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Equilibrium geometry and electron detachment energies of anionic Cr_2O_4, Cr_2O_5, and Cr_2O_6 clusters

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Abstract

Theoretical calculations are performed to study $Cr_2O_n^-$ ($n = 4 - 6$) clusters. The sequential oxidation of these clusters tends to quench the spin configuration of the ground state. For $Cr_2O_6^-$, the bonding orbitals dominate the higher valence molecular orbitals leading to a very high value of electron detachment energy for the cluster. Calculations also find the symmetric and asymmetric stretching of the terminal Cr–O bonds to be associated with the high frequency region of the vibrational spectrum of these clusters. Analysis of Mulliken charges and atomic spin density reveals two Cr atoms to be chemically equivalent but magnetically inequivalent atoms in these clusters.
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1. Introduction

Oxides of chromium are well known for their applications in polymerization of un-saturated hydrocarbons [1,2] and as coating materials [3,4]. Due to their immense applications, these materials are widely studied in the bulk form. In recent years, gas-phase chromium oxide clusters have also received attention due to their interesting magnetic behavior at the molecular level. Many of the previous investigations in the literature have studied ground state geometries, electronic structure and vibrational frequencies of small clusters of chromium oxide [5–10]. Initial experimental [5] and theoretical [6,7] studies were performed on Cr_mO_n ($m = 1, 2$ and $n = 2, 3$, and 4) clusters to determine their structural and vibrational properties in the ground state. In subsequent years, the focus was shifted to magnetic and electronic properties of chromia clusters. For example, calculations have predicted an oscillatory magnetic coupling between two Cr sites in Cr_2O_n ($n = 1 - 6$) clusters [8,9]. Oxygen-excess CrO_n^- ($n = 1 - 5$) clusters have also been

subject of a combined theoretical and experimental study yielding the information about their structures and photoelectron detachment energies [10]. Very recently, the results of a detailed study on $Cr_2O_n^-$ ($n = 1 - 3$) clusters have been reported [11]. In this work, the negatively-charged dichromium oxide clusters were generated by the laser ablation technique. Photoelectron spectroscopy, in conjunction with density functional theory were employed to study the electronic and geometric structures of these anionic oxide clusters. In a more recent experimental study [16], two classes of stable chromia clusters (Cr_nO_{2n+2} and Cr_nO_{3n}) were generated under different formation conditions. Theoretical DFT calculations performed for these two series of clusters revealed that the Cr_nO_{2n+2} class of clusters are ferro-magnetic in nature, while the Cr_nO_{3n} class is non-magnetic. Due to their high stability and inertness, these magnetic clusters were predicted as potential nanomagnets.

Our interest in the negatively-charged Cr_2O_n clusters arises from a recent experimental study on the reaction of chromium oxyanions ($Cr_xO_yH_z^-$) with water which is of vital importance in view of the resulting environmental and biological toxicity [12]. In the experimental

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study, the $Cr_xO_yH_z^-$ ($x = 1 - 3$, $y = 2 - 4$, $z = 0, 1$) ions were generated using an ion trap secondary ion mass spectrometer. Among the $Cr_2O_yH_z^-$ clusters, $Cr_2O_4^-$, $Cr_2O_5^-$, and $Cr_2O_5H_2^-$ clusters were found to react with the water molecule. A similar investigation was carried out to study the reaction of an O_2 molecule with $Cr_xO_yH_z^-$ ($x = 1 - 3$, $y = 2 - 4$, $z = 0, 1$) clusters. In order to understand the different reaction pathways of the chromium oxyanions with H_2O and O_2, we have initiated a systematic study of chromium oxyanionic clusters and report the results on anionic Cr_2O_y ($y = 4 - 6$) clusters in this Letter. We are not aware of any other experimental or theoretical study on $Cr_2O_4^-$, $Cr_2O_5^-$, and $Cr_2O_6^-$. Hence, it is noteworthy that this is the first systematic theoretical work to report the equilibrium geometries, ground-state spin multiplicities, and energetics of negatively-charged Cr_2O_n clusters ($n = 4 - 6$). In our subsequent studies, we will focus on the reactions of chromium oxyanions with H_2O and O_2.

The rest of the Letter, is organized as follows: the computational method employed in this work is presented in Section 2, followed by the discussion on the accuracy of our theoretical scheme and basis set. In Section 3, we present the equilibrium geometry, vibrational frequency, and vertical detachment energy values of $Cr_2O_4^-$, $Cr_2O_5^-$, and $Cr_2O_6^-$. Finally, we summarize the results in Section 4.

2. Computational method

The ground-state configurations of anionic Cr_2O_n ($n = 4 - 6$) clusters were obtained by density functional theory (DFT) based total energy calculations using GAUSSIAN 98 program [13]. The Becke three parameter hybrid exchange functional combined with LYP correlation (referred to as B3LYP) [14] and a double-ζ basis set (6–31G**) were employed in these calculations. Doublet, quartet, and sextet unrestricted spin configurations of a given cluster were considered for DFT calculations.

In the geometry optimization procedure, the convergence criteria for gradient and energy are set to 10^{-4} hartree/Å and 10^{-9} hartree, respectively. The lowest-energy configurations of anionic Cr_2O_n ($n = 4 - 6$) clusters are tested for stability by computing their vibrational frequencies.

The reliability and accuracy of 6–31G** basis set for anionic systems has been established in our previous calculations on group III nitride clusters [15]. However, the B3LYP exchange and correlational functional form has so far not been tested in identifying the ground state of negatively-charged transition metal oxide clusters. Hence, we have first tested the reliability of B3LYP functional form by calculating the equilibrium geometry and vertical electron detachment energy of anionic CrO_5 cluster.

The ground state of anionic CrO_5 was reported [10] to be consisted of a superoxo-type configuration with a CrO_3 unit (with C_{3v} symmetry) attached to the O_2 molecule. The structure with a doublet spin multiplicity was obtained using a combination of Becke's exchange and Perdew–Wang's correlation functionals (i.e. BPW91) and 6–311+G* basis sets for Cr and O atoms. In the present study, the modeling elements, namely B3LYP functional and 6–31G** basis sets reproduce the ground state configuration of anionic CrO_5 very well. For example, our values of $R_{Cr-O\,(base)}$, $R_{Cr-O(top)}$, R_{O-O}, A_{O-Cr-O} are 1.59, 1.91, 1.32 Å, and 108.5°, respectively, agree well with the respective values (BPW91/6-311+G*) in [10] of 1.62, 1.93, 1.32 Å, and 108°. The calculated (B3LYP/6–31G**) vertical electron detachment energy comes out to be 4.63 eV which is in excellent agreement with the experimental value of 4.69 eV [10]. The good agreement obtained between our theoretical results and the widely tested values by Gustev et al. [10] establishes the reliability of our theoretical scheme and the basis set.

3. Results and discussion

3.1. Ground state configuration

Since the ground state properties of the neutral Cr_2O_n ($n = 1 - 6$) clusters were extensively investigated in previous studies [6–9], the choice of cluster configurations for the geometry optimization in the negatively-charged state becomes relatively simple. Several planar and non-planar structural configurations, along with previously reported [6–9] ground state geometries of neutral Cr_2O_n clusters, were considered as candidates for geometry optimization. The choice of each of these cluster configurations was based on various structural motifs containing different combinations of Cr–O, Cr–Cr, and O–O bonds. In the following discussion, we only present the results for the lowest-energy configuration with different spin states. The structural details and energetics of the other configurations considered in this study can be obtained from the authors.

The lowest-energy configuration of $Cr_2O_4^-$ has C_1 symmetry, which consists of a Cr_2O_2 rhombic unit, with the remaining two oxygen atoms bound to each of the chromium atoms (Fig. 1). The rhombic unit is non-planar with a dihedral angle of 6.5°. The symmetry of the Cr–O–Cr–O ring is broken and the respective $R_{Cr-O(bridge)}$ are 1.75 and 1.91 Å. For the terminal oxygen atoms, $R_{Cr-O(terminal)}$ are 1.60 and 1.62 Å. In this configuration, one of the terminal oxygen atoms moved away from the plane making an angle of 36°, whereas the other terminal oxygen is just 6 degrees above the plane of the ring. The breaking of symmetry in the Cr–O–Cr–O ring can be seen as an attempt to reduce the strain in the symmetric ring to accomodate an extra
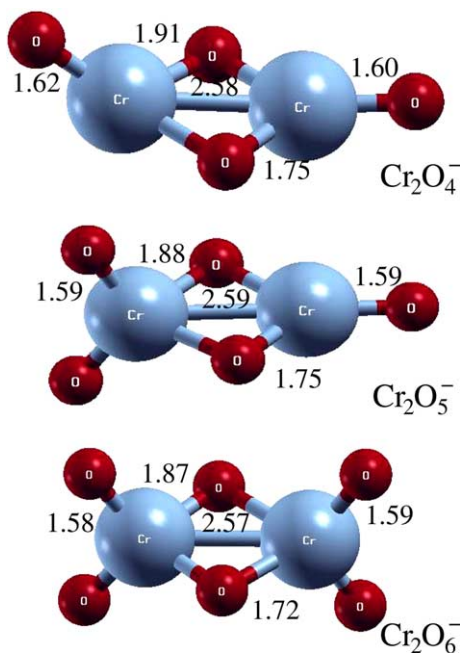
Fig. 1. The structural configurations of the ground state of $Cr_2O_n^-$ ($n = 4 - 6$) clusters. Here, Cr is represented by a large sphere and O is represented by a small sphere.

electron. The corresponding neutral Cr_2O_4 has C_{2v} symmetry with $R_{Cr-O(bridge)}$ of 1.80 Å and $R_{Cr-O(terminal)}$ of 1.56 Å. We note here that the oxygen atoms in the Cr_2O_2 rhombic unit are referred to as $O_{(bridge)}$.

The spin multiplicity of the ground state of $Cr_2O_4^-$ is found to be a doublet. However, configurations with sextet and quartet spin state are about 0.06 and 0.25 eV higher in energy than the doublet spin state, respectively (Table 1).

The predicted ground state of $Cr_2O_5^-$ can be viewed as an extension of $Cr_2O_4^-$ in which the additional oxygen atom is attached to a chromium atom. In this configuration, the metal atoms now have different coordination from each other, which resulted in an asymmetry in the Cr_2O_2 rhombic unit (Fig. 1). The ground state spin multiplicity of this lowest-energy configuration of C_s symmetry is again found to be doublet. A quartet spin

state with nearly identical geometry as that of the doublet state is 0.02 eV higher in energy (Table 1). However, the sextet electronic spin state has a very close geometry, its energy is relatively high (2.40 eV) indicating a preference of the lower spin states in this cluster.

The ground state configuration of $Cr_2O_6^-$ is a doublet spin state with C_s symmetry (Fig. 1). This ground state geometry can also be seen as an extension of $Cr_2O_5^-$ cluster with an additional oxygen added to the three-fold coordinated Cr atom. The $Cr-O_{(terminal)}$ and $Cr-O_{(bridge)}$ bond distances in this stable geometry are 1.58, 1.59, and 1.72, 1.87 Å, respectively. At the same level of theory, R_{Cr-O} in the CrO molecule, is calculated to be 1.63 Å in its quintet ground state. This fact makes the $Cr-O_{(bridge)}$ bond distance larger due to the increasing oxygen radius.

The calculated results of the present study find that the doublet and sextet states in $Cr_2O_4^-$ and the quartet and doublet spin states in $Cr_2O_5^-$ are competing with each other in stabilizing the respective cluster configurations. As shown in Table 1, the sextet is about 0.06 eV higher in energy than the doublet in $Cr_2O_4^-$ and the quartet is about 0.02 eV higher in energy than the doublet in $Cr_2O_5^-$. We note here that the energy differences between singlet and triplet states in neutral Cr_2O_4, Cr_2O_5 and Cr_2O_6 were reported to be 0.17, 0.17, and 1.58 eV, respectively [9].

Analysis of the chemical bonding in the dichromium oxide clusters can be performed reasonably well by considering only the four and six valence electrons of oxygen and chromium, respectively. Thus, the higher molecular orbitals of Cr_2O_n clusters can be classified, in order of increasing energy, into non-bonding $2p_O$, bonding $2p_O–3d_{Cr}$, bonding $3d_{Cr}–3d_{Cr}$ and non-bonding $3d_{Cr}$ orbitals. In the absence of oxygen, the ground state of Cr_2 and Cr_2^- has been assigned to singlet and doublet spin states, respectively in which bonding $3d_{Cr}–3d_{Cr}$ orbitals form the higher molecular orbitals. With the addition of oxygen atoms to Cr_2 (in either neutral or negative charge state), there exists a possibility of hybridization of $3d_{Cr}$ and $2p_O$ orbitals in dichromium oxide clusters. This, in turn, would result in the ferro-

Table 1
Spin multiplicity (2S + 1), symmetry, bond length (Å), and energies ΔE relative to the most stable isomer of $Cr_2O_n^-$ ($n = 4 - 6$) cluster configurations

System	(2S + 1)	Symmetry	$R_{Cr-O(terminal)}$	$R_{Cr-O(bridge)}$	R_{Cr-Cr}	ΔE (eV)
$Cr_2O_4^-$	2	C_1	1.62, 1.60	1.91, 1.75	2.58	0.00
	6	C_1	1.62, 1.60	1.91, 1.76	2.58	0.06
	4	C_1	1.62, 1.60	1.92, 1.73	2.56	0.25
$Cr_2O_5^-$	2	C_s	1.59, 1.59, 1.59	1.88, 1.75	2.59	0.00
	4	C_s	1.59, 1.59, 1.60	1.87, 1.76	2.58	0.02
	6	C_s	1.59, 1.59, 1.90	1.85, 1.77	2.54	2.40
$Cr_2O_6^-$	2	C_s	1.58, 1.58, 1.59, 1.59	1.72, 1.87	2.57	0.00
	4	C_s	1.59, 1.59, 1.59, 1.59	1.86, 1.86	2.84	1.87
	6	C_s	1.59, 1.59, 1.59, 1.83	1.86, 1.87	2.85	3.89

magnetic coupling of two Cr atoms in which the higher valence molecular orbitals are associated with (singly occupied) non-bonding $3d_{Cr}$ orbitals. The spin polarization of the $3d_{Cr}$ orbitals via oxygen atoms yields a high-spin multiplicity in the ground state of the $Cr_2O_n^-$ clusters ($n = 1, 2, 3$). This is what has been reported for anionic Cr_2O^-, $Cr_2O_2^-$ and $Cr_2O_3^-$ in the DFT/GGA-based study [11], where the respective spin multiplicity was predicted to be 10, 10, and 8 for the ground state.

The sequential oxidation of $Cr_2O_3^-$ to $Cr_2O_6^-$, on the other hand, would make the bonding $2p_O$–$3d_{Cr}$ orbitals to be energetically preferred in forming the higher valence molecular orbitals. This is a consequence of strong hybridization between $3d_{Cr}$ and $2p_O$ orbitals together with the shift of non-bonding $3d_{Cr}$ orbitals to higher energy: this is consistent with the increase in the *ligand field* gap due to the increase in the number of oxygen ligands per chromium atom. It is therefore, expected to lower the spin multiplicity in the ground state of the oxygen-rich clusters. This behavior is what we have found for $Cr_2O_4^-$, $Cr_2O_5^-$ and $Cr_2O_6^-$, where the energetically favored spin configuration decreases from sextet to quartet to doublet. The dominance of the bonding $2p_O$–$3d_{Cr}$ orbitals is further reflected in $Cr_2O_6^-$ where the quartet and sextet spin states lie well above (1.9 and 3.9 eV, respectively), the doublet spin configuration (Table 1).

In $Cr_2O_3^-$, the doublet spin state, however, was found to be very close in energy (0.04 eV) to the ground state of the octet spin configuration [11]. The stability of the doublet state was then attributed to the asymmetric structure of $Cr_2O_3^-$ in which the Cr atoms carry different valence states [11]. Our results provide only a partial support to this conjecture of different valence states for the Cr atoms in the clusters considered here. On one hand, analysis of Mulliken atomic charges given in Table 2 finds the two inequivalent chromium atoms to carry positive charges of (0.9, 0.8), (1.1, 1.0), and (1.2, 1.1) electrons in the doublet spin state of $Cr_2O_4^-$, $Cr_2O_5^-$, and $Cr_2O_6^-$, respectively. The very similar charges support chemically equivalent atoms in these clusters. On the other hand, the Mulliken-partitioned atomic spin densities (Table 2) show very dissimilar Cr atoms for all clusters except for the quartet state of $Cr_2O_5^-$, thus supporting an image of magnetically inequivalent Cr atoms. Given the unrestricted nature of our orbitals, we cannot extract a unique picture in this respect.

Nevertheless, our calculated results clearly show the interplay between non-bonding and bonding orbitals in forming the higher molecular orbitals of the clusters. The composition of the highest occupied molecular orbital shifts from the non-bonding $3d_{Cr}$ orbitals to the bonding $2p_O$–$3d_{Cr}$ orbitals as we go from $Cr_2O_4^-$ to $Cr_2O_6^-$. This is further reinforced by the reduction in the spin polarization of the $3d_{Cr}$ orbitals in the high-spin oxygen-rich clusters (Table 2). For example, the total

Table 2
Mulliken atomic charge Q (e) and atomic spin density (μ_B) associated with Cr atoms in $Cr_2O_n^-$ with $n = 4 - 6$

	Spin state	Cr_1	Cr_2	Total (Cr_1+Cr_2)
$Cr_2O_4^-$:Q (e)	Doublet	+0.93	+0.77	+1.70
	Quartet	+0.84	+0.81	+1.65
	Sextet	+0.79	+0.91	+1.70
$Cr_2O_5^-$:Q (e)	Doublet	+1.09	+1.00	+2.09
	Quartet	+1.12	+0.96	+2.08
	Sextet	+1.15	+0.86	+2.01
$Cr_2O_6^-$:Q (e)	Doublet	+1.21	+1.12	+2.32
	Quartet	+1.14	+1.14	+2.28
	Sextet	+1.14	+1.09	+2.23
$Cr_2O_4^-$:spin density	Doublet	−2.22	+3.23	+1.01
	Quartet	+0.13	+3.14	+3.27
	Sextet	+2.45	+3.05	+5.50
$Cr_2O_5^-$:spin density	Doublet	−1.14	+2.24	+1.10
	Quartet	+0.96	+2.40	+3.36
	Sextet	+0.90	+3.33	+4.23
$Cr_2O_6^-$:spin density	Doublet	+0.11	+1.04	+1.15
	Quartet	+0.99	+0.99	+1.98
	Sextet	+1.00	+1.81	+2.81

spin density associated with the Cr atoms in the quartet spin state changes from 3.27 to 1.98 in going from $Cr_2O_4^-$ to $Cr_2O_6^-$. As discussed later in this Letter, dominance of the bonding orbitals would also result in a very high value of the electron affinity of the $Cr_2O_6^-$ cluster.

3.2. Photoelectron detachment energy

In the photoelectron spectroscopy experiments on anions, the electron affinity of the corresponding neutral cluster is estimated by photodetachment of the electron from the ground state geometry of the anion. In order to have a realistic comparison between theory and experiment, we have defined the vertical electron affinity (EA) of dichromium oxide clusters as the energy difference between the anionic and neutral clusters, both at the optimized geometry of the anionic cluster (i.e. EA $= E_{q=0} - E_{q=-1}$, where E is the total energy of the cluster and q is the charge of the cluster). Following this definition, the calculated electron affinity can also be termed as vertical detachment energy.

In $Cr_2O_4^-$, the vertical EA corresponding to the transition from the (anion) doublet spin state to the singlet spin state of the neutral cluster is calculated to be 3.44 eV; whereas the detachment energy corresponding to transition from (anion) doublet spin state to the neutral triplet spin state is calculated to be 3.22 eV. However, it has been reported earlier [9] that singlet is the ground sate spin multiplicity of neutral Cr_2O_4 cluster, with triplet being 0.17 eV higher in energy. So, in

anionic photoelectron spectroscopic experiments, it can be expected that the *spin-flip*, which is observed in calculations here would manifest itself in the spectra as a very broad spectrum without any distinct features. This phenomena of *spin-flips* usually occur via spin–orbit coupling, by which the singlet and triplet states are coupled.

On the other hand, the vertical EA from the (anion) doublet to the (neutral) triplet in $Cr_2O_5^-$ is calculated to be 3.90 eV. In $Cr_2O_6^-$ cluster, the calculated vertical EA of 4.71 eV corresponds to the transition energy from the (anion) doublet to the (neutral) singlet. By considering the adiabatic electron affinity (adiabatic EA) in this case, the calculated value is 4.27 eV. Hence, it is noteworthy that the adiabatic EA is consistent with the trend found in the species correspond to the oxygen-rich Cr_nO_{3n} composition [16]. It is to be noted here that doublet/sextet and doublet/quartet spin states are predicted to be nearly energetically degenerate for $Cr_2O_4^-$ and $Cr_2O_5^-$, respectively, in the present study.

The calculated vertical EA values exhibit an increasing trend with the successive addition of oxygen atoms to the dichromium oxide clusters. This is consistent with the fact that the highest occupied molecular orbitals (HOMOs) begin to change their character from the nonbonding $3d_{Cr}$ to the bonding $2p_O$–$3d_{Cr}$ orbitals with the sequential oxidation of the clusters. We note here that the vertical detachment energies from the photoelectron spectroscopy were reported as follows: Cr_2O^-, 1.3 eV; $Cr_2O_2^-$, 1.4 eV; $Cr_2O_3^-$, 2.0 eV [11]. We are not aware of any experimental or theoretical vertical electron detachment energy data for Cr_2O_n ($n = 4 - 6$) clusters.

3.3. Vibrational frequencies

The distributions of the calculated normal vibrational frequencies of $Cr_2O_n^-$ ($n = 4 - 6$) clusters are shown in Fig. 2. Instead of giving an exhaustive description of the different vibrational movements in each compound, we will extract general features. The lower region of the frequency spectra corresponds to the bending modes
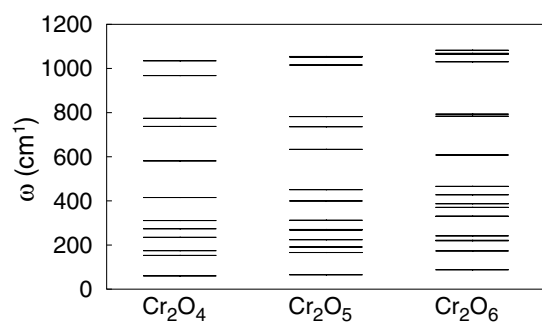
(below 581, 451, and 427 cm^{-1} for $n = 4$, 5, and 6, respectively), as one would expect for these open structures. The lowest bending mode (60, 65, and 88 cm^{-1} for $Cr_2O_4^-$, $Cr_2O_5^-$, and $Cr_2O_6^-$, respectively), is relatively separated in all compounds from rest of the bending modes. Again as expected, these lowest energy modes correspond to the symmetric bending of the terminal oxygen atoms in a perpendicular movement to the ring unit. The remaining bending modes are distributed as follows: first, the bending movements of the terminal oxygen atoms, and then the bending displacements of the bridge oxygen atoms.

After the bending modes, there is a frequency gap, and then come the three stretching modes involving the ring Cr–O bonds. The lowest one is always the symmetric stretching of the largest Cr–O bonds in the ring unit (581, 633, and 608 cm^{-1} for $n = 4$, 5, and 6, respectively), followed by the asymmetric stretching of the largest bond length Cr–O bonds and by the stretching of the other Cr–O bonds in the ring. The highest frequency region in the spectra is related with the symmetric and asymmetric stretching of the terminal Cr–O bonds. It is to be noted that the stretching frequency of the CrO molecule is 922 cm^{-1}, with 1.63 Å as the internuclear distance. This value is situated in between the last two regions of the spectra. This is in perfect agreement with the distance criteria (Fig. 1), since the longer ring bonds will have smaller frequencies and the shorter terminal bonds will have larger frequencies than the diatomic, and corresponds to the splitting of the frequency values after the coupling of the different stretching movements.

4. Summary

The ground state of $Cr_2O_n^-$ with $n = 4 - 6$ prefers to keep the Cr_2O_2 rhombic unit as the basic structural motif, as the case was with the corresponding neutral clusters. The calculated results find the lowering of spin multiplicity with the addition of the oxygen atoms to these clusters. It is attributed to the dominance of the bonding $2p_O$–$3d_{Cr}$ orbitals in forming the higher molecular orbitals in the oxygen-rich clusters. It also leads to a very high value of electron affinity of $Cr_2O_6^-$.

Fig. 2. Vibrational frequency spectra of anionic Cr_2O_n ($n = 4 - 6$) clusters.

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