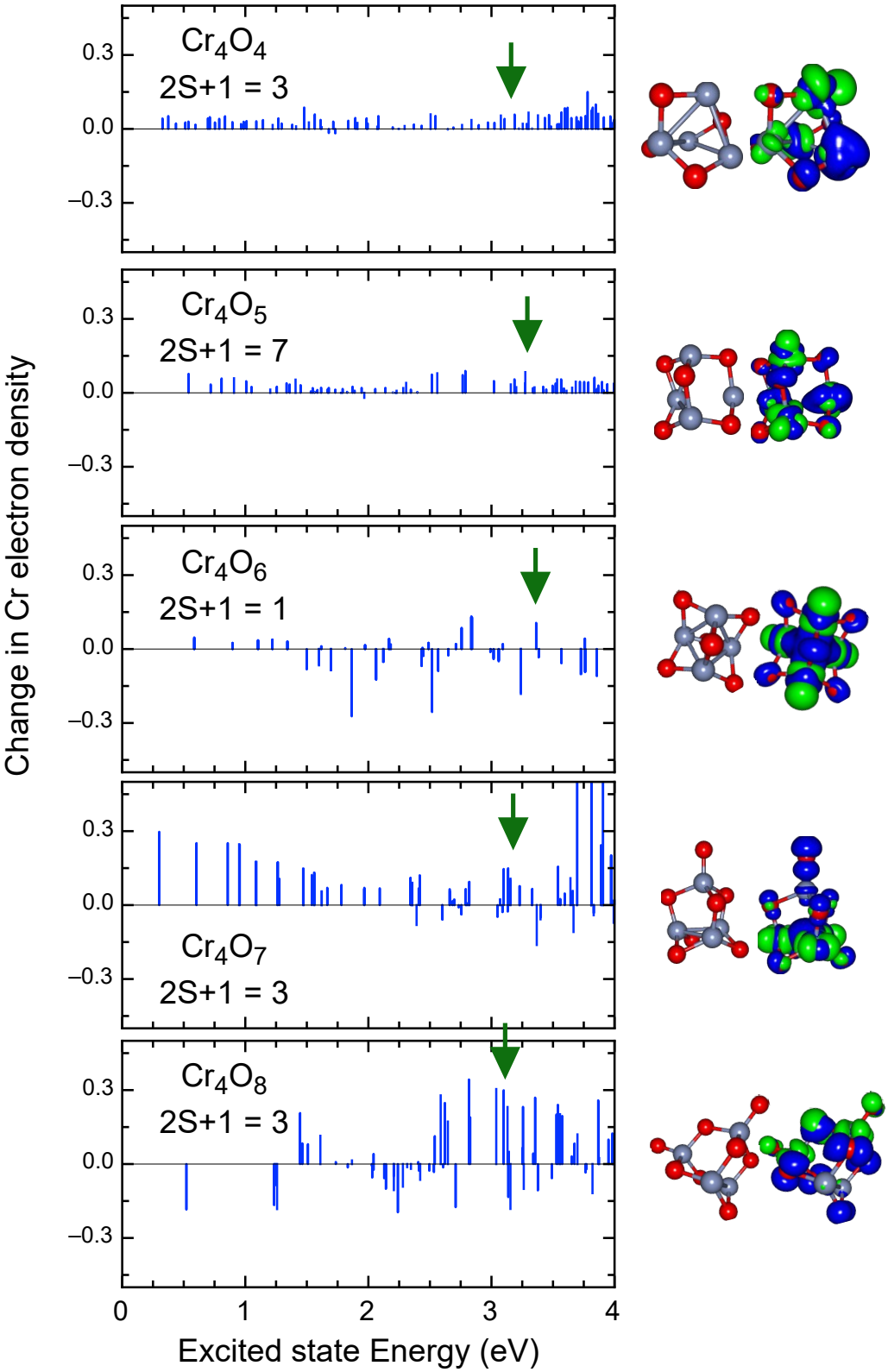

Fig. S4. Change in Cr electron density (LMCT character) for the $Cr_4O_{4\text{-}8}$ clusters, with properties listed similar to Fig.S1.

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian16 (Revision C.01). Gaussian Inc. Wallingford CT, 2016.