

# A theoretical investigation on the $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$ ( $n = 1\text{--}4$ ) clusters by density functional theory methods

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## Abstract

The first systematic study of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1\text{--}4$ ) series of clusters is herein presented at the level of the unrestricted DFT B3LYP level in conjunction with electron core potential basis sets. The present structures are relevant for laser-induced and laser-ablation syntheses of chromium compounds, and also for fundamental spectroscopy studies of metal-bearing species in the gas phase. Calculated properties include optimal geometries, total energies, bond lengths, bond angles, natural orbital analysis charges, hydration dissociation energies, and HOMO–LUMO gaps inter alia. Present results reveal a strict correlation between the clusters total energy and their spin state. Except for  $\text{Cr}(\text{H}_2\text{O})_4^{0+}$ , the most stable clusters in each  $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1\text{--}4$ ) series are high-spin states. Comparisons with a few available theoretical results show good agreement.

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**Keywords:** Density functional theory; Chromium–water clusters; Electron core potential; van der Waals interactions

## 1. Introduction

The cluster state of matter, consisting of aggregates of relatively weakly bonded atoms and/or molecules, is widely viewed as a bridge between the gas and condensed phases [1]. Accordingly, the study of gas-phase clusters having one metal ion or atom coordinated with a few water molecules can elucidate many details of water–metal interactions in both solution (solvation) and on metallic surfaces (adsorption). For example, the investigation of small water–metal clusters with the central metal in one of its stable oxidation states [e.g. Cr(III) in  $\text{Cr}(\text{H}_2\text{O})_n^{3+}$  ( $n=1\text{--}6$ )] can be used as probes for the ion successive solvation processes in a size-dependent way over a relatively narrow range of cluster sizes. The reason for this lies in the relatively short extension of the Debye length, i.e. the minimum separation over which neighboring ions in solution screen from each other. On the other hand, the study of small water–metal (or non-metal–metal [2]) clusters with the central atom at a very low or zero oxidation state [e.g. Cr(I) and Cr(0) in  $\text{Cr}(\text{H}_2\text{O})_n^{1+}$  and  $\text{Cr}(\text{H}_2\text{O})_n^{0+}$  ( $n=1\text{--}4$ , respectively)] is highly relevant for laser-induced and laser-ablation syntheses

of chromium compounds, and for fundamental spectroscopy studies of metal-bearing species in the gas phase.

A considerable number of both experimental and theoretical studies of aqueous clusters are known in the literature. Many of those recent investigations have focused on aqueous clusters bearing cations, (oxo) anions or small molecules of representative elements. For instance, Lisy and collaborators have exhaustively studied solvation effects in several clusters containing alkali metal ions coordinated with both water and non-aqueous solvents. These investigators have synthesized and characterized the first genuine hexa-coordinated  $\text{Na}^{1+}$  ion cluster in the gas phase [3], prepared and measured the infrared spectra of the  $\text{Cs}^{1+}(\text{H}_2\text{O})_{1\text{--}5}$  series of clusters [4], inferred ion selectivity mechanisms in channel proteins by preparing and studying cluster prototypes of the form  $\text{M}^{1+}(\text{C}_6\text{H}_6)_n(\text{H}_2\text{O})_m$  with  $\text{M}=\text{Na}$  and  $\text{K}$  [5,6], and studied theoretically both metallic ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ag}^+$ ) and organic [ $\text{NH}_4^+$ ,  $\text{C}(\text{NH}_2)_3^+$  and  $\text{N}(\text{CH}_3)_4^+$ ] cations solvated with different classes of  $\pi$  systems (e.g. ethene, benzene and pyrrole) [7]. Duncan and collaborators [9] have investigated experimentally aqueous clusters containing alkaline-earth metal ions with their pioneering studies of  $\text{Ca}^{1+}(\text{H}_2\text{O})$  [8] and  $\text{Mg}^{1+}(\text{H}_2\text{O})$  complexes via photodissociation spectroscopy. Johnson and collaborators have also conducted extensive research on numerous aqueous clusters containing anions and small molecules, with special attention to solvation and dissociation mechanisms. Quite remarkably, these investigators could determine experimentally that the first

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primary hydration shells of the  $\text{OH}^-(\text{H}_2\text{O})_n$  and  $\text{F}^-(\text{H}_2\text{O})_n$  clusters in the gas phase do consist of exactly three and four  $\text{H}_2\text{O}$  molecules ( $n=3$  and 4). Other important contributions by this group include their spectroscopic and theoretical studies of the  $\text{NO}^-(\text{H}_2\text{O})_{n=1-3}$  [10,11],  $\text{OH}^-(\text{H}_2\text{O})$  [12],  $(\text{H}_2\text{O})_6$  and  $(\text{H}_2\text{O})_6^-$  (*magic*) [13,14],  $\text{SO}_2^-(\text{H}_2\text{O})$  [15], and  $\text{X}^-(\text{H}_2\text{O})_2$ , ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ) clusters [16,17] *inter alia*. The mentioned experiments have spurred a plethora of theoretical research on gas-phase aqueous clusters. Among several recent theoretical contributions, it is worth mentioning the quite successful application of the effective fragment potential (EFP) model by Gordon et al. [18] to study aqueous clusters as shown by the investigations on oxyanion–water clusters  $\text{A}^-(\text{H}_2\text{O})_{1-4}$  ( $\text{A}^-=\text{ClO}_4^-, \text{HSO}_4^-, \text{NO}_3^-, \text{H}_2\text{PO}_4^-, \text{HCO}_3^-, \text{HCO}_2^-, \text{SO}_4^{2-}, \text{HPO}_4^{2-}, \text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ ) [19], alkali and alkaline-earth metal cation water clusters  $\text{M}(\text{H}_2\text{O})_{1-6}$  ( $\text{M}=\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) [20], and anion–water clusters  $\text{A}^-(\text{H}_2\text{O})_{1-6}$  ( $\text{A}=\text{OH}, \text{F}, \text{SH}, \text{Cl}$  and  $\text{Br}$ ) [21] by Merrill et al., and by the study on  $\text{LiOH}$  dissociation in the  $\text{LiOH}(\text{H}_2\text{O})_n$ ,  $n=1-6$ , 8 clusters by Yoshikawa and Morales [22].

More recently, substantial efforts have been devoted to investigate different types of aqueous clusters containing transition metals as a way to elucidate chemical processes in both catalytic and biochemical systems [23]. Several experimental and theoretical studies of those types of clusters do exist in the literature but most of them deal with species having metals from the right half of the first transition row: Mn–Cu (e.g. the iron-bearing aqueous clusters:  $\text{Fe}^{+1}(\text{H}_2\text{O})_{1-4}$  [24],  $\text{Fe}^{+2}(\text{H}_2\text{O})$  [25], and  $\text{Fe}^{+1}(\text{H}_2\text{O})$  [26] *inter alia*). In contrast, studies of aqueous clusters with metals from the left half of the first transition row: Sc–Cr, are somewhat less common. Notable exceptions to that trend are the calculations on the  $\text{M}^{1,2+}(\text{H}_2\text{O})_{1-2}$ ,  $\text{M}=\text{Sc–Zn}$ , at the self-consistent field modified coupled pair functional (SCF-MCPF) level by Rosi and Bauschlicher [27], and the experimental investigations on the  $\text{V}(\text{H}_2\text{O})^{+1}$  complex by Brucat et al. [28], and on the  $\text{M}^{+1}(\text{H}_2\text{O})_{1-4}$ ,  $\text{M}=\text{Ti–Cu}$ , series of clusters by the Armentrout group [29]. In the specific case of chromium, aqueous clusters corresponding to its water-soluble salts at its most stable oxidation state in solution, Cr(III), have been predominantly studied by theoretical methods because of these compounds use for tanning processes, pigments manufacturing, and chromium plating. Conversely, their low-charged counterparts exhibiting Cr(I) and Cr(0) oxidation states, which are relevant in adsorption studies, have received far less attention. For instance, Varnali et al. have recently modeled several water-soluble Cr(III) complexes including  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ ,  $\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4^+$  and  $\text{Cr}(\text{OH})\text{SO}_4(\text{H}_2\text{O})_3$  by using the ZINDO/1 semiempirical method [30]. Martinez et al. have conducted a quite systematic series of molecular dynamics (MD) simulations and additional theoretical studies of the  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  complex in solution [31–35]. In one of their most interesting investigations [34], both the  $\text{Cr}^{3+}-\text{H}_2\text{O}$  [first shell in  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ] and the  $\text{Cr}(\text{H}_2\text{O})_6^{3+}-\text{H}_2\text{O}$  (extra first shell) interactions were described by ab initio potentials whereas the interactions among the water molecules in the bulk solvent were described by the TIP4P model [34]. Finally, a few

chromium-bearing clusters have been investigated with full ab initio methods at different levels of sophistication as is the case of the all-electron, complete active space self-consistent field (CASSCF) calculations of the  $\text{Cr}^+(\text{NO})$  [Cr(I)], and  $\text{Cr}(\text{H}_2\text{O})_5\text{NO}^{2+}$  [Cr(II)] clusters by Shim et al. [36], the Hartree–Fock (HF) calculations of the  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  [Cr(II)], complex by Akesson et al. [37] and the density functional theory (DFT) studies of ligand-to-metal charge transfers and of  $\sigma/\pi$  acceptor/donor trends in the  $\text{M}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{M}=\text{Sc–Fe}$  series of complexes by Kallies and Meier [38].

The theoretical understanding of the water-soluble Cr(III) clusters and their corresponding solvation mechanisms can be deemed satisfactory. However, the theoretical characterization of their low-charged  $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$  ( $n=1-4$ ) counterparts is far from being complete. These types of chromium-bearing clusters are relevant for laser-induced and laser-ablation syntheses of chromium compounds and also for fundamental spectroscopy studies of metal-bearing species in the gas phase, as those previously conducted by the Duncan [8,9], Brucat [28], and Armentrout [29] groups. Therefore, this article intends to provide the first complete theoretical description of the geometries, molecular properties and relative stabilities of the whole series of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$  ( $n=1-4$ ) clusters as a guide for future experimental studies of these fascinating structures.

## 2. Computational details

The explicit treatment of all the electrons in this type of clusters constitutes a demanding computational task. One of the best ways to surmount this difficulty is to make use of electron core potentials (ECP), also known as pseudo-potentials [39], by means of which only the valence electrons are treated explicitly. Therefore, the complete series of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$  ( $n=1-4$ ) clusters are herein calculated at the DFT level of theory with the unrestricted (U), hybrid Becke (B3) [40] exchange and the Lee, Yang and Parr (LYP) [41] correlation functionals [DFT-(U)B3LYP] in conjunction with the Los Alamos ECP double-zeta basis sets (LanL2DZ) [42,43] for the Cr atom and with the ordinary, non-ECP, all-electron 6-31+G\* basis set for the H and O atoms [DFT-(U)B3LYP/LanL2DZ/6-31+G\*]. The combination of an ECP basis set with DFT exchange-correlation functionals might give rise to some reservations because those functionals were originally formulated for core-and-valence electrons basis sets and not for a combination of an ECP with valence electrons. However, the validity and accuracy of the proposed methodology have been established in previous theoretical investigations on similar systems [44–46] and finally summarized in Ref. [2].

All the present DFT computations are performed with the GAUSSIAN 98 program [47]. Each cluster in the  $\text{Cr}(\text{H}_2\text{O})_n^{0,1+}$  ( $n=1-4$ ) series is first geometry optimized at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level for different spin states and the converged structures are subsequently tested for stability by harmonic vibrational frequency analysis. The unrestricted Kohn–Sham (KS) single determinant implicit in the present method is not a spin eigenfunction in general and therefore the obtained states might be spin-contaminated. However, the degree of spin

contamination in all the presently calculated species turns out to be relatively low. For instance, in the attempted septet ( $S=3$ ) state of the  $\text{Cr}(\text{H}_2\text{O})_1^{0+}$  cluster, and in the quartet ( $S=3/2$ ) and sextet ( $S=5/2$ ) states of the  $\text{Cr}(\text{H}_2\text{O})_1^{0+}$  cluster, the KS single determinant expectation values of the total spin operator  $\hat{S}^2$  are successively:  $\langle \hat{S}^2 \rangle = 12.001 \approx S(S+1) = 3(3+1) = 12$ ,  $\langle \hat{S}^2 \rangle = 3.746 \approx S(S+1) = 3/2(3/2+1) = 3.75$ , and  $\langle \hat{S}^2 \rangle = 8.755 \approx S(S+1) = 5/2(5/2+1) = 8.75$ . If an attempted cluster is found to be unstable, efforts are made to obtain a stable structure by deformation along its unstable coordinates. After stable structures are found, their different molecular properties, including bond lengths and angles, total energies, natural orbital population analysis charges, and HOMO–LUMO energy gaps are subsequently calculated. In addition, two important properties to ascertain the stability of the studied structures are their successive hydration dissociation energies  $\text{DE}_C(n,n-1)$  and  $\text{DE}_N(n,n-1)$  for the charged and neutral clusters, respectively, defined according to

$$\text{DE}_C(n,n-1) = E(\text{H}_2\text{O}) + E_T[\text{Cr}(\text{H}_2\text{O})_{n-1}^{1+}] - E_T[\text{Cr}(\text{H}_2\text{O})_n^{1+}];$$

$$\text{DE}_N(n,n-1) = E(\text{H}_2\text{O}) + E_T[\text{Cr}(\text{H}_2\text{O})_{n-1}^{0+}] - E_T[\text{Cr}(\text{H}_2\text{O})_n^{0+}]$$

where  $E(\text{H}_2\text{O})$  is the energy of an isolated  $\text{H}_2\text{O}$  molecule at the B3LYP/6-31+G\* level ( $-76.4213$  hartree), and  $E_T[\text{Cr}(\text{H}_2\text{O})_n^{0,+}] / E_T[\text{Cr}(\text{H}_2\text{O})_{n-1}^{0,+}]$  are the total energies of the

calculated  $\text{Cr}(\text{H}_2\text{O})_n^{0,+}/\text{Cr}(\text{H}_2\text{O})_{n-1}^{0,+}$  clusters at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level. Some relevant values of  $\text{DE}_C(n,n-1)$  and  $\text{DE}_N(n,n-1)$  are presented and discussed below.

### 3. Results and discussion

The most relevant calculated properties of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,+}$  ( $n=1-4$ ) series of clusters at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level are listed in [Tables 1 and 2](#). The clusters total energies  $E_T$  along with their representative bond lengths  $R_1-R_4$  and bond angles  $a_1-a_4$  are presented in [Table 1](#); additionally, the clusters natural orbital population analysis charges on the Cr and O atoms are listed in [Table 2](#). The structures of the most stable spin state  $\text{Cr}(\text{H}_2\text{O})_n^{0,+}$  ( $n=1-4$ ) clusters per each number  $n$  of coordinated  $\text{H}_2\text{O}$  molecules along with their representative bond lengths  $R_1-R_4$  and bond angles  $a_1-a_4$  are depicted in [Fig. 1](#). Additional calculated properties, such as HOMO–LUMO energy gaps and hydration dissociation energies, are presented and discussed below.

In order to preliminarily assess the accuracy of the proposed method in the description of chromium-bearing compounds, the simple  $\text{Cr}_2$  molecule is first optimized at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level; the obtained Cr–Cr bond

**Table 1**  
Geometries and total energies of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,+}$  ( $n=1-4$ ) clusters at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level

Cluster	Symmetry	Spin	$R_1$	$R_2$	$R_3$	$R_4$	$a_1$	$a_2$	$a_3$	$a_4$	$E_T$
$\text{Cr}(\text{H}_2\text{O})^{0+}$	$C_s$	0	1.987				113.1				-162.5402773
		1	2.112				111.2				-162.6026981
		2	2.127				111.8				-162.6836526
		3	2.439				122.5				-162.6958523
$\text{Cr}(\text{H}_2\text{O})^{1+}$	$C_s$	1/2	2.076				126.3				-162.4067265
		3/2	2.043				126.0				-162.4339085
		5/2	2.114				126.6				-162.4895809
$\text{Cr}(\text{H}_2\text{O})_2^{0+}$	$C_1$	0	2.044	2.044			176.4				-239.0147721
		1	2.135	2.135			105.0				-238.9931505
		2	2.094	2.094			179.8				-239.1351098
$\text{Cr}(\text{H}_2\text{O})_2^{1+}$	$C_1$	1/2	2.084	2.084			180.0				-238.8850527
			2.075	2.077			179.7				-238.8890082
			3/2	2.064	2.064		180.0				-238.9189427
$\text{Cr}(\text{H}_2\text{O})_3^{0+}$	$C_1$		2.075	2.101	2.101		180.0				-238.9679874
		0	2.037	2.087	2.262		170.4	74.4	114.5		-315.4484958
		1	2.074	2.098	2.422		176.6	82.1	101.2		-315.5096102
$\text{Cr}(\text{H}_2\text{O})_3^{1+}$	$C_1$	2	2.104	2.138	2.528		174.6	75.4	110.0		-315.5608274
		1/2	2.074	2.051	1.720		87.9	127.7	141.6		-315.3336992
		3/2	2.073	2.073	2.302		173.8	105.6	80.5		-315.3680615
$\text{Cr}(\text{H}_2\text{O})_4^{0+}$	$C_1$	5/2	2.121	2.124	2.461		171.6	77.3	111.2		-315.4142276
		0	2.145	2.119	2.127	2.135	81.3	95.6	81.2	102.0	-391.9208248
		1	2.082	2.082	2.075	2.072	86.6	90.5	91.4	91.4	-391.9448687
$\text{Cr}(\text{H}_2\text{O})_4^{1+}$	$C_1(a)$	2	2.179	2.180	2.179	2.180	89.8	89.8	89.8	89.8	-391.9164939
		1/2	2.113	2.173	2.117	2.179	103.4	76.5	103.5	76.6	-391.7851825
		3/2	2.092	2.083	2.094	2.079	91.1	97.6	86.6	84.6	-391.8206527
	$C_1(b)$	1/2	2.426	2.104	2.147	2.385					-391.7796134
		3/2	2.219	2.092	2.045	4.154					-391.8164625
		5/2	2.531	2.143	2.167	2.522					-391.8566816

Units: Cr–O bond lengths  $R_1-R_4$ , Å; bond angles  $a_1-a_4$ , degree; total energy  $E_T$ , hartree.

Table 2

Natural orbital population analysis charges of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,+}$  ( $n=1-4$ ) clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level

System	Symmetry	Spin	Cr	O(1)	O(2)	O(3)	O(4)
$\text{Cr}(\text{H}_2\text{O})^0+$	$C_s$	0	-0.082	-0.973			
		1	-0.030	-1.022			
		2	-0.016	-1.03			
		3	0.016	-1.040			
$\text{Cr}(\text{H}_2\text{O})^1+$	$C_s$	1/2	0.970	-0.534			
		3/2	0.925	-1.055			
		5/2	0.956	-1.075			
$\text{Cr}(\text{H}_2\text{O})_2^0+$	$C_1$	0	-0.109	-0.981	-0.981		
		1	0.024	-1.023	-1.023		
		2	-0.043	-1.010	-1.010		
$\text{Cr}(\text{H}_2\text{O})_2^1+$	$C_1$	1/2	0.851	-1.042	-1.042		
		3/2	0.841	-1.040	-1.040		
		5/2	0.875	-1.050	-1.050		
$\text{Cr}(\text{H}_2\text{O})_3^0+$	$C_1$	0	-0.107	-0.986	-0.984	-1.025	
		1	-0.039	-1.007	-1.012	-1.044	
		2	0.010	-1.019	-1.032	-1.041	
$\text{Cr}(\text{H}_2\text{O})_3^1+$	$C_1$	1/2	1.159	-0.998	-0.984	-0.885	
		3/2	0.808	-1.025	-1.024	-1.050	
		5/2	0.875	-1.054	-1.043	-1.043	
$\text{Cr}(\text{H}_2\text{O})_4^0+$	$C_1$	0	-0.031	-1.038	-1.000	-1.002	-1.036
		1	0.277	-1.006	-1.013	-1.038	-1.017
		2	0.210	-1.024	-1.024	-1.024	-1.024
$\text{Cr}(\text{H}_2\text{O})_4^1+$	$C_1(a)$	1/2	0.695	-0.999	-1.006	-0.999	-1.008
		3/2	0.668	-0.996	-1.003	-1.003	-0.991
	$C_1(b)$	1/2	0.817	-1.046	-1.022	-1.025	-1.050
		3/2	0.787	-1.049	-1.018	-1.047	-1.016
		5/2	0.869	-1.047	-1.034	-1.040	-1.055

length of 1.799 Å in that  $\text{Cr}_2$  dimer agrees well with both experimental and theoretical results [48,49].

### 3.1. $\text{Cr}(\text{H}_2\text{O})^{0,1+}$ clusters

Neutral  $\text{Cr}(\text{H}_2\text{O})^{0,+}$  clusters with  $C_s$  point-group symmetry and with spin states  $S=0, 1, 2, 3$  and 4 are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged

structures are stable except for the one with  $S=4$ , which exhibits some imaginary frequencies. Inspection of the theoretical results listed in Table 1 shows that in the  $\text{Cr}(\text{H}_2\text{O})^{0,+}$  clusters, the Cr-O bond length  $R_1$  monotonically increases and the total energy  $E_T$  monotonically decreases as the spin number  $S$  increases from 0 to 3. Therefore, the  $\text{Cr}(\text{H}_2\text{O})^{0,+}$  cluster with spin state  $S=3$  is the most stable structure in this series of  $\text{Cr}(\text{H}_2\text{O})^{0,+}$  clusters. In that structure, the Cr atom retains its isolated atomic electronic configuration

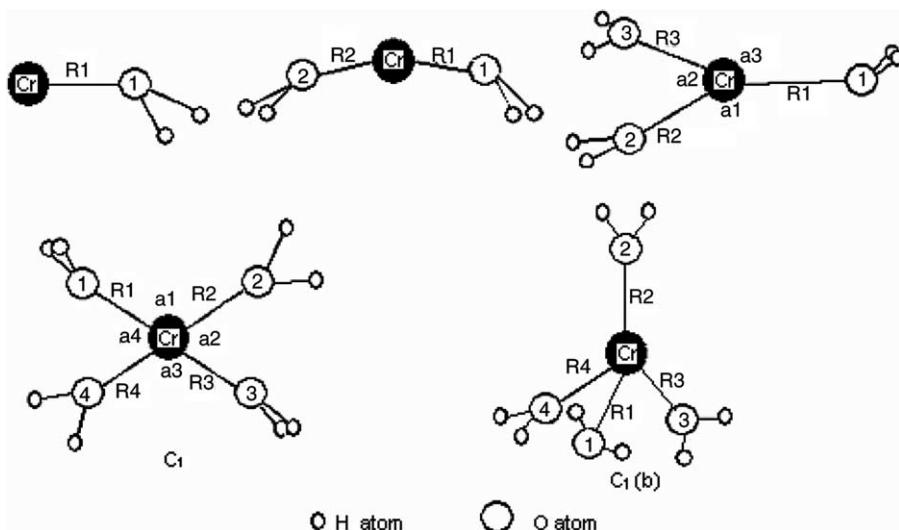


Fig. 1. Structures, bond lengths  $R_1-R_4$ , and bond angles  $a_1-a_4$ , of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,+1}$  ( $n=1-4$ ) clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level.

( $^7\text{A}'$ ). The Cr–O bond length in the most stable  $\text{Cr}(\text{H}_2\text{O})^{0+}$  cluster with  $S=3$  is of 2.439 Å, a value perceptibly longer than the average Cr–O bond length of 1.7 Å [27]. This fact suggests that the interaction between the Cr atom and the  $\text{H}_2\text{O}$  molecule is mainly via weak van der Waals forces as expected if both the Cr and the  $\text{H}_2\text{O}$  remain uncharged upon coordination as seen below. The calculated natural orbital population analysis charges in the  $\text{Cr}(\text{H}_2\text{O})^{0+}$  clusters reveal that the charge on the Cr atom is always negligible but slightly and monotonically increases with the spin number  $S$ . Conversely, the charge on the O atom monotonically and more appreciably decreases with the spin number  $S$  via electron transfers from the H atoms. Despite this internal rearrangements, the net charges on both the Cr and  $\text{H}_2\text{O}$  moieties in all the investigated  $\text{Cr}(\text{H}_2\text{O})^{0+}$  clusters remain close to zero. In addition, the HOMO–LUMO gaps in the  $\text{Cr}(\text{H}_2\text{O})^{0+}$  clusters with spin numbers  $S=0, 1, 2, 3$  are 2.29, 2.76, 2.46 and 2.84 eV, respectively.

Cation  $\text{Cr}(\text{H}_2\text{O})^{1+}$  clusters with  $C_s$  point-group symmetry and spin states  $S=1/2, 3/2, 5/2$  and  $7/2$  are optimized at the (U) B3LYP/LanL2DZ/6-31 + G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable except for the one with  $S=7/2$ , which exhibits some imaginary frequencies. Inspection of the theoretical results listed in Table 1 shows that the total energy  $E_T$  of these  $\text{Cr}(\text{H}_2\text{O})^{1+}$  clusters decreases monotonically as the spin number  $S$  increases from  $1/2$  to  $5/2$ . Therefore, the cluster with spin state  $S=5/2$  is the most stable structure in this series of  $\text{Cr}(\text{H}_2\text{O})^{1+}$  clusters. In that structure, the Cr atom takes a  $^6\text{A}'$  electronic configuration, a result in agreement with previous calculations at the self-consistent field modified coupled pair functional (SCF-MCPF) level [27]. In the most stable  $\text{Cr}(\text{H}_2\text{O})^{1+}$  cluster with  $S=5/2$ , the Cr–O bond length is of 2.114 Å, a value that also agrees well with a previous theoretical result of 2.145 Å at the SCF-MCPF level [27]. Like in the case of the neutral species, the Cr–O bond lengths in the  $\text{Cr}(\text{H}_2\text{O})^{1+}$  clusters are again longer than the average Cr–O chemical bond [27]. The calculated net natural orbital populations for the electrons in the 4 s and 3d subshells of the Cr atom in the most stable  $\text{Cr}(\text{H}_2\text{O})^{1+}$  cluster with  $S=5/2$  are 0.15 and 4.89, respectively, values in good agreement with the previous SCF-MCPF results of 0.15 and 4.90, respectively [27]. In addition, the hydration dissociation energy  $\text{DE}_C(1,0)$  in the most stable  $\text{Cr}(\text{H}_2\text{O})^{1+}$  cluster with  $S=5/2$  is of 34.54 kcal/mol, a value that confirms a previous theoretical result of 31.8 kcal/mol at the SCF-MCPF level [27]. Contrastingly, the hydration dissociation energy  $\text{DE}_N(1,0)$  in the most stable  $\text{Cr}(\text{H}_2\text{O})^{0+}$  cluster with  $S=3$  is of only 4.8 kcal/mol. The fact that  $\text{DE}_N(1,0) \ll \text{DE}_C(1,0)$  is consistent with the view that the Cr– $\text{H}_2\text{O}$  interaction in the  $\text{Cr}(\text{H}_2\text{O})^{0+}$  cluster is mainly of a weaker van der Waals type whereas the  $\text{Cr}^+-\text{H}_2\text{O}$  interaction in the  $\text{Cr}(\text{H}_2\text{O})^{1+}$  cluster is predominantly of a stronger permanent charge ( $\text{Cr}^+$ )–permanent dipole ( $\text{H}_2\text{O}$ ) kind. The good agreement found between several molecular properties at the SCF-MCPF and (U)B3LYP/LanL2DZ/6-31 + G\* levels gives additional support to the use of the latter method for accurately describing the present systems.

### 3.2. $\text{Cr}(\text{H}_2\text{O})_2^{0,1+}$ clusters

Neutral  $\text{Cr}(\text{H}_2\text{O})_2^{0+}$  clusters with  $C_1$  point-group symmetry and with spin states  $S=0, 1, 2$ , and 3 are optimized at the (U) B3LYP/LanL2DZ/6-31 + G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable except for the one with  $S=3$ , which exhibits some imaginary frequencies. On the basis of the calculated total energies  $E_T$ , the  $\text{Cr}(\text{H}_2\text{O})_2^{0+}$  cluster with spin number  $S=2$  is the most stable structure in the present series of  $\text{Cr}(\text{H}_2\text{O})_2^{0+}$  clusters. In that structure, both Cr–O bond lengths are of 2.094 Å, a value that is somewhat longer than the average Cr–O bond length of 1.7 Å. In addition, the hydration dissociation energy  $\text{DE}_N(2,1)$  in the  $\text{Cr}(\text{H}_2\text{O})_2^{0+}$  with  $S=2$  is of 34.74 kcal/mol.

Cation  $\text{Cr}(\text{H}_2\text{O})_2^{1+}$  clusters with  $C_1$  point-group symmetry and with spin numbers  $S=1/2, 3/2$ , and  $5/2$  are optimized at the (U)B3LYP/LanL2DZ/6-31 + G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable without exception. The total energy  $E_T$  in the series of  $\text{Cr}(\text{H}_2\text{O})_2^{1+}$  clusters decreases monotonically as the spin number  $S$  increases from  $1/2$  to  $5/2$ . Therefore, the  $\text{Cr}(\text{H}_2\text{O})_2^{1+}$  cluster with spin number  $S=5/2$  is the most stable structure in this series of  $\text{Cr}(\text{H}_2\text{O})_2^{1+}$  clusters. In that structure, both Cr–O bond lengths are of 2.101 Å, a value that is in good agreement with a previous theoretical result of 2.103 Å at the SCF-MCPF level [27]. In addition, the hydration dissociation energy  $\text{DE}_C(2,1)$  in the most stable  $\text{Cr}(\text{H}_2\text{O})_2^{1+}$  cluster with  $S=5/2$  is of 35.88 kcal/mol, a value that is 1.98 kcal/mol higher than a previous theoretical result at the SCF-MCPF level [27]. Finally, the net natural orbital populations in the 4 s and 3d subshells of the Cr atom in the most stable  $\text{Cr}(\text{H}_2\text{O})_2^{1+}$  cluster with  $S=5/2$  are 0.34 and 4.78, respectively, values that again are close to the SCF-MCPF results of 0.41 and 4.74 [27]. Once again, all these good agreements between the SCF-MCPF and the (U)B3LYP/LanL2DZ/6-31 + G\* results confirm the adequacy of the latter method in the description of the present clusters.

### 3.3. $\text{Cr}(\text{H}_2\text{O})_3^{0,1+}$ clusters

Neutral  $\text{Cr}(\text{H}_2\text{O})_3^{0+}$  clusters with  $C_1$  point-group symmetry and with spin states  $S=0, 1$ , and 2 are optimized at the (U) B3LYP/LanL2DZ/6-31 + G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable without exception. Inspection of the results in Table 1 shows that in this series of clusters, the Cr–O bond lengths  $R_1$ ,  $R_2$  and  $R_3$  monotonically increase and the total energy  $E_T$  monotonically decreases as the spin number  $S$  increases from 0 to 2. Therefore, the  $\text{Cr}(\text{H}_2\text{O})_3^{0+}$  cluster with spin number  $S=2$  is the most stable structure in this series of  $\text{Cr}(\text{H}_2\text{O})_3^{0+}$  clusters. In that structure, the hydration dissociation energy  $\text{DE}_N(3,2)$  is of only 2.822 kcal/mol, a low value suggesting weak van der Waals interactions between the Cr and  $\text{H}_2\text{O}$  moieties.

Cation  $\text{Cr}(\text{H}_2\text{O})_3^{1+}$  clusters with  $C_1$  symmetry and with spin states  $S=1/2, 3/2$ , and  $5/2$  are optimized at the (U)

B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable without exception. Inspection of the calculated results in Table 1 shows that in this series of clusters, the Cr–O bond lengths  $R_1$ ,  $R_2$  and  $R_3$  almost monotonically increase and the total energy  $E_T$  monotonically decreases as the spin number  $S$  increases from 1/2 to 5/2. Therefore, the  $\text{Cr}(\text{H}_2\text{O})_3^{1+}$  cluster with spin number  $S=5/2$  is the most stable structure in this series of  $\text{Cr}(\text{H}_2\text{O})_3^{1+}$  clusters. Additionally, the hydration dissociation energy  $\Delta E_C(3,2)$  in that structure is of 17.0 kcal/mol.

### 3.4. $\text{Cr}(\text{H}_2\text{O})_4^{0,+}$ clusters

Neutral  $\text{Cr}(\text{H}_2\text{O})_4^0$  clusters with  $C_1$  point-group symmetry and with spin states  $S=0, 1, 2$  and  $3$  are optimized at the (U) B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable except for the one with spin number  $S=3$ , which exhibits some imaginary frequencies. Inspection of the calculated results in Table 1 shows that the  $\text{Cr}(\text{H}_2\text{O})_4^0$  cluster with spin number  $S=1$  is the most stable structure in this series of  $\text{Cr}(\text{H}_2\text{O})_4^0$  clusters. In that structure, the four Cr–O bond lengths are about 2.07–2.08 Å, values that are again somewhat longer than the average Cr–O bond length. Remarkably, the natural orbital population analysis charges on the Cr and O atoms in the  $\text{Cr}(\text{H}_2\text{O})_4^0$  clusters with spin numbers  $S=1$  and  $2$  (Table 2) are 0.277, −1.006, −1.013, −1.038 and −1.017; and 0.210, −1.024, −1.024, −1.024 and −1.024, respectively. The charges on the Cr atom in these structures are markedly higher than those in the previously investigated neutral clusters. Therefore, the Cr–O interaction in the  $\text{Cr}(\text{H}_2\text{O})_4^0$  clusters with  $S=1$  and  $2$  must have an increased electrostatic character.

Two isomers of the cation  $\text{Cr}(\text{H}_2\text{O})_4^{1+}$  clusters both with  $C_1$  point-group symmetry, the ‘planar’ and the ‘tetrahedral’  $C_1(a)$  and  $C_1(b)$  structures, respectively, and with spin states  $S=1/2, 3/2$ , and  $5/2$  are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable except for the  $C_1(a)$  isomer with spin number  $S=5/2$ , which exhibits some imaginary frequencies. Inspection of the calculated total energies  $E_T$  listed in Table 1 shows that the stable isomers  $C_1(a)$  and  $C_1(b)$  with the highest spin numbers  $S=3/2$  and  $5/2$ , respectively, are the most stable structures in each isomeric series, being the  $C_1(b)$   $\text{Cr}(\text{H}_2\text{O})_4^{1+}$  isomer with spin number  $S=5/2$  the most stable structure in the whole series of  $\text{Cr}(\text{H}_2\text{O})_4^{1+}$  clusters. In that structure, the hydration dissociation energy  $\Delta E_C(4,3)$  is of 12.486 kcal/mol. Once again, all these ionic clusters exhibit noticeably elongated Cr–O bond lengths. Some attempts have been made to obtain an analogous ‘tetrahedral’  $\text{Cr}(\text{H}_2\text{O})_4^0$  cluster but no stable structure having that geometry has been found yet.

## 4. Concluding remarks

The full series of the  $\text{Cr}(\text{H}_2\text{O})_n^{0,+}$  ( $n=1–4$ ) clusters have been herein systematically investigated at the (U)

B3LYP/LanL2DZ/6-31+G\* level of theory for the first time. Several molecular properties have been calculated for the clusters stable structures, including optimal geometries, total energies, bond lengths, bond angles, natural orbital population analysis charges, hydration dissociation energies, and HOMO–LUMO gaps inter alia. Due to the weak interactions between the Cr ( $\text{Cr}^{1+}$ ) atom (ion) and the  $\text{H}_2\text{O}$  molecules, specially in the case of the neutral clusters, convergence by the self-consistent field algorithm of the (U)B3LYP/LanL2DZ/6-31+G\* method is difficult to reach. In addition, a few converged structures were proven to be unstable under subsequent harmonic vibrational frequency analysis. The present results show a strong correlation between the clusters total energy  $E_T$  and their spin states. Except for the  $C_1$   $\text{Cr}(\text{H}_2\text{O})_2^0$  and  $C_1$   $\text{Cr}(\text{H}_2\text{O})_4^0$  structures, the clusters total energies  $E_T$  decrease monotonically with the spin number  $S$  in both neutral and cationic species. Also, except for the  $C_1$   $\text{Cr}(\text{H}_2\text{O})_4^0$  structure, the most stable clusters are always high-spin in both neutral and cationic species. For all the structures, the Cr–O bond lengths are always in the range of about 2.0–2.5 Å, values that are longer than the average Cr–O bond length. In most of the neutral clusters, natural orbital population analysis charges on the Cr atom are negligible thereby indicating no appreciable electron transfers with the coordinated  $\text{H}_2\text{O}$  molecules. Relevant hydration dissociation energies have been reported and discussed as well. The calculated properties suggest very weak interactions between the Cr ( $\text{Cr}^{1+}$ ) atom (ion) and the  $\text{H}_2\text{O}$  molecules, predominantly of the van der Waals and of the charge-permanent dipole types in the neutral and the cationic clusters, respectively. Comparison of the present results for the  $\text{Cr}(\text{H}_2\text{O})_{1–2}^{1+}$  clusters at the (U)B3LYP/LanL2DZ/6-31+G\* level with available results at the self-consistent field modified coupled pair functional (SCF-MCPF) method [27] shows a good agreement. Present research efforts are directed to a further theoretical characterization of aqueous chromium-bearing clusters and also of related aqueous clusters containing other transition metals (e.g. Ti [50]).

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