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Theoretical study of the structure and stability of Nb$_x$O$_y$ and Nb$_x$O$_y^+$ ($x = 1$–3; $y = 2$–5, 7, 8) clusters

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Abstract

Geometric, thermodynamic and electronic properties of cluster neutrals Nb$_x$O$_y$ and cations Nb$_x$O$_y^+$ ($x = 1$–3; $y = 2$–5, 7, 8) have been characterized theoretically. A DFT calculation using a hybrid combination of B3LYP with contracted Huzinaga basis sets. Numerical results of the relative stabilities, ionization potentials and band gaps of different clusters are in agreement with experiment. Analysis of dissociation channels supports the more stable building blocks as formed by NbO$_2$, NbO$_2^+$, NbO$_3$ and NbO$_3^+$ stoichiometries. The net atomic charges suggest that oxygen donor molecules can interact more favorably on central niobium atoms of cluster cations, while the interaction with oxygen acceptor molecules is more favorable on the terminal oxygen atoms of neutral clusters. A topological analysis of the electron localization function gradient field indicates that the clusters may be described as having a strong ionic interaction between Nb and O atoms. Published by Elsevier Science B.V.

1. Introduction

Considerable effort has been devoted to the characterization of different kinds of clusters from an experimental and theoretical perspective [1]. Knowledge of the cluster structure is a prerequisite for a quantitative discussion of many physical and chemical properties, providing valuable insight on the development of the properties of condensed matter from those of isolated atoms or molecules [2,3].

Recently, Castleman et al. [4] have studied the clusters belonging to the niobium oxide family using a triple-quadrupole mass spectrometer, finding the building blocks and the corresponding cluster stoichiometry of the most stable species. The study of these structures add to their intrinsic interest, the fact that they constitute surfaces whose study can provide

a proper understanding of their behavior at an atomic scale. Therefore, a complementary theoretical study of bond properties, such as the determination of the equilibrium geometry and dissociation energies and the understanding of the nature of bonding as a function of the size of the clusters is thus of importance in order to have a precise idea of the evolution of the cluster properties. This study affords an opportunity for the interplay between theory and experiment.

Reliable and accurate ab initio calculations on these kinds of systems would be useful since this information is complementary to that obtained using experimental techniques. The density functional theory (DFT) method has gained widespread recognition due to its ability to achieve a considerable degree of success in the computation of molecular

properties on medium to large size molecules [5–8]. DFT has emerged as a computational approach of comparable accuracy to the traditional correlated quantum mechanical methods [9]. In this formalism exchange and correlation are described by a functional of the density and the computational cost is comparable to a Hartree–Fock calculation. Since the precise form of the exchange-correlation functional is unknown, several exchange-correlation functionals have been proposed to approximate the exact functional [10]. Among various proposed functionals, the combination of Becke's three-parameter hybrid exchange functional [11] with the Lee, Yang and Parr correlation functional [12,13], B3LYP [14], is widely used and generally yields good results in the study of various chemical problems [15–22].

Motivated by a desire to provide a bridge between experimental and theoretical works, we present a DFT study for neutral Nb_xO_y and cation $Nb_xO_y^+$ clusters ($x = 1–3$; $y = 2–5, 7, 8$). Moreover, we applied some innovative ideas on the bonding in such clusters, based on the topological analysis of the electron localization function (ELF) [23], following recent achievements in applying this methodology to the understanding of some physical and chemical properties relevant to condensed matter.

The following aspects are considered in this Letter: (i) evaluation of cluster properties, such as equilibrium distances and bond angles and the electronic structure energy as function of cluster size; (ii) calculation of the relative energy and ionization potential of the different clusters; (iii) the understanding of the nature of the chemical bond by using a topological analysis based on the ELF representation; (iv) comparison between our results and experimental data. The layout of this Letter is as follows. The methods and cluster models are summarized in Section 2. The results and discussion are presented in Section 3. Section 4 closes this Letter.

2. Method and model

The calculations have been carried out with the GAUSSIAN 94 program package [24]. The DFT method with a hybrid combination of B3LYP [14] and contracted basis sets for representing atomic centers on niobium $(43333/433/43)$ and oxygen

$(33/3)$ atoms developed by Huzinaga and co-workers [25,26] has been used. Analytical gradient geometry optimizations have been performed for the Nb_xO_y and $Nb_xO_y^+$ ($x = 1–3$; $y = 2–5, 7, 8$) cluster models to obtain the geometry, ionization potential (IP), band gap. The different dissociation channels for each cluster, Mulliken population analysis, natural bond orbital (NBO) [27–29] and atomic density in the sense of Bader [30] for niobium and oxygen atoms have been analyzed. Additionally, geometry optimizations and energy calculations were repeated using B3LYP/3-21G∗. Since these results are very similar, they are not discussed here.

The neutral clusters are doublet electronic states, except Nb_2O_5 which is a singlet electronic state and the corresponding Nb_2O_4 with a triplet electronic state. The cation clusters are singlet electronic states, except $Nb_2O_4^+$ which is a doublet.

Recently Becke and Edgecombe [31] proposed an electron localization function (ELF), which appears to be useful in describing the bonds in a rigorous way. The ELF has been defined as:

$$ELF = \frac{1}{1 + \left(\dfrac{D_\sigma(r)}{D_\sigma^0(r)} \right)^2}$$

where D_σ and D_σ^0 represent the curvature of the electron pair density for electrons of identical spins (Fermi hole) for the actual system and a homogeneous electron gas with the same density, respectively. Savin et al. [32] have proposed an alternative interpretation of the ELF, based on the excess local kinetic energy due to Pauli repulsion. They identified D_σ as the local kinetic energy of the studied fermionic system with respect to a bosonic behavior of the electron density. In the space regions where electrons of opposite spin are found, the excess local kinetic energy is small. Therefore, the ELF is close to 1. However, space regions where electrons of parallel spin are found are characterized by an ELF close to 0. Thanks to the topological analysis of the ELF field, Silvi and Savin [23] proposed a new classification of chemical bonds. The ELF gradient field attractors are called localization attractors and divide themselves in three groups: core, valence bonding and non-bonding attractors. This theory allows the definition of shared and unshared-electron interac-

tions. Shared-electron interactions are characterized with polysinaptic (synaptic order $\geqslant 2$) valence bonding attractors which lie between two (or more) core attractors.

In this Letter, we have adopted a nomenclature of attractors which has been previously defined by Savin et al. [33]. $C(X_i)$ denotes core attractors, where X_i represents the corresponding atom label. $V(X_i)$ and $V(X_i, Y_i)$ represent monosynaptic valence attractors (lone pairs) and disynaptic valence attractors, respectively.

The integration of the density over the basins has been performed with the TopMod program [34], it provides an indication of the ratio of the total electron density involved in a particular bond, a particular lone pair region. However, a strong relative fluctuation of the basin population is related with an important electron delocalization (for more details see Savin et al. [33]). This topological partition of

the electron density provides an alternative to the standard methods of analysis of wavefunctions based on projection techniques. Among such population analysis, the natural population analysis [28,35] does not depend so much upon the nature of the basis set. In particular, the approach based on Weinhold's natural bond orbital (NBO) provides a useful additional tool [27–29].

3. Results and discussion

The structure of the different neutral and cation clusters and the corresponding atom numbering are displayed in Fig. 1. The continuing addition of NbO_2 and NbO_3 onto the niobium and oxygen atoms would be expected to lead the formation of different clusters. Detailed discussion of the structures, relative stability, dissociation energies, band gap, ionization
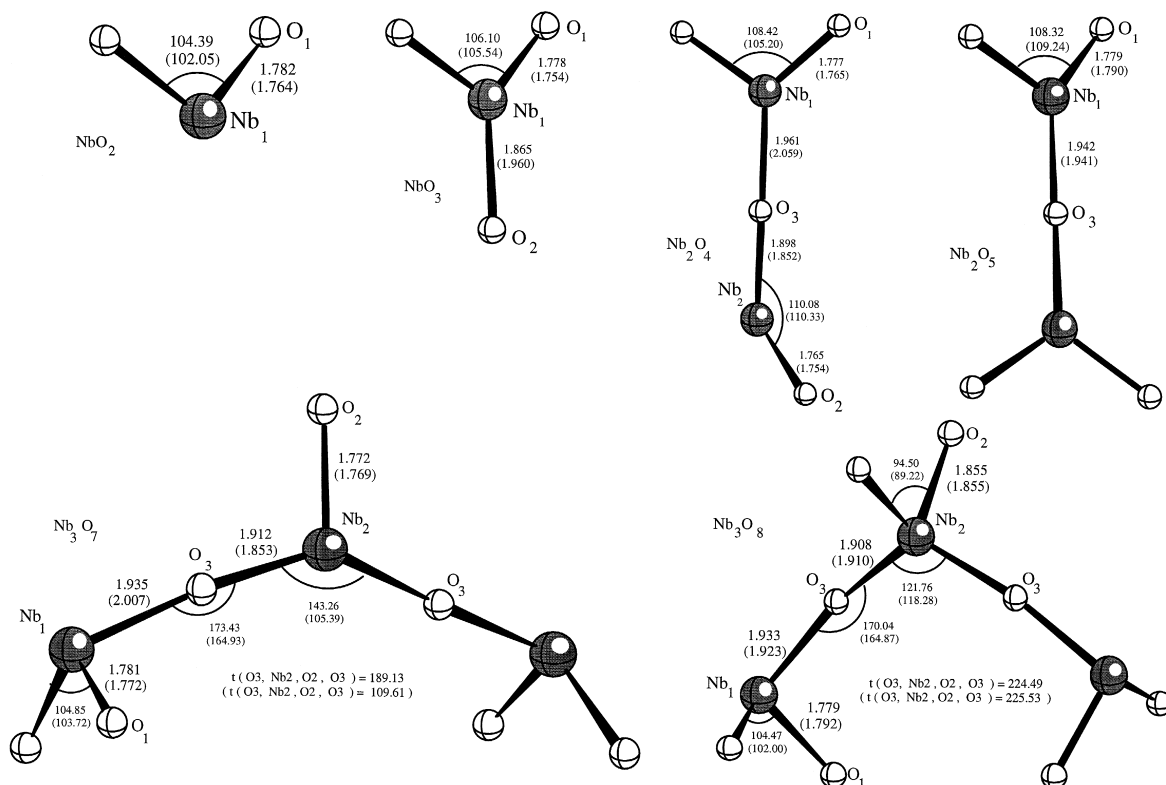

Fig. 1. Selected geometrical parameters for the Nb_xO_y clusters ($x = 1, 2, 3$; $y = 2, 3, 4, 5, 7, 8$). The values in parentheses correspond with the cation system.

potentials and net atomic charges of these clusters are given in the following subsections.

3.1. Optimized geometries

An analysis of the results shows that the bond lengths of bridged Nb_1-O_3 and Nb_2-O_3 bonds are larger than terminal Nb_2-O_2 and Nb_1-O_1 bonds, following the order: $Nb_1-O_3 > Nb_2-O_3 > Nb_2-O_2 > Nb_1-O_1$. The values of the distance for the bridged Nb_1-O_3 bond are in the range of 1.865–2.037 and 1.921–2.059 Å for the neutral and cation niobium oxide clusters, respectively; while, the distance values for the bridged Nb_2-O_3 are within 1.849–1.928 and 1.853–1967 Å for the neutral and cation clusters, respectively. Terminal Nb_2-O_2 and Nb_1-O_1 bonds present shorter values in the range of 1.772–1.958 and 1.772–1.779 Å for neutral clusters, while the corresponding values are within 1.767–1.966 and 1.764–1.790 Å for the cation clusters, respectively. Therefore, the terminal Nb_2-O_3 and Nb_1-O_1 distances have double bond character while the bridged Nb_1-O_3 and Nb_2-O_3 distances correspond with single bonds. For neutral and cation clusters with the same stoichiometry, the values of the $O_1-Nb_1-O_1$ bond angle decrease from the neutral to cation cluster, except for the Nb_2O_5 and $Nb_2O_5^+$ systems.

The niobium atoms of the neutral and cation Nb_xO_y clusters ($x = 1, 2; y = 2, 3, 5$) present a planar arrangement with a coordination number of two or three. However, the central Nb_2 and the terminal Nb_1 niobium atoms of the Nb_3O_7 and $Nb_3O_7^+$ clusters present a three coordination number with a non-planar arrangement. The more complex system Nb_3O_8 shows that the central niobium has a tetrahedral conformation, while a non-planar arrangement with coordination number of three is presented on the terminal niobium centers.

3.2. Energetics

The dissociation energies (ΔE) have been theoretically evaluated as the difference of the total energy of the cluster and the total energy of the corresponding dissociation products in the appropriate spin state. Total energies of the different clusters and ΔE values for the corresponding dissociation channels are given in Table 1. All dissociation channels correspond to exothermic processes.

The results point out that the stability order and therefore the dissociation energies are dependent on the corresponding dissociation channels. The reactive channels that render NbO_3, NbO_3^+, NbO_2 and NbO_2^+ clusters as dissociation products present the larger values of the dissociation energies. Thus, it would be reasonable to conclude that these clusters should be stable systems, being the building blocks of the different clusters.

Important information can be obtained from the relative trends in the ionization potential (IP) and band gap values that are listed in Table 2. The results show that the IP value decreases in the order for the neutral clusters: $NbO_3 > Nb_2O_5 > Nb_3O_8 > Nb_3O_7 > NbO_2 > Nb_2O_4$, indicating that neutral clusters with a larger number of oxygen atoms with respect niobium atoms have higher value of IP. A similar trend is obtained by Castleman et al. [4]. For the cation clusters the results show that the IP value decreases in the order: $NbO_2^+ > NbO_3^+ > Nb_2O_5^+ > Nb_3O_8^+ > Nb_3O_7^+ > Nb_2O_4^+$. The band gap values, computed as the difference HOMO–LUMO, follow the order: $NbO_3 > Nb_3O_8 > NbO_2 > Nb_2O_5 > Nb_3O_7 > Nb_2O_4$ and for the cation clusters: $Nb_2O_5^+ > Nb_3O_7^+ > NbO_2^+ > NbO_3^+ > Nb_2O_4^+ > Nb_3O_8^+$.

Table 1
Total energies (au) and dissociation energies (eV) for the different dissociation channels

Clusters	Total energy (au)	Dissociation channels	ΔE (eV)
(NbO_2)	-3902.048042	–	–
$(NbO_2)^+$	-3901.763601	–	–
(NbO_3)	-3976.775432	–	–
$(NbO_3)^+$	-3976.434211	–	–
(Nb_2O_4)	-7804.165278	$(NbO_2)+(NbO_2)$	-1.88
$(Nb_2O_4)^+$	-7803.912758	$(NbO_2)^+ +(NbO_2)$	-2.75
(Nb_2O_5)	-7878.928476	$(NbO_2)+(NbO_3)$	-2.86
$(Nb_2O_5)^+$	-7878.600421	$(NbO_2)^+ +(NbO_3)$	-1.67
		$(NbO_3)^+ +(NbO_2)$	-3.22
(Nb_3O_7)	-11781.128129	$(NbO_2)+(Nb_2O_5)$	-4.13
$(Nb_3O_7)^+$	-11780.900864	$(NbO_2)^+ +(Nb_2O_5)$	-5.68
		$(Nb_2O_5)^+ +(NbO_2)$	-6.87
(Nb_3O_8)	-11855.863695	$(Nb_2O_5)+(NbO_3)$	-4.35
$(Nb_3O_8)^+$	-11855.502796	$(Nb_2O_5)^+ +(NbO_3)$	-3.45
		$(NbO_3)^+ +(Nb_2O_5)$	-3.81

Table 2
Calculated ionization potentials (eV) and values of band gap (eV) for the different clusters

Clusters	IP (eV)	Band gap (eV)
(NbO_2)	4.90	3.00
$(NbO_2)^+$	14.97	3.35
(NbO_3)	7.01	4.86
$(NbO_3)^+$	14.33	2.68
(Nb_2O_4)	4.63	1.64
$(Nb_2O_4)^+$	10.61	1.63
(Nb_2O_5)	6.64	2.97
$(Nb_2O_5)^+$	13.33	4.17
(Nb_3O_7)	5.24	2.91
$(Nb_3O_7)^+$	10.93	3.49
(Nb_3O_8)	6.59	4.07
$(Nb_3O_8)^+$	11.37	0.52

3.3. Mulliken population, NBO and topological analysis

Some interesting observations emerge from the Mulliken populations and NBO analysis. Both methods render similar results and Mulliken atomic charges are listed in Table 3. The terminal niobium atom Nb_1 has a larger value of positive net atomic charge than the central niobium atom Nb_2 except for the $Nb_3O_7^+$ cation cluster. The Nb_1 center can acts as a Lewis acid. The bridged oxygen atom O_3 presents a larger value of the negative net atomic charge than the terminal oxygen atoms, O_1 or O_2, except for the Nb_3O_8 and $Nb_3O_8^+$ clusters. On going from

Table 3
Net atomic charges (au) on different niobium and oxygen centers of the different clusters

Clusters	Nb_1	Nb_2	O_1	O_2	O_3
(NbO_2)	0.78	–	−0.39	–	–
$(NbO_2)^+$	1.46	–	−0.23	–	–
(NbO_3)	1.14	–	−0.36	–	−0.43
$(NbO_3)^+$	1.55	–	−0.17	–	−0.23
(Nb_2O_4)	1.20	0.69	−0.44	−0.40	−0.60
$(Nb_2O_4)^+$	1.31	1.25	−0.34	−0.32	−0.56
(Nb_2O_5)	1.21	–	−0.44	–	−0.68
$(Nb_2O_5)^+$	1.41	–	−0.30	–	−0.61
(Nb_3O_7)	1.23	0.95	−0.43	−0.43	−0.65
$(Nb_3O_7)^+$	1.31	1.36	−0.35	−0.35	−0.62
(Nb_3O_8)	1.17	1.33	−0.42	−0.37	−0.62
$(Nb_3O_8)^+$	1.31	1.43	−0.33	−0.28	−0.59

Table 4
Basin population ($\bar{N}$) and relative fluctuations ($\lambda(\Omega)$) of NbO_2^+

	$\bar{N}$	$\lambda(\Omega)$
$C(Nb_1)$	10.28	0.19
$C(O_1) \times 2$	2.21	0.15
$V(Nb_1)$	27.66	0.15
$V(O_1) \times 2$	6.80	0.22

neutral to the cation cluster with the same stoichiometry, the net atomic charges of the Nb_1 and Nb_2 centers increases while the negative net atomic charge for the oxygen atoms O_1, O_2 and O_3, decreases. The possible interaction of oxygen donor molecules with these clusters is more favorable on central Nb_2 center of the cation clusters, while the interaction with oxygen acceptor molecules is more favorable on the terminal O_1 center of neutral clusters. We emphasize that the partitioning of the charge density among individual atoms is arbitrary and, in Mulliken analysis, depends on the local basis functions used. In this case the basis set is the same in all calculations and therefore this analysis provide a reasonable measure of charge redistribution.

The localization basins of the ELF gradient field attractors are summarized in Tables 4–6. The basin populations and their relative fluctuations have been calculated for NbO_2^+, Nb_2O_5 and $Nb_3O_7^+$. An analysis of the results shows that the valence basins are only monosynaptic associated with the lone pairs. Therefore, the interactions between Nb and O atoms can be described as purely ionic. In addition, the relative fluctuation of the basin populations is small, indicating that the electrons are not delocalized. In particular there is no noticeable interatomic delocalization since the relative fluctuations of the valence

Table 5
Basin population ($\bar{N}$) and relative fluctuations ($\gamma(\Omega)$) of Nb_2O_5

	$\bar{N}$	$\lambda(\Omega)$
$C(Nb_1) \times 2$	10.52	0.19
$C(O_1) \times 4$	2.22	0.16
$C(O_3)$	2.22	0.16
$V(Nb_1) \times 2$	27.57	0.16
$V(O_1) \times 4$	6.88	0.21
$V(O_3)$	7.24	0.20

Table 6
Basin population ($\bar{N}$) and relative fluctuations ($\lambda(\Omega)$) of $Nb_3O_7^+$

	$\bar{N}$	$\lambda(\Omega)$
$C(Nb_1) \times 2$	10.38	0.19
$C(Nb_2)$	10.40	0.21
$C(O_1) \times 4$	2.22	0.15
$C(O_3) \times 2$	2.21	0.15
$C(O_2)$	2.22	0.16
$V(Nb_1) \times 2$	27.64	0.18
$V(Nb_2)$	27.58	0.18
$V(O_1) \times 4$	6.88	0.21
$V(O_3) \times 2$	6.80	0.20
$V(O_2)$	7.20	0.20

basin of the oxygen lone pairs are of the same order of magnitude as that of the Nb and O cores.

4. Conclusions

A theoretical study on Nb_xO_y and $Nb_xO_y^+$ ($x = 1, 2, 3$; $y = 2, 3, 5, 7, 8$) clusters has been carried out in the present work. The equilibrium geometries, thermodynamic parameters and electronic properties have been calculated. The results of the present study can be summarized as follows:

(i) The relative stabilities, ionization potential and band gap of the different clusters obtained by computer simulation are in agreement with the reported experimental values.

(ii) An analysis of the different dissociation channels supports that the more stable building blocks as formed by NbO_2, NbO_2^+, NbO_3 and NbO_3^+ stoichiometry.

(iii) The net atomic charges points out that the oxygen donor molecules can interact more favorably on terminal niobium atoms of cation clusters, while the interaction with oxygen acceptor molecules is more favorable on the terminal oxygen atoms of neutral clusters.

(iv) A structural and topological analysis shows the absence of disynaptic attractor basins and the interaction between Nb and O atoms can be described as purely ionic.

Acknowledgements

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