A theoretical study of the Y₃O clusters

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Abstract. Hybrid density functional calculations are performed to study the structural and electronic properties of neutral, anionic and cationic Y₃O clusters. The most stable structures of these clusters are found to be triply bridging oxygen atom structures with Cs symmetry. The ground states of Y₃O, Y₃O⁻ and Y₃O⁺ are doublet (1A¹), triplet (1A²) and singlet (1A¹), respectively. The calculated electron affinities and ionization potentials are in good agreement with the available experimental data. Time-dependent density functional theory is used to calculate the low-lying excited states. A theoretical assignment for the features in the experimental photoelectron spectra is given.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 31.15.Ew Density-functional theory – 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.)

1 Introduction

Because of wide applications in many areas, such as high-temperature chemistry, nanotechnology, material science and microelectronics [1–3], transition metal clusters, especially transition metal oxide clusters, have attracted a lot of attention in decades from both theory and experiment. However, our knowledge of transition metal clusters is far from completeness, especially on their excited states. At the same time, the studies about second- or third-row transition metal and transition metal oxide clusters are quite scarce because these clusters have a large number of electrons and electronic states, which makes both spectroscopy studies and theoretical calculations rather difficult.

Photoelectron spectroscopy (PES) is an effective experimental method to study the electronic structure of free molecules and clusters, especially their low-lying excited states. Recently, there are several experimental studies on small yttrium oxide clusters. Knickelbein [4] probed the PES of Y₉O⁺ clusters and measured their electron vertical ionization potentials (IP). Wu and Wang [5] have carried out executed vibrationally resolved photodetachment studies on YO₅⁻ (n = 1–5) clusters. Pramann et al. [6] presented the PES of Y₉O_m−, measured the electron affinities and vertical detachment energies, and discussed some of their structures quantitatively.

From a theoretical point of view, time-dependent density functional theory (TDDFT) methodology [7] has been proved not only to be more satisfactory than CI-Single [8], but also to be a reliable method for calculating excitation energies for the open-shell transition metal oxides clusters [9,10]. Recently, Dai et al. [11] made an assignment based on the TDDFT method for the features in the PES of Y₃O⁻, and got an excellent agreement with the PES.

In this paper we perform a systematic study on Y₃O in its neutral, anionic and cationic charge states using hybrid density functional theory (DFT) and then calculate the excitation energies to assign the features in the available PES using TDDFT. All the calculated results are in good agreement with the available experimental data.

2 Computational detail

All computations are performed with Gaussian98 [12] programs. The hybrid DFT is used in the ground state calculations and the TDDFT in excited states. Both the ground states of Y₃O, Y₃O⁻ and Y₃O⁺, and the excited states of Y₃O are calculated within unrestricted Kohn-Sham formalism with a three-parameter exchange and correlation functional B3LYP [13]. The standard LANL2DZ in Gaussian98 is employed as the basis set, which has been proved to be suitable for the transition metal systems [9,14]. Geometry optimizations are carried out until the gradient forces vanished with respect to a threshold value of 10⁻⁶ a.u. All calculations are performed with (75, 302) pruned grid.

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Pramann et al. [6] presented PES of $Y_3O^-$ and proposed that the geometry structure of $Y_3O$ is most probably a planar $C_{2v}$ structure, very similar as in the case of $V_3O$, $Nb_3O$ and $Ta_3O$ [15]. This conjecture needs to be verified.

When we optimize the structure of $Y_3O^-$, several various initial structures are chosen, such as linear structures (straight or bend), planar structures (rhombic or monocyclic), a triangular $Y_3$ trimer with an oxygen atom at a vertex or with the oxygen inside) and three-dimensional structures. Some of them are transition states with imaginary frequencies. Two stable isomers, a doubly bridging oxygen atom structure with $C_{2v}$ symmetry and a triply bridging oxygen atom structure with $C_{3v}$ symmetry, are found, shown in Figure 1. For both singlets and triplets of $Y_3O^-$, the total energies of $C_{2v}$ structures are higher than those of the triply bridging oxygen atom structures, and are considerably more stable than the doubly bridging oxygen atom structures.

The ground states of the most stable $Y_3O$, $Y_3O^-$ and $Y_3O^{+}$ isomers are doublet ($2\Lambda'$), triplet ($3\Lambda'$) and singlet ($1\Lambda'$), respectively. Figure 1 shows that all the three ground state structures have the same $C_3$ symmetry.

The vibrational frequencies of the $Y_3O$, $Y_3O^-$ and $Y_3O^{+}$ ground states are listed in Table 1. The absence of imaginary frequency indicates that the triply bridging oxygen atom structures indeed correspond to local minima of the potential energy surface. Because of the minor difference for geometries of the three clusters, there exists only a little difference of vibrational frequencies among them.

The electronic configurations are useful to analyze the electronic transitions. For neutral $Y_3O$, the configuration is $2\Lambda''$, i.e., ($1A'^2$ ($2\Lambda''$) ($2\Lambda''$) ($3\Lambda''$) ($4\Lambda''$) ($5\Lambda''$) ($6\Lambda''$) ($7\Lambda''$) ($8\Lambda''$) ($9\Lambda''$) ($10\Lambda''$) ($11\Lambda''$) ($12\Lambda''$) ($7\Lambda''$) ($13\Lambda''$) ($8\Lambda''$))$^1$, for anionic $Y_3O^-$, the configuration is $3\Lambda''$, i.e., ($1A''$) ($2\Lambda''$) ($3\Lambda''$) ($4\Lambda''$) ($5\Lambda''$) ($6\Lambda''$) ($7\Lambda''$) ($8\Lambda''$) ($9\Lambda''$) ($10\Lambda''$) ($11\Lambda''$) ($12\Lambda''$) ($13\Lambda''$) ($14\Lambda''$))$^1$; for cationic $Y_3O^{+}$, the configuration is $1\Lambda'$, i.e., ($1A'$) ($2\Lambda'$) ($3\Lambda'$) ($4\Lambda'$) ($5\Lambda'$) ($6\Lambda'$) ($7\Lambda'$) ($8\Lambda'$) ($9\Lambda'$) ($10\Lambda'$) ($11\Lambda'$) ($12\Lambda'$) ($13\Lambda'$) ($14\Lambda'$) $^1$; for anionic $Y_3O^-$, the configuration is $3\Lambda''$, i.e., ($1A''$) ($2\Lambda''$) ($3\Lambda''$) ($4\Lambda''$) ($5\Lambda''$) ($6\Lambda''$) ($7\Lambda''$) ($8\Lambda''$) ($9\Lambda''$) ($10\Lambda''$) ($11\Lambda''$) ($12\Lambda''$) ($13\Lambda''$) ($14\Lambda''$) $^1$.

Table 2 lists the adiabatic and vertical electron affinities (EAs) and ionization potentials (IPs) for $Y_3O$. Two types of vertical EAs and IPs are defined as follows: in type I, the total energy differences of the neutral molecule and ions are calculated at the optimized molecular geometry; and in type II, they are calculated at the optimized ionic geometry. The vertical EAs and IPs are corresponding to the different experimental processes. For example, the EA$_{vert}$ is corresponding to the measured EA in PES of anions, and the IP$_{vert}$ is corresponding to the measured IP in PES of cations. Our calculated EA$_{ad}(1.22 \text{ eV})$, EA$_{vert}(1.33 \text{ eV})$ and IP$_{vert}(4.84 \text{ eV})$ are in good agreement with experimental value (1.10 ± 0.19) eV [6], (1.33 ± 0.8) eV [6] and 4.92 eV [4], respectively. The calculated

![Figure 1](image-url)