Another Look at Photoelectron Spectra of the Anion Cr_2O_2^- : Multireference Characters and Energetic Degeneracy

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Abstract

Geometrical and electronic structures of the chromium oxide dimer in both charge states $\text{Cr}_2\text{O}_2^{-/0}$ were carefully and thoroughly studied using the restricted active space RASSCF/RASPT2 and density matrix renormalization group followed by second-order perturbation theory DMRG-CASPT2 methods in conjunction with large basis sets. The anionic and neutral clusters $\text{Cr}_2\text{O}_2^{-/0}$ are characterized by a D_{2h} structure and high spin ground states (10 and 9, respectively). RASSCF wave functions point out strong multireference characters of their electronic ground state. The two lowest-lying states $^{10}\text{A}_g$ and $^{10}\text{B}_{2g}$ of the anion Cr_2O_2^- are nearly degenerate and both were proven to be populated and involved in the anion photoelectron spectra of Cr_2O_2^- . The neutral cluster exhibits a $^9\text{B}_{2g}$ ground state. Within the active space of 20 electrons in 18 orbitals

used, thirty electronic transitions starting from both lower-lying anionic states to corresponding neutral states were predicted. Transitions from the anionic ground state $^{10}A_g$ cause most of visible bands in the anion photoelectron spectra of Cr_2O_2^- , while the first band with low intensity is determined to arise from a transition starting from the nearly degenerate state $^{10}B_{2g}$. Furthermore, multi-dimensional Franck-Condon Factor simulations were carried out to further support our band assignments.

1 Introduction

With several applications in industry^{1,2} and chemical reactions as catalysts,³⁻⁵ chromium oxides have been widely studied. Many new chromium oxide clusters were synthesized,⁶⁻¹⁴ and their properties such as magnetic behaviors, geometrical structures and electronic states were also investigated.^{6-9,14-17} Several electronic, magnetic and energetic features of chromium oxides are known to be dependent on chemical compositions and geometrical structures. Therefore, geometries of their lowest-lying states must be accurately identified. For this purpose, calculated results obtained using reliable quantum chemical methods still need to be rechecked by comparison with experimental data such as infrared signals and ionization energies.

Similar to a large number of clusters containing transition metals, theoretical studies of unsaturated chromium oxides are known to be computationally challenging. In fact, such clusters need to be described by wave functions that can accurately address their inherently strong multireference characters. As a result, specific methods, such as the multi-reference configuration interaction MRCI, multiconfigurational complete active space followed by perturbation theory CASSCF/CASPT2, and n-electron valence state perturbation theory NEVPT2 are necessary to recover enough correlation energy. When lower levels of theory (usually single reference methods) were employed, the results obtained for geometric and electronic structures of chromium oxides were frequently not consistent with each other, leading to confusing conclusions.^{6,7,11,15-19}

A case in point in which a typical chromium oxide gives rise to conflicting results is dichromium dioxide ($\text{Cr}_2\text{O}_2^{-/0}$). Two independent groups probed the electronic structures and magnetic interactions of Cr_2O_2 by using anion photoelectron spectroscopy.^{6,11} The anion photoelectron spectra recorded by Wang and coworkers¹¹ in general reproduced all four distinguished bands reported previously by Tono et al.,⁶ and interestingly two additional clear bands were also observed.^{6,11} On the one hand, the studies of both groups agreed with each other that both the anionic and neutral clusters $\text{Cr}_2\text{O}_2^{-/0}$ have high-spin ground states of 10 and 9, respectively, in which two chromium atom sites are ferromagnetically coupled. On the other hand, both reports completely disagreed on the band assignments. In addition to two above reports, several theoretical reports pointed out a low spin state (singlet) electronic ground states of Cr_2O_2 .^{16–18,20} In contrast, some more recent studies again reached the conclusion of a high-spin ground state (dectet) for Cr_2O_2^- .^{16,21} Even more surprisingly, the geometrical form of Cr_2O_2 determined by Ashman and coworkers²⁰ is not consistent with those given in other reports mentioned.^{6,16–18,20}

As summarized above, although experimental spectra obtained from two studies^{6,11} appear quite similar, the band assignments differed completely from each other. Tono et al.⁶ used energies obtained from density functional theory (DFT) for assignments of the four visible bands noted as X' (1.20 vs. 1.40 eV), X (1.69 vs. 1.80 eV), A (2.52 vs. 2.60 eV), B (2.99 vs. 3.10 eV) or C (3.14 vs. 3.10 eV) as shown in Figure 1¹¹ (the first and second values given in parentheses are vertical detachment energies (VDEs) taken from ref. 11 and ref. 6, respectively). Wang and coworkers¹¹ applied an energetic shift of 0.56 eV to VDEs calculated⁶ to ascribe all transition bands including two new observed ones (B or C and D (3.81 eV)), leading to a complete disregard of the very first band X' located at ~ 1.20 eV. As a consequence, the identity of the first band (X') with extremely low intensity remains to be determined. While this low intensity band was believed in ref. 11 to be raised from a lowly populated isomer,¹¹ it was attributed in ref. 6 to a transition from a highly populated isomer.⁶

Overall, correct and reliable conclusions on the most stable isomers, electronic ground states and ionization processes appearing in the anion photoelectron spectra of Cr_2O_2^- are still matter of debate. In this context, we set out to carry out a set of high accuracy quantum chemical computations with the aims of reinvestigating the geometrical and electronic structures of both $\text{Cr}_2\text{O}_2^{-/0}$. Subsequently, all electronic transitions causing the appearance of bands in the photoelectron spectra of the anion Cr_2O_2^- are predicted and assigned. A further step, which is multi-dimensional Franck-Condon Factor simulations of the first two bands with lowest ionization energies, is also conducted to corroborate our band assignments.

Figure 1: Anion photoelectron spectra of Cr_2O_2^- at two different photon energies of 266 and 193 nm (reproduced with permission from ref 11, Copyright 2006, AIP Publisher).

2 Computational Methods

Generally, the computational procedure includes three steps involving geometry optimizations, additional energy single point calculations, and Franck-Condon factor simulations. The RASSCF/RASPT2 method was first used to optimize geometries of the oxides in both charge states $\text{Cr}_2\text{O}_2^{-/0}$. Single point electronic energy calculations were subsequently conducted using the density-matrix renormalization group DMRG method, also followed by second-order perturbation treatment CASPT2 and DFT computations using different functionals. The last step involving Frank-Condon simulations was performed on the basis of equilibrium structures and harmonic vibrational frequencies obtained from DFT optimizations. To treat the $\text{Cr}_2\text{O}_2^{-/0}$ clusters with the RASSCF/RASPT2 method,²² a predefined coordinate system was applied to a particular isomer of $\text{Cr}_2\text{O}_2^{-/0}$. The four different isomers considered with their predefined coordinate systems are given in Figure 2.

Figure 2: Coordinate systems used for RASSCF/RASPT2 calculations of four different Cr_2O_2 isomers in both neutral and anionic states.

All RASSCF/RASPT2²² calculations were conducted using the OpenMolcas program.²³

The active space used for generations of RASSCF wave functions consists of three subspaces,

noted as RAS1, RAS2 and RAS3. While RAS1 contains all six $2p$ orbitals of two oxygen atoms, RAS3 has no orbitals. Theoretically, some more virtual orbitals can be added to the RAS3 subspace. For transition metals with a more-than-half filled $3d$ -shell, a set of additional $4d$ orbitals should be the first choice to account for the $3d$ double-shell effect.²⁴ The inclusion of such an additional d shell would make our computations harder to get convergence and require higher computing resources. More importantly, all metallic $3d$ MOs of $\text{Cr}_2\text{O}_2^{-/0}$ are singly occupied and unoccupied, and as a result occupation numbers of all $4d$ orbitals are negligible. Hence, these $4d$ MOs are not important and RAS3 is kept empty with insignificant sacrifice of accuracy. RAS2 is basically comprised of 12 metallic orbitals arising from two chromium atoms, namely two $4s$ orbitals and ten $3d$ ones. Maximum two electrons were excited from RAS1 to take further static correlation energy into account. Depending on the charged state of Cr_2O_2 , the total number of electrons in the active spaces is 20 (for the neutral) or 21 (for the anion). Two RASSCF calculation schemes can be written in a short way as $\text{RAS}(20,2,0;6,12,0)$ and $\text{RAS}(21,2,0;6,12,0)$ for the neutral and anionic clusters, respectively. Dynamic correlation energy was subsequently calculated employing the second-order perturbation theory on the basis of RASSCF wave functions obtained above. All core orbitals of oxygen ($1s$) and chromium ($3p$ and inner ones) atoms were not considered in the perturbative step. Because the optimization step can be only performed using numerical gradient evaluations at the RASPT2 level, many electronic states of the mentioned isomers are, first, roughly optimized with a small basis set ANO-RCC-VDZ,^{25,26} and some selected low-lying states were reoptimized with a larger basis set ANO-RCC-VQZP.^{25,26} Energetic minima of optimizations were subsequently confirmed by vibrational calculations. However, due to technical shortcomings, only the totally symmetric vibrational modes with respect to the molecular symmetries (C_{2v} and D_{2h}) were obtained at the RASPT2 level.

The first result revealed from RASSCF calculations is strong multireference features of the wave functions of the $\text{Cr}_2\text{O}_2^{-/0}$ systems. Therefore, in order to assure that the RASPT2 computations correctly identified ground and important low-lying states, some

DMRG-CASPT2²⁷⁻³¹ single point calculations were also conducted. Single point energies of some selected low-lying states were thus calculated employing the previous optimized RASPT2 geometries. A larger active space with 28 orbitals including all $2s$ and $2p$ ones of two oxygen atoms, and $3s$, $3p$, $3d$ and $4s$ orbitals of two chromium atoms was used for DMRG calculations. The numbers of electrons in the active space amount to 40 and 41 for the neutral and anionic clusters, respectively. The number of renormalized state m in all DMRG calculations was set to $m = 2000$. It is known that to obtain more accurate energies, m needs to be > 2000 , but the resulting DMRG-CASPT2 calculations become computationally expensive, and they go beyond our computing resources. Correlation energy recovered from CASPT2 calculations on the basis of DMRG wave functions did not include the core orbitals excluded in the DMRG step. The ANO-RCC-VQZP basis set was used for all DMRG-CASPT2 calculations that were done with the CHEMPS2 code³² interfaced with the OpenMolcas package.

Dozens of DFT single points calculations were also conducted by using the TPSS³³ and BP86^{34,35} functionals in combination with the correlation consistent quintuple- ζ aug-cc-pV5Z (for Cr)³⁶ and cc-pV5Z (for O)³⁷ basis sets implemented in the Molpro 2015 package.³⁸ All single point energy calculations and RASPT2 optimizations took all electron scalar relativistic effects into account by use of the 2nd Douglas-Kroll-Hess Hamiltonian (DKH2).³⁹ As proven elsewhere, the zero-point vibrational energies ZPEs insignificantly affect positions of small cluster states on their potential energy hypersurfaces;⁴⁰ hence all energies considered in this work are purely electronic energies without ZPE corrections.

To give more details to and support the photoelectron band assignments, equilibrium geometries and corresponding harmonic vibrational frequencies of four states involved in the first two bands X' and X were calculated analytically using DFT with the TPSS functional in conjunction with the def2-TZVP basis set⁴¹ available in the Gaussian 09 program.⁴² All obtained information was used to simulate the Franck-Condon factors. The integrals between vibrational wave functions were calculated with the MolFC program.⁴³ As a side note,

optimal geometrical parameters of these four states obtained at this DFT level were compared to those optimized at the RASPT2 (see Table S3) to ensure that the TPSS functional is appropriate for Franck-Condon factor simulations.

3 Results and Discussion

3.1 Ground State Identification

Electronic ground states of both $\text{Cr}_2\text{O}_2^{-/0}$ clusters were determined after two rounds of optimizations. The results of the first round employing the ANO-RCC-VDZ basis set are collected in Table S1 of the Supporting Information (SI) file. We can rule out all low-spin states as candidates for the ground states of both the neutral and anionic clusters. Some high-spin states of the isomers **a**, **b** and **d** (Figure 2) tended to geometrically converge to the same motif of geometry **c** in Figure 2, belonging to the D_{2h} point group. Therefore, in the second round of optimizations, only high-spin states of the isomer *c* with the spatial symmetry of D_{2h} were selected for geometry reoptimizations using the larger ANO-RCC-VQZP basis set.

As mentioned above, all electronic states with spin multiplicities of 8, 9, 10, and 11 were reoptimized using the RASPT2 method with the ANO-RCC-VQZP basis set, and their relative energies are given in Table 1. Clearly, the RASPT2 method identified a dectet state $^{10}\text{A}_g$ as the most stable electronic structure of the anionic cluster Cr_2O_2^- . Interestingly, another dectet state of Cr_2O_2^- , namely the $^{10}\text{B}_{2g}$, was determined to be energetically very close to the $^{10}\text{A}_g$, being about 0.02 eV less stable than the state $^{10}\text{A}_g$ computed with the RASPT2 method. The RASPT2 potential energy curves for the two lowest-lying states of the anionic cluster Cr_2O_2^- in Figure 3 strongly corroborate their degeneracy. Due to the very small difference in energy between two lowest-lying anionic states, DMRG-CASPT2 calculations were carried out and the results obtained confirmed the RASPT2 finding. Additionally, to ensure ZPE corrections do not affect energetic ordering of these two lowest-lying

states, their RASPT2 and DMRG-CASPT2 energies corrected with the CASSCF and TPSS ZPEs were evaluated (see Table 2). Both states $^{10}A_g$ and $^{10}B_{2g}$ are nearly degenerate, in which the $^{10}B_{2g}$ state is only 0.01 eV energetically higher than the ground state. With DFT methods, the results calculated with the TPSS functional seem to be consistent with the RASPT2 and DMRG-CASPT2 methods, whereas the BP86 produced a bit of confusion over the ground state of Cr_2O_2^- . Overall, one can conclude that the two high-spin dectet states $^{10}A_g$ and $^{10}B_{2g}$ are degenerate with a marginal energy difference in favor of the $^{10}A_g$ state as the ground state of the anionic cluster Cr_2O_2^- .

Figure 3: Potential energy curves for the ground and first excited states of $\text{Cr}_2\text{O}_2^{-/0}$ along the Cr-Cr distance at the RASPT2 level.

For the neutral cluster, all used methods consistently agree with each other that the $^9B_{2g}$ state is the most stable one. The difference in energy of this state with respect to the anionic ground state $^{10}A_g$ yielded an adiabatic electron affinity of ~ 1.30 eV for the neutral oxide. The first excited state of the neutral Cr_2O_2 was determined to be the 9A_g state at all employed levels of theory. The RASPT2 relative energy of this state with respect to the neutral ground state is 0.33 eV, placing it at the first excited position on the potential surface

Table 1: Relative energies (eV) of all electronic states with spin multiplicities of 8, 9, 10 and 11 determined using different methods. Coefficient weights of leading configurations are noted as wt.

isomer	wt.	state	RASPT2 geometry ($\text{\AA}$) r_{Cr-Cr}, r_{Cr-O}	method		
				RASPT2 ^a	TPSS ^b	BP86 ^b
c-anion	0.26	8A_g	2.55, 1.83	1.10		
	0.08	$^8B_{3u}$	2.42, 1.84	0.62		
	0.09	$^8B_{2u}$	2.23, 1.84	1.32		
	0.10	$^8B_{1g}$	2.65, 1.82	1.20		
	0.10	$^8B_{1u}$	2.60, 1.82	1.45		
	0.14	$^8B_{1g}$	2.39, 1.83	0.78		
	0.16	$^8B_{3g}$	2.53, 1.83	2.45		
	0.13	8A_u	2.63, 1.81	1.24		
	0.44	$^{10}A_g$	2.57, 1.84	0.00 (0.00)	0.00	0.00
	0.21	$^{10}B_{3u}$	2.54, 1.88	1.53	1.51	1.40
	0.36	$^{10}B_{2u}$	2.48, 1.86	1.26	0.84	0.70
	0.34	$^{10}B_{1g}$	2.48, 1.87	1.29	1.14	1.08
	0.96	$^{10}B_{1u}$	2.66, 1.85	3.47		
	0.34	$^{10}B_{2g}$	2.45, 1.83	0.02 (0.01)	0.11	-0.01
	0.42	$^{10}B_{3g}$	2.25, 1.84	2.24	0.67	0.57
	0.34	$^{10}A_u$	2.29, 1.92	2.28	0.96	0.99
c-neutral	0.59	9A_g	2.56, 1.82	1.68 (1.40)	1.38	1.43
	0.30	$^9B_{3u}$	2.53, 1.87	3.13	2.41	2.41
	0.69	$^9B_{2u}$	2.39, 1.85	3.04	1.92	2.01
	0.32	$^9B_{1g}$	2.36, 1.88	2.21	1.67	1.83
	0.34	$^9B_{1u}$	2.39, 1.90	2.90	2.41	2.50
	0.37	$^9B_{2g}$	2.45, 1.83	1.35 (1.25)	1.28	1.33
	0.34	$^9B_{3g}$	2.61, 1.83	2.42	2.18	2.25
	0.36	9A_u	2.56, 1.84	2.81	2.70	2.87
	0.41	$^{11}A_g$	2.50, 1.93	6.46	5.70	5.83
	0.53	$^{11}B_{3u}$	2.40, 2.02	6.77	5.12	5.33
	0.72	$^{11}B_{2u}$	2.66, 2.25	5.76	4.30	4.56
	0.65	$^{11}B_{1g}$	2.45, 2.00	5.97	4.49	4.73
	0.60	$^{11}B_{1u}$	2.90, 1.90	7.52	6.03	6.24
	0.46	$^{11}B_{2g}$	2.58, 1.91	5.99	4.37	4.50
	0.80	$^{11}B_{3g}$	2.51, 2.19	6.78	5.91	6.13
	0.40	$^{11}A_u$	2.51, 1.93	6.59	6.05	6.33

^a Values in parentheses are the DMRG-CASPT2 relative energies

^b Because coefficient weights (wt.) of some octet states are too small, their DFT energies are not calculated.

Table 2: Insignificant effects of ZPEs on energetic ordering of the two lowest anionic states. All relative energies are in eV.

method	without ZPE		with CASSCF ZPE ^c		with TPSS ZPE	
	¹⁰ A _g	B _{2g}	¹⁰ A _g	¹⁰ B _{2g}	¹⁰ A _g	¹⁰ B _{2g}
RASPT2	0.000	0.020	0.000	0.022	0.000	0.023
DMRG-CASPT2	0.000	0.010	0.000	0.012	0.000	0.013

^c To obtain CASSCF ZPE values, CASSCF calculations were conducted using 12 orbitals (two 4s and ten 3d) only.

of the neutral Cr₂O₂. The other levels (DMRG-CASPT2, TPSS and BP86) estimated that this relative energy is ~ 0.15 eV.

Our results on the ground state of the anion Cr₂O₂⁻ are in agreement with one of previous reports,⁶ whereas the ground state ⁹B_{2g} of the neutral is completely different from that given in the same report (⁹A_g).⁶ In a recent work,¹⁶ the neutral ground state was identified using DFT computations to have a low spin multiplicity of 1 (singlet state), which is totally different from our present results. For the anion, the difference becomes more significant because a twisted geometrical chain of the anion Cr₂O₂⁻ was found in ref. 16 to be the most stable one.¹⁶ Such an inconsistency in the most stable geometry and electronic ground states can be explained by strong multireference characters of wave functions describing the clusters Cr₂O₂^{-/0}, that can be deduced from the small coefficient weights of the dominant configuration state functions listed in Table 1. These values are around 0.30 – 0.50 for important states (ground and some excited states involved in the anion photoelectron processes). This suggests that quantum chemical methods with high capability of recovering static correlation energy are necessary for treatments of Cr₂O₂^{-/0} systems. Single reference methods are less suitable for the study of Cr₂O₂, resulting in less accurate, if not confusing, results. This is the reason why several DFT studies are not consistent with each other in determination of the geometric and electronic structures of Cr₂O₂⁻ as mentioned above.

3.2 Electronic Structures and One-electron Removals

The two most stable anionic states $^{10}\text{A}_g$ and $^{10}\text{B}_{2g}$ are now analyzed on the basis of their leading electronic configurations extracted from corresponding RASSCF wave functions. Table 3 lists the leading configurations of these two anionic and some selected neutral states. Detailed analysis of the anionic ground state from pseudonatural active orbitals points out that all nine singly occupied orbitals are strongly metallic, in which the $11a_g$ MO is mainly composed of the metallic $4s$ AOs of chromium atoms and other singly occupied ones originate from $3d$ AOs. Within the active space used, there are also six doubly occupied MOs resulted from six $2p$ AOs of the two oxygen atoms. The orbital features of the nearly degenerate state $^{10}\text{B}_{2g}$ are quite similar to those of the ground state, except for the occupation schemes of two MOs $2b_{1g}$ and $4b_{3g}$. Figure 4 shows some characteristics of the 18 active-space MOs of both lowest-lying anionic states.

It is worth noting that from the leading configurations in Table 3 and the electronic features in Figure 2, one can easily figure out the formal oxidation states of both oxygen and chromium atoms in each state of $\text{Cr}_2\text{O}_2^{-/0}$. For example, the anionic ground state $^{10}\text{A}_g$ has nine singly metallic occupied orbitals and six doubly $2p$ occupied ones, which means each oxygen atom captures 2 electrons, and two chromium atoms donate 3 electrons. Thus, the formal oxidation state of oxygen in the anionic ground state $^{10}\text{A}_g$ is -2, and each chromium atom is +1.5. Formal oxidation states of oxygen and chromium in the anionic $^{10}\text{B}_{2g}$ state are also -2 and +1.5, respectively. Because one metallic electron is removed from Cr_2O_2^- to form the neutral ground state $^9\text{B}_{2g}$, the formal oxidation state of oxygen is unchanged (-2), and the formal oxidation state of each chromium atom is +2.

Generally, one can divide the 15 occupied orbitals into three different types ($4s$, $3d$ and $2p$ types) depending on their original AOs. Such origins of orbitals can somehow explain the ionization ordering of MOs in the photoelectron spectroscopic measurements. With three types of MOs found, electrons in the $4s$ -type MOs are associated with the lowest ionization energy, while the $2p$ -type MOs are expected to be at the highest ionization energy. The $3d$ -

type orbitals are in the middle range of ionization energies. This is understandable because for a specific transition metal atom, the $4s$ AO is energetically higher than $3d$ orbitals, and as a result, ionization from $4s$ -type MOs likely occurs first. Therefore, three ranges of electron signals are expected to be observed in the anion photoelectron spectra of Cr_2O_2^- , in which the first and second band regions correspond to electrons removed from the $4s$ -type and $3d$ -type MOs, respectively. The last region of anion photoelectron spectra is expected to be higher in terms of energy because all relevant electrons correspond to higher ionization energies of $\text{O}(2p)$ electrons. It should be noted that all predictions are made on the basis of active orbitals constructed and are for a certain upper limit of ionization energy.

Table 3: Leading configurations of the two most stable anionic ground states and of neutral ones

state	wt.	leading configuration	ionization	orbital
$^{10}\text{A}_g$	0.44	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$		
$^{10}\text{B}_{2g}$	0.34	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$		
$^1\text{A}_g$	0.59	$8a_g^2 9a_g^1 10a_g^1 11a_g^0 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$	$^{10}\text{A}_g \longrightarrow ^1\text{A}_g$	$11a_g \text{ (X)}$
2^9A_g	0.21	$8a_g^2 9a_g^0 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$	$^{10}\text{A}_g \longrightarrow 2^9\text{A}_g$	$9a_g \text{ (C)}$
3^9A_g	0.16	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{A}_g$	$3b_{2g} \text{ (D')}$
4^9A_g	0.24	$8a_g^2 9a_g^1 10a_g^0 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$	$^{10}\text{A}_g \longrightarrow 4^9\text{A}_g$	$10a_g \text{ (D)}$
$^1\text{B}_{3u}$	0.22	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^0 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$	$^{10}\text{A}_g \longrightarrow ^1\text{B}_{3u}$	$4b_{3u} \text{ (C)}$
2^9B_{3u}	0.22	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^0 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$	$^{10}\text{B}_{2g} \longrightarrow 2^9\text{B}_{3u}$	$8b_{1u} \text{ (B')}$
3^9B_{3u}	0.14	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^0 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{B}_{3u}$	$7b_{1u} \text{ (D')}$
$^1\text{B}_{2u}$	0.69	$8a_g^2 9a_g^1 10a_g^1 11a_g^0 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^0 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$		
2^9B_{2u}	0.36	$8a_g^2 9a_g^1 10a_g^1 11a_g^0 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^0 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$		
3^9B_{2u}	0.30	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^0$	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{B}_{2u}$	$1a_u \text{ (C')}$
$^1\text{B}_{1g}$	0.32	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$	$^{10}\text{A}_g \longrightarrow ^1\text{B}_{1g}$	$2b_{1g} \text{ (A)}$
2^9B_{1g}	0.32	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$	$^{10}\text{B}_{2g} \longrightarrow 2^9\text{B}_{1g}$	$4b_{3g} \text{ (A')}$
$^1\text{B}_{1u}$	0.34	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^0 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^1 1a_u^1$	$^{10}\text{A}_g \longrightarrow ^1\text{B}_{1u}$	$8b_{1u} \text{ (B)}$
2^9B_{1u}	0.19	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^0 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^2 4b_{3g}^0 1a_u^1$	$^{10}\text{A}_g \longrightarrow 2^9\text{B}_{1u}$	$7b_{1u} \text{ (B)}$

Continued on next page

Table 3 – continued from previous page

state	wt.	leading configuration	ionization	orbital
3^9B_{1u}	0.19	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^0 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9B_{2g} \longrightarrow 3^9B_{1u}$	$4b_{3u} (D')$
1^9B_{2g}	0.37	$8a_g^2 9a_g^1 10a_g^1 11a_g^0 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9B_{2g} \longrightarrow 1^9B_{2g}$	$11a_g (X')$
2^9B_{2g}	0.11	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^0 3b_{2g}^1 4b_{3g}^0 1a_u^1$	$10^9A_g \longrightarrow 2^9B_{2g}$	$3b_{2g} (C)$
3^9B_{2g}	0.14	$8a_g^2 9a_g^1 10a_g^0 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9B_{2g} \longrightarrow 3^9B_{2g}$	$10a_g (D')$
4^9B_{2g}	0.17	$8a_g^2 9a_g^0 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9B_{2g} \longrightarrow 4^9B_{2g}$	$9a_g (D')$
1^9B_{3g}	0.34	$8a_g^2 9a_g^1 10a_g^0 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$		
1^9A_u	0.34	$8a_g^2 9a_g^1 10a_g^1 11a_g^0 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$		
2^9A_u	0.15	$8a_g^2 9a_g^1 10a_g^0 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$		
3^9A_u	0.17	$8a_g^2 9a_g^0 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$		
4^9A_u	0.12	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9A_g \longrightarrow 4^9A_u$	$1a_u (con.)$
$1^{11}A_g$	0.50	$8a_g^1 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9A_g \longrightarrow 1^{11}A_g$	$8a_g (con.)$
$1^{11}B_{3u}$	0.53	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^1 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9A_g \longrightarrow 1^{11}B_{3u}$	$3b_{3u} (con.)$
$2^{11}B_{3u}$	0.18	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9B_{2g} \longrightarrow 2^{11}B_{3u}$	$6b_{1u} (con.)$
$1^{11}B_{2u}$	0.72	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^1 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9A_g \longrightarrow 1^{11}B_{2u}$	$5b_{2u} (con.)$
$1^{11}B_{1g}$	0.65	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^1 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9A_g \longrightarrow 1^{11}B_{1g}$	$1b_{1g} (con.)$
$2^{11}B_{1g}$	0.33	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10^9B_{2g} \longrightarrow 2^{11}B_{1g}$	$3b_{3g} (con.)$

Continued on next page

Table 3 – continued from previous page

state	wt.	leading configuration	ionization										orbital
1^1B_{1u}	0.60	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^1 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^0 1a_u^1$	$10\text{A}_g \longrightarrow 1^1\text{B}_{1u}$										$6b_{1u}$ (con.)
2^1B_{1u}	0.23	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^1 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10\text{B}_{2g} \longrightarrow 2^1\text{B}_{1u}$										$3b_{3u}$ (con.)
1^1B_{2g}	0.19	$8a_g^1 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10\text{B}_{2g} \longrightarrow 1^1\text{B}_{2g}$										$8a_g$ (con.)
1^1B_{3g}	0.80	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^1 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^0 1a_u^1$	$10\text{A}_g \longrightarrow 1^1\text{B}_{3g}$										$3b_{3g}$ (con.)
2^1B_{3g}	0.28	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^2 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10\text{B}_{2g} \longrightarrow 2^1\text{B}_{3g}$										$1b_{1g}$ (con.)
1^1A_u	0.40	$8a_g^2 9a_g^1 10a_g^1 11a_g^1 3b_{3u}^2 4b_{3u}^1 5b_{2u}^1 6b_{2u}^0 1b_{1g}^2 2b_{1g}^0 6b_{1u}^2 7b_{1u}^1 8b_{1u}^1 9b_{1u}^0 3b_{2g}^1 3b_{2g}^1 4b_{3g}^1 1a_u^1$	$10\text{B}_{2g} \longrightarrow 1^1\text{A}_u$										$5b_{2u}$ (con.)

In an anion photoelectron spectrum, the strongest bands in spectra are caused by removals of electrons from an anionic ground state. Let us stress again that in this analysis, all inner core orbitals of Cr_2O_2^- were not considered. A close look at the leading configurations of the anionic ground state ($^{10}\text{A}_g$) in Table 3 reveals all possible one-electron removals. In detail, nine singly occupied orbitals ($9a_g$, $10a_g$, $11a_g$, $4b_{3u}$, $2b_{1g}$, $7b_{1u}$, $8b_{1u}$, $3b_{2g}$, and $1a_u$) ionized at relatively low energy and six doubly occupied counterparts ($8a_g$, $3b_{3u}$, $5b_{2u}$, $1b_{1g}$, $6b_{1u}$, and $3b_{3g}$) with higher one-electron removal energy give rise to 15 ionization processes. Because all ionization processes originate from the most populated anionic ground state $^{10}\text{A}_g$ of the anion, they should be all observed in the anion photoelectron spectra of Cr_2O_2^- .

As the $^{10}\text{B}_{2g}$ state is very close to the anionic ground state in terms of its relative energy, this state will have a significant population. Thus, one-electron removals from this nearly degenerate state can also give rise to observed bands in the experimental spectra. This phenomenon was observed elsewhere.^{44,45} Taking into account all occupied MOs of the $^{10}\text{B}_{2g}$ state, another set of 15 orbitals can be equally ionized under a relevant energy of laser beams. Because these 15 ionization processes are predicted to start from a formal excited state, their signals are also predicted to be relatively lower in comparison to those from the anionic ground state. This means some weak signals can be seen if the experimental spectra are well resolved. Also, these signals can be overshadowed by signals of electrons removed from the ground state or even by the noise. For the sake of understanding, 30 ionization processes and corresponding ionized MOs are given in Table 3, in which the coefficient weights of several final neutral states are also collected, that will be analyzed in a following section on the low-intensity bands caused by electrons of the ground state.

Figure 4: Pseudonatural orbitals within the active spaces of the ground and first excited states of Cr_2O_2^- . In parentheses are the occupation numbers.

3.3 Anion Photoelectron Spectra

The anion photoelectron spectra of Cr_2O_2^- recorded at four photon beam energies¹¹ (two of them provided in Figure 1) look more complicated than those measured earlier.⁶ In the earlier report,⁶ two energetic regions of electron signals, in which one region is below 2.0 eV and the other one is over 2.5 eV, were recorded. In the more recent report, one more continuous region over 4.0 eV is present (see Figure 1).¹¹ As predicted above, electron removals from three different types of orbitals can give signals to the anion spectra. Obviously, ionization

from these three types of MOs are completely reflected by the observation of three visible regions of signals in the experimental spectra of Cr_2O_2^- .¹¹ This also implies that the active space used in our RASSCF calculations are sufficient to allow us to assign all visible bands.

In the range of under 2.00 eV, starting from the anionic ground state $^{10}\text{A}_g$, one electronic transition $^{10}\text{A}_g \longrightarrow ^{1^9}\text{A}_g$ was predicted at the RASPT2 level. The $^{10}\text{A}_g \longrightarrow ^{1^9}\text{A}_g$ vertical (VDE) and adiabatic (ADE) were determined to be both 1.68 eV, which correspond to the X band with its experimental VDE and ADE of 1.69 and 1.65 eV, respectively (see Table 4). In this range of ionization energy, starting from the first excited state $^{10}\text{B}_{2g}$, one more ionization $^{10}\text{B}_{2g} \longrightarrow ^{1^9}\text{B}_{2g}$ was found. The calculated VDE of this electronic transition is 1.35 eV. The experimental spectra recorded one band at around 1.20 – 1.40 eV, noted as X' in Table 4 and in Figure 1. Therefore, this band can be energetically ascribed to the $^{10}\text{B}_{2g} \longrightarrow ^{1^9}\text{B}_{2g}$ transition.

One more interesting fact which further supports such assignments for the first two bands is the relative intensities between two experimental bands in the spectra. The X' band is much less intense as compared to the X band. This suggests that the X' band is likely caused by an experimentally less populated electronic state. Indeed, the $^{10}\text{B}_{2g} \longrightarrow ^{1^9}\text{B}_{2g}$ transition originates from the first excited state $^{10}\text{B}_{2g}$ which may have, according to Maxwell - Boltzmann statistics, $\sim 10\%$ of probability to be populated in the ionization region of the spectrometer at 110 K,⁶ the lowest temperature of the cluster-growth room reported in ref 6. As a result, all ionization signals coming from this anionic excited state are expected to be lower in intensity, and this is probably what happened to the X' band. To make all electronic transitions starting from the first anionic excited state $^{10}\text{B}_{2g}$ clear with regard to band assignments, corresponding bands are noted with the prime symbol in Table 4.

The second region ranging from 2.00 to 4.00 eV in the spectra (Figure 1) shows four visible bands, denoted as A, B, C, and D, in which the B and C bands are not well resolved. At first, for the A band, the electronic transition $^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{1g}$ has a calculated VDE of 2.41 eV, which is ~ 0.10 eV smaller than the experimental VDE of the A band. The neutral $^{1^9}\text{B}_{3g}$

Table 4: RASPT2 ADE and VDE values of electronic transitions starting from the nearly degenerate anionic states. Formal bands with the prime symbol are due to transitions starting from the state $^{10}\text{B}_{2g}$.

state	ADE (eV)	VDE (eV)	expt. VDE (eV)		band ^d	ionization
			ref. 11 ^c	ref. 6		
1^9A_g	1.68	1.68	1.69 (1.65)	1.80	X	$^{10}\text{A}_g \longrightarrow 1^9\text{A}_g$
2^9A_g		3.16	3.16	3.10	C	$^{10}\text{A}_g \longrightarrow 2^9\text{A}_g$
3^9A_g		3.88	3.81		D'	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{A}_g$
4^9A_g		4.06	3.81		D	$^{10}\text{A}_g \longrightarrow 4^9\text{A}_g$
1^9B_{3u}	2.67	3.02	3.16	3.10	C	$^{10}\text{A}_g \longrightarrow 1^9\text{B}_{3u}$
2^9B_{3u}		2.90	2.99	3.10	B'	$^{10}\text{B}_{2g} \longrightarrow 2^9\text{B}_{3u}$
3^9B_{3u}		3.97	3.81		D'	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{B}_{3u}$
1^9B_{2u}		3.04				
2^9B_{2u}		3.11				
3^9B_{2u}		3.33	3.16	3.10	C'	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{B}_{2u}$
1^9B_{1g}	2.22	2.41	2.52	2.60	A	$^{10}\text{A}_g \longrightarrow 1^9\text{B}_{1g}$
2^9B_{1g}	2.18	2.49	2.52	2.60	A'	$^{10}\text{B}_{2g} \longrightarrow 2^9\text{B}_{1g}$
1^9B_{1u}	2.9	2.93	2.99	3.10	B	$^{10}\text{A}_g \longrightarrow 1^9\text{B}_{1u}$
2^9B_{1u}		3.01	2.99	3.10	B	$^{10}\text{A}_g \longrightarrow 2^9\text{B}_{1u}$
3^9B_{1u}		3.78	3.81		D'	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{B}_{1u}$
1^9B_{2g}	1.35	1.35	1.20	1.40	X'	$^{10}\text{B}_{2g} \longrightarrow 1^9\text{B}_{2g}$
2^9B_{2g}		3.21	3.16	3.10	C	$^{10}\text{A}_g \longrightarrow 2^9\text{B}_{2g}$
3^9B_{2g}		3.58	3.81		D'	$^{10}\text{B}_{2g} \longrightarrow 3^9\text{B}_{2g}$
4^9B_{2g}		4.06	3.81		D'	$^{10}\text{B}_{2g} \longrightarrow 4^9\text{B}_{2g}$
1^9B_{3g}	2.42	2.66				
1^9A_u	2.81	3.25				
2^9A_u		3.37				
3^9A_u		4.38				
4^9A_u		4.53	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 4^9\text{A}_u$
1^{11}A_g		7.69	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 1^{11}\text{A}_g$
1^{11}B_{3u}	6.77	7.07	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 1^{11}\text{B}_{3u}$
2^{11}B_{3u}		8.49	> 4.00		con.	$^{10}\text{B}_{2g} \longrightarrow 2^{11}\text{B}_{3u}$
1^{11}B_{2u}	5.76	6.66	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 1^{11}\text{B}_{2u}$
1^{11}B_{1g}	5.97	6.36	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 1^{11}\text{B}_{1g}$
2^{11}B_{1g}		8.15	> 4.00		con.	$^{10}\text{B}_{2g} \longrightarrow 2^{11}\text{B}_{1g}$
1^{11}B_{1u}	7.52	7.78	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 1^{11}\text{B}_{1u}$
2^{11}B_{1u}		7.76	> 4.00		con.	$^{10}\text{B}_{2g} \longrightarrow 2^{11}\text{B}_{1u}$
1^{11}B_{2g}		8.25	> 4.00		con.	$^{10}\text{B}_{2g} \longrightarrow 1^{11}\text{B}_{2g}$
1^{11}B_{3g}		7.58	> 4.00		con.	$^{10}\text{A}_g \longrightarrow 1^{11}\text{B}_{3g}$
2^{11}B_{3g}		8.09	> 4.00		con.	$^{10}\text{B}_{2g} \longrightarrow 2^{11}\text{B}_{3g}$
1^{11}A_u		7.73	> 4.00		con.	$^{10}\text{B}_{2g} \longrightarrow 1^{11}\text{A}_u$

^c The value in parentheses is the experimental ADE

^d Continuous bands are noted as con.

state with a VDE of 2.66 eV energetically matches the band A, but a comparison between the leading configurations of $^{10}A_g$ and $^{19}B_{3g}$ listed in Table 3 indicates this ionization is not a one-electron process. Hence, the A band is assigned to the $^{10}A_g \longrightarrow ^{19}B_{1g}$ ionization. Let us note that the $^{29}B_{1g}$ state, formed by the $^{10}B_{2g} \longrightarrow ^{29}B_{1g}$ ionization process can also be ascribed to the A band in view of its relative energy. However, this ionization is caused by a transition from the first excited state, and therefore its signal can be overshadowed by ionization processes from the ground state.

Moving on to the next two bands B and C, these bands are energetically quite close to each other with a difference in energy of ~ 0.15 eV. Such a difference in energy is too small to make distinguishable band assignments. Thus, the assignments for the B and C bands can be interchangeable within the error bar of the RASPT2 method. To assign these two bands, all electronic transitions from the anionic ground state should be considered first. Within the range of experimental VDEs from 2.99 to 3.16 eV, our calculated VDEs show that five ionization processes, namely $^{10}A_g \longrightarrow ^{19}B_{1u}$, $^{10}A_g \longrightarrow ^{29}B_{1u}$, $^{10}A_g \longrightarrow ^{29}A_g$, $^{10}A_g \longrightarrow ^{19}B_{3u}$, and $^{10}A_g \longrightarrow ^{29}B_{2g}$ from the anionic ground state can be attributed to these two bands. Each calculated VDE value of these five electronic transitions lies within an energetic range of 2.93 – 3.21 eV. Electronic transitions corresponding to each band noted as B and C in this region are listed in Table 4, and the assignments here are in fact totally interchangeable. Besides, two more additional ionization processes $^{10}B_{2g} \longrightarrow ^{29}B_{3u}$ and $^{10}B_{2g} \longrightarrow ^{39}B_{2u}$ arising from two singly occupied 3d-type MOs of the nearly degenerate state $^{10}B_{2g}$ are likely to take place and give rise to lower intensity bands (noted as B' and C') dominated by the bands B and C.

The last well-resolved band in the anion photoelectron spectra of Cr_2O_2^- was centered at ~ 3.81 eV. Because of its relatively high ionization energy, this band could not be observed in the earlier report, where the limit is set to ~ 3.20 eV.⁶ The intensity of this band is obviously lower than those of the X, A, B, and C bands. However, it is much higher than the intensity of the X' band (see Figure 1). Such relative intensity of the D band suggests that a one-electron

transition starting from the ground state $^{10}A_g$ may underlie this band. Because the D band vertically lies at 3.81 eV, the $^{10}A_g \rightarrow 4^9A_g$ transition with a computed VDE of 4.06 eV seems to be a good candidate to be responsible for this band. Such a predicted VDE slightly overestimates the experimental value, but this is the only energetically appropriate transition in Table 4. The D band is assigned to the $^{10}A_g \rightarrow 4^9A_g$ ionization process. In Table 4, five electronic transitions starting from the lowly populated state $^{10}B_{2g}$ are theoretically found in the range of 3.78 – 4.06 eV. Although all of them can contribute to the experimental band D, their extremely low intensities would be overshadowed by signals of the $^{10}A_g \rightarrow 4^9A_g$ transition. Note that the leading configuration of the final state 4^9A_g has a relatively smaller coefficient weight than those of other final states causing X and A bands. Therefore, the intensity of the D band is lower than those of both the X and A bands.

In Figure 1, a continuous region of signals is present at over 4.00 eV. As analyzed above, due to higher ionization energy, these unwell-resolved signals are expected to come from the ionization processes of electrons in $2p$ -type MOs. In Table 4, twelve $2p$ -type electronic transitions are listed together with their calculated VDEs of above 6.30 eV. All these twelve one-electron transitions lead to the high spin 11-tet states of the neutral Cr_2O_2 . In addition, one $3d$ -type transition ($^{10}A_g \rightarrow 4^9A_u$) contributes to the continuous region. The vertical ionization energy of this transition was computed to be 4.53 eV. If the anion photoelectron spectra of Cr_2O_2^- is more resolved, this band is believed to become pronounced and appear more clearly in the spectrum.

Obviously, most of our present band assignments are different from those reported in two previous studies.^{6,11} The nearly degenerate state of the anion Cr_2O_2^- , causing the extremely low intensity X' band, was not recognized and completely ignored in these two reports. A detailed comparison of relative energies between the present RASPT2 results and those of Tono and coworkers shows that DFT relative energies reported by these authors are significantly underestimated. This tends to explain the remarkable difference in band assignments. Using an empirical energetic shift of 0.56 eV, Wang and coworkers ruled out the 9A_g as the

final state underlying the X' band identified by Tono et al., but the X band, which is in agreement with our present RASPT2 assignment for this band. However, such an empirical energy correction seems not completely effective for the remaining bands (see Table 5).

Let us note that the electronic transition, $^{10}A_g \longrightarrow 1^9B_{3g}$, is not a one-electron process found in Tono's report, but a two-electron one. A few additional two-electron processes involving electronic transitions from both degenerate anionic states to the unassigned neutral counterparts can be predicted from Table 3. Two-electron processes usually appear as low-intensity peaks in anion photoelectron spectra.⁴⁶⁻⁴⁸ Because of low intensities, two-electron signals can be overshadowed by strong and well-resolved bands of the same energy regions. If spectra of strong electron correlation anionic systems are well-resolved and no one-electron processes underlie bands in the energy region of two-electron processes, two-electron detachment signals can be seen even clearly like those in the UO_2^- and Cu^- anion photoelectron spectra reported by Wang and co-workers.^{47,49}

3.4 Franck-Condon Factor Simulations

To further support the band assignments discussed above and give more details to band progressions, multidimensional Franck-Condon factor simulations were conducted. Because only the harmonic vibrational frequencies of four states involved in the first two bands ($^{10}A_g$, 9A_g , $^{10}B_{2g}$, and $^9B_{2g}$) were accessible from DFT computations, both X' and X bands were simulated. The equilibrium structures and harmonic vibrational frequencies of the involved states are tabulated in the SI. Two simulated bands are presented in Figure 5. The intensity of the X band is much higher than that of the X' band, which is in good agreement with the experiment (Figure 5). With regard to band broadening, although the simulated bands do not well reproduce the absolute values of band widths, their relative band width is in good correlation with the experiment. The simulation results not only well reflect the experiment in terms of relative intensities and band widths, but also confirm the band assignments for these two bands.

Table 5: A comparison of band assignments from this work and two refs 11 and 6. All electronic transitions starting from the anionic ground state $^{10}\text{A}_g$ and one giving rise to the X' band are listed.

band	assignment		
	this work	ref. 11	ref. 6
X'	$^{10}\text{B}_{2g} \longrightarrow ^{1^9}\text{B}_{2g}$		$^{10}\text{A}_g \longrightarrow ^{1^9}\text{A}_g$
X	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{A}_g$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{A}_g$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{3g}$
A	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{1g}$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{3g}$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{3u}$ $^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{1u}$
B	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{1u}$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{3u}$	
	$^{10}\text{A}_g \longrightarrow ^{2^9}\text{B}_{1u}$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{1u}$	
C	$^{10}\text{A}_g \longrightarrow ^{2^9}\text{A}_g$	$^{10}\text{A}_g \longrightarrow ^{2^9}\text{A}_g$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{2g}$
	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{3u}$		$^{10}\text{A}_g \longrightarrow ^{2^9}\text{B}_{3u}$
	$^{10}\text{A}_g \longrightarrow ^{2^9}\text{B}_{2g}$		
D	$^{10}\text{A}_g \longrightarrow ^{4^9}\text{A}_g$	$^{10}\text{A}_g \longrightarrow ^{1^9}\text{B}_{2g}$ $^{10}\text{A}_g \longrightarrow ^{2^9}\text{B}_{3u}$	
con.	$^{10}\text{A}_g \longrightarrow ^{4^9}\text{A}_u$		
	$^{10}\text{A}_g \longrightarrow ^{1^{11}}\text{A}_g$		
	$^{10}\text{A}_g \longrightarrow ^{1^{11}}\text{B}_{3u}$		
	$^{10}\text{A}_g \longrightarrow ^{1^{11}}\text{B}_{2u}$		
	$^{10}\text{A}_g \longrightarrow ^{1^{11}}\text{B}_{1g}$		
	$^{10}\text{A}_g \longrightarrow ^{1^{11}}\text{B}_{1u}$		
	$^{10}\text{A}_g \longrightarrow ^{1^{11}}\text{B}_{3g}$		

As explained before, the first two bands are the results of one-electron removals from 4s-type MOs of Cr_2O_2^- . Therefore, vibrational modes including vibrations of Cr atoms are expected in the final states. Indeed, all vibrational modes in the insets show harmonic vibrations of Cr atoms. A deeper investigation into the integrals describing the intensity of the band X' indicates significant involvement of the first excited vibrational state of the Cr-Cr stretching mode, while for the X band the results mainly come from 0-0 transitions of the same mode.

Figure 5: Franck-Condon factor simulations of the first two bands X' and X in the anion photoelectron spectra of Cr_2O_2^- . Vibrational modes obtained from DFT computations giving rise to significant integrals can be seen in the insets.

4 Concluding Remarks

In the present theoretical study, detailed electronic and geometrical structures of the chromium oxides $\text{Cr}_2\text{O}_2^{0/-}$ were reinvestigated. Geometrical structures of both anionic and neutral clusters of Cr_2O_2 have a D_{2h} diamond form. Competition for the anionic ground state of the anion Cr_2O_2^- between the two lowest-lying electronic states $^{10}\text{A}_g$ and $^{10}\text{B}_{2g}$ was found, in which the $^{10}\text{A}_g$ state is marginally more stable, and within the expected accuracy of the methods employed both states are basically degenerate.

A high-spin state $^9\text{B}_{2g}$ is confirmed to be the ground state of the neutral cluster. Both lowest anionic states ($^{10}\text{A}_g$ and $^{10}\text{B}_{2g}$) have contributions to the anion photoelectron spectra of the anion Cr_2O_2^- . All well-resolved bands with high intensities denoted as X, A, B, C, and D were determined to be the results of one-electron transitions starting from the anionic ground state $^{10}\text{A}_g$. The lower intensity X' band is likely caused by the nearly degenerate state $^{10}\text{B}_{2g}$ when one electron is removed to form the neutral ground state $^9\text{B}_{2g}$. The degenerate state $^{10}\text{B}_{2g}$ is also found to undergo several ionization processes and to produce photoelectron signals overshadowed by those originating from the anionic ground state. Overall, most of our spectral assignments for Cr_2O_2^- done in this work turn out to be completely different from those given in previous reports. Additionally, band simulations for the first two bands X' and X confirm the anionic ground state and reinforce the band assignments for these two bands.

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Supporting Information Available

Relative energies among electronic states of four different isomers in both neutral and anionic states. Equilibrium geometries and harmonic vibrational frequencies of states involved in the first two bands X' and X. Comparison of geometrical parameters between the RASPT2 and TPSS methods.

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Note

The authors declare no competing financial interest

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Graphical TOC Entry