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A theoretical investigation on the $Cr(H_2O)_n^{0,1+}$ ($n = 1$–4) clusters by density functional theory methods

Ju-Guang Han, Jorge A. Morales *

Department of Chemistry and Biochemistry, Texas Tech University, P.O. Box 41061, Lubbock, TX 79409-1061, USA

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Abstract

The first systematic study of the $Cr(H_2O)_n^{0,1+}$ ($n = 1-4$) 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 $Cr(H_2O)_4^{0+}$, the most stable clusters in each $Cr(H_2O)_n^{0,1+}$ ($n = 1$–4) series are high-spin states. Comparisons with a few available theoretical results show good agreement.

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 $Cr(H_2O)_n^{3+}$ ($n = 1$–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 $Cr(H_2O)_n^{1+}$ and $Cr(H_2O)_n^{0+}$ ($n = 1$–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 Na^{1+} ion cluster in the gas phase [3], prepared and measured the infrared spectra of the $Cs^{1+}(H_2O)_{1-5}$ series of clusters [4], inferred ion selectivity mechanisms in channel proteins by preparing and studying cluster prototypes of the form $M^{1+}(C_6H_6)_n(H_2O)_m$ with M = Na and K [5,6], and studied theoretically both metallic (Li^+, Na^+, K^+ and Ag^+) and organic [NH_4^+, $C(NH_2)_3^+$ and $N(CH_3)_4^+$] cations solvated with different classes of π 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 $Ca^{1+}(H_2O)$ [8] and $Mg^{1+}(H_2O)$ 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

* Corresponding author. Tel.: +1 806 742 3094; fax: +1 806 742 1289.
E-mail address: jorge.morales@ttu.edu (J.A. Morales).

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primary hydration shells of the $OH^-(H_2O)_n$ and $F^-(H_2O)_n$ clusters in the gas phase do consist of exactly three and four H_2O molecules ($n=3$ and 4). Other important contributions by this group include their spectroscopic and theoretical studies of the $NO^-(H_2O)_{n=1-3}$ [10,11], $OH^-(H_2O)$ [12], $(H_2O)_6$ and $(H_2O)_6^-$ *(magic)* [13,14], $SO_2^-(H_2O)$ [15], and $X^-(H_2O)_2$, (X=F, Cl, Br, 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 $A^-(H_2O)_{1-4}$ ($A^- = ClO_4^-$, HSO_4^-, NO_3^-, $H_2PO_4^-$, HCO_3^-, HCO_2^-, SO_4^{2-}, HPO_4^{2-}, $CO_3^{2-}$and PO_4^{3-}) [19], alkali and alkaline-earth metal cation water clusters $M(H_2O)_{1-6}$ ($M=Li^+$, Na^+, K^+, Mg^{2+}, and Ca^{2+}) [20], and anion–water clusters $A^-(H_2O)_{1-6}$ (A=OH, F, SH, Cl and Br) [21] by Merril et al., and by the study on LiOH dissociation in the $LiOH(H_2O)_n$, $n=1$–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: $Fe^{+1}(H_2O)_{1-4}$ [24], $Fe^{+2}(H_2O)$ [25], and $Fe^{+1}(H_2O)$ [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 $M^{1,2+}(H_2O)_{1-2}$, M=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 $V(H_2O)^{+1}$ complex by Brucat et al. [28], and on the $M^{+1}(H_2O)_{1-4}$, M=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 $Cr(H_2O)_6^{3+}$, $Cr(OH)(H_2O)_5^{2+}$, $Cr(OH)_2(H_2O)_4^+$ and $Cr(OH)SO_4(H_2O)_3$ 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 $Cr(H_2O)_6^{3+}$ complex in solution [31–35]. In one of their most interesting investigations [34], both the Cr^{3+}–H_2O [first shell in $Cr(H_2O)_6^{3+}$] and the $Cr(H_2O)_6^{3+}$–H_2O (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 $Cr^+(NO)$ [Cr(I)], and $Cr(H_2O)_5NO^{2+}$ [Cr(II)] clusters by Shim et al. [36], the Hartree–Fock (HF) calculations of the $Cr(H_2O)_6^{2+}$ [Cr(II)], complex by Akesson et al. [37] and the density functional theory (DFT) studies of ligand-to-metal charge transfers and of σ/π acceptor/donor trends in the $M(H_2O)_6^{3+}$, M=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 $Cr(H_2O)_n^{0,1+}$ ($n=1$–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 $Cr(H_2O)_n^{0,1+}$ ($n=1$–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 $Cr(H_2O)_n^{0,1+}$ ($n=1$–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 $Cr(H_2O)_n^{0,1+}$ ($n=$ 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