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The interplay of the electronic and atomic structure on the stability of cationic $Li_{5+p}O_2^+$ clusters

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Abstract. Cationic $Li_{5+p}O_2^+$ clusters ($0 \leq p \leq 5$) are studied by the use of *ab initio* molecular dynamics within the local spin density approximation and compared to neutral $Li_{4+p}O_2$ species. The topologies of the most stable Li_7O_2 and $Li_{10}O_2$ isomers are shown to change upon ionization. An enhanced stability is obtained in the neutral or ionized clusters whenever the number of the lithiums not bounded to oxygen atoms is equal to half the number p of excess electrons. This results in odd–even oscillations both in the Li detachment energies for the cationic species and the adiabatic ionization potentials of the neutral clusters.

PACS. 36.40.Wa Charged clusters – 71.24.+q Electronic structure of clusters and nanoparticles – 71.15.Pd Molecular dynamics calculations (Car–Parrinello)

1 Introduction

Oxide clusters play an important role in catalysis and oxidation processes, where they are often found as supported nanoparticles or embedded in solid matrices. In addition, free oxide clusters can be considered as prototype systems for understanding the evolution of the oxygen-metal bonding as a function of the cluster size and for comparing the reactivity of small molecular systems to that of bulk compounds.

Among these clusters, metal-rich oxide clusters have attracted the attention of several groups. A nontrivial behavior of the ionization potential in relation to the number of excess metal atoms has been detected in suboxide alkali metal clusters [1, 2], and examined versus the evolution of the work function of thin oxidized alkali films as a function of their degree of oxidation. The first theoretical explanation of the lowering of the work function upon oxidation, based on a quantum confinement effects [3], has been recently confirmed by density functional calculations on small lithium suboxide neutral clusters [4]. In these simulations, the excess electronic states turn out to be preferentially localized around the Li atoms not bound to O, whenever they exist. A correlation between the geometry and the electronic properties has been also invoked to explain the observed electronic shell structure in $Cs_{2m+p}O_m$ clusters [5] and the dissociation behavior of Li-rich Li–O cationic clusters [6]. Both these experimental studies suggest that metal-rich clusters are likely made of an inner ionic core around which the excess metal atoms arrange themselves, giving a quasi-spherical geometry. Density functional studies of $Li_{2m+p}O_m$ clusters [4, 7] have confirmed this picture for a not too small amount of excess metal atoms, while in the small p/m regime, the excess Li atoms are all bound to oxygen; this is in agreement with experimental findings for the Li_4O and Li_5O molecules [8]. On the other hand, both neutral A_p and cationic A_{p+1}^+ elemental alkali metal clusters show an enhanced stability for an even number of electrons ($p = 2n$) [9, 10]. Recent mass spectra of $Li_{2m+p}O_m^+$ clusters show that odd–even alternation depends upon the ratio between the number of excess metal atoms and the total number of lithium atoms [11]. The interplay between the geometrical structure, the degree of delocalization of the excess electrons, and the electron pairing on the stability of these clusters still remains an open question.

In this study, we carry out *ab initio* molecular dynamics simulations [12] of small $Li_{5+p}O_2^+$ clusters ($0 \leq p \leq 5$). We compare the cationic low-energy isomers issued from the present simulations with those previously determined for neutral $Li_{4+p}O_2$ clusters [4]. We discuss the influence of the removal of an electron upon the stability of $Li_{4+p}O_2$ and the difference between the computed vertical and adiabatic ionization potentials, in comparison with elemental Li_p and Li_{p+1}^+ clusters.

2 Computational method

The Car–Parrinello method has widely been applied to the study of metallic, semiconducting, and oxide clusters [7, 13]. Its success relies on the coupling of molecular dynamics, useful for exploring the configuration space of low-symmetry structures, with the use of reliable interatomic forces, derived from the density functional theory (DFT) without *ad hoc* assumptions about the analytical form of the atomic interactions. Various bonding configurations may thus in principle be accounted for with the same accuracy.

The electronic structure is described within the DFT through the use of the local spin density approximation for the exchange and correlation functional [14]. The interaction between valence electrons and ionic cores (consisting of nuclei plus the $1s$ atomic levels for Li and O) is described by the use of soft norm-conserving pseudopotentials [15]. Periodic boundary conditions are used throughout in the calculations. The Kohn–Sham orbitals are thus expanded in plane waves with a kinetic energy cutoff equal to 39 Ry. This approach has already been used, in the study of stoichiometric and nonstoichiometric lithium oxide clusters [16, 17], where the reader can find further computational details.

The charged clusters are simulated by the introduction of a compensating uniform background, and the finite contribution of the background self interaction to the long-range part of the electrostatic energy is taken into account [18]. This method allows a faster convergence of the total energy as a function of the size of the unit cell, as confirmed by extensive tests on charged molecules. In practice, a face-centered cubic cell included in a cubic box 35 a.u. wide was found to be sufficient to ensure that spurious interactions between neighboring periodic images do not bias the computed energy differences between the various isomers and the calculated interatomic distances.

In order to find out the low-energy isomers of $Li_{5+p}O_2^+$ clusters, we start from the geometries previously determined for $Li_{4+p}O_2$ [4], and perform local geometry optimizations. In addition, for most of the composition studied, we carry out a few simulated annealing cycles to look for other possible low-energy configurations. Many isomers are thus found. Among them, we focus on those having the lowest internal energy at zero temperature.

3 Results and discussion

3.1 Description of lowest-energy isomers

The geometries of the lowest-energy cationic $Li_{5+p}O_2^+$ clusters resulting from our simulations are drawn in Fig. 1. In the following, we will use the notations $Li^{(j)}$ to indicate Li atoms which are j-fold coordinated with O. As was already found in neutral $Li_{4+p}O_2$ species [4], the inner cores of all clusters are made up of two oxygens which are linked by either two or three $Li^{(2)}$. Up to and including $Li_6O_2^+$ and Li_7O_2, the Li enrichment of the clusters proceeds by formation of Li–O bonds. For $Li_7O_2^+$ and larger sizes, lithiums, unbound to oxygens, are present in the clusters.

For $p = 0, 1, 3, 4$, the most stable isomers of $Li_{5+p}O_2$ and $Li_{5+p}O_2^+$ show the same configurations, apart from small variations of the bond-lengths. At variance, there is a noteworthy change of topology for Li_7O_2 and $Li_{10}O_2$ upon ionization, as represented in Fig. 1. The $Li_7O_2^+$ isomer is obtained by attachment of a $Li^{(0)}$ atom on $Li_6O_2^+$, while, in Li_7O_2, all lithium atoms are bound to oxygens. The neutral $Li_{10}O_2$ stable isomer has three $Li^{(0)}$, while $Li_{10}O_2^+$ has only two. We can therefore conclude that the number of $Li^{(0)}$ atoms in the most stable isomers depends sensitively upon the charge state of the species. An implication of this result regards the growth mode of lithium oxide clusters. The transition to a growth driven by $Li^{(0)}$–Li bonding occurs earlier in cationic than in neutral lithium oxide clusters.

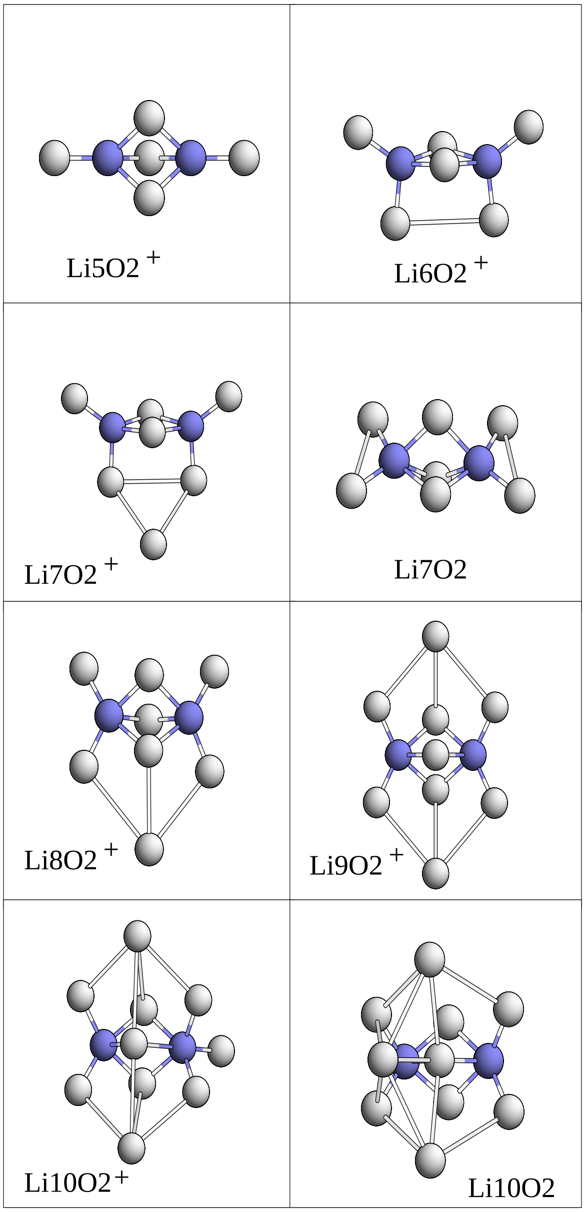

Fig. 1. Geometry of most stable clusters. O atoms are drawn in dark grey, Li in light grey. From the top to the bottom, and from the left to the right (the group symmetry is given in brackets): $Li_5O_2^+$ (C_{3v}), $Li_6O_2^+$ (C_{2v}), $Li_7O_2^+$ (C_s), Li_7O_2 (C_s), $Li_8O_2^+$ (C_s), $Li_9O_2^+$ (C_{2v}), $Li_{10}O_2^+$ (C_s), and $Li_{10}O_2$ (C_s).

As regards the influence of the charge state on bond lengths, we find that the O–$Li^{(1)}$ and O–$Li^{(2)}$ interatomic distances are changed by less than 1%, while dilations of the $Li^{(0)}$–Li distances as large as 4% occur. On general grounds, bond dilation is induced by ionization, since the electrostatic repulsion between the ions is less effectively screened. In this particular case, it helps us to anticipate that the lack of one electron mainly affects the $\mathrm{Li}^{(0)}$–Li bonds.

As in the case of $\mathrm{Li}_{4+p}\mathrm{O}_2$ neutral clusters, the key in a discussion of isomer stability is the distinction among inequivalent $\mathrm{Li}^{(j)}$. We have stressed previously [4] that the excess electrons are preferentially accomodated around the available $\mathrm{Li}^{(0)}$, because of the weakest electrostatic potential felt by the latter. Thus, the isomers having as many $\mathrm{Li}^{(0)}$ as half the number p of excess electrons show an enhanced stability when the $\mathrm{Li}^{(0)}$ can be coordinated with a large number of other lithiums. This occurs for $\mathrm{Li}_7\mathrm{O}_2^+$ ($p=2$ and 1 $\mathrm{Li}^{(0)}$), $\mathrm{Li}_9\mathrm{O}_2^+$ ($p=4$ and 2 $\mathrm{Li}^{(0)}$), and $\mathrm{Li}_{10}\mathrm{O}_2$ ($p=6$ and 3 $\mathrm{Li}^{(0)}$). It should be noted that $\mathrm{Li}_8\mathrm{O}_2$ represents an exception to this rule, according to which a topology with two $\mathrm{Li}^{(0)}$, rather than one, would be predicted. Actually, the $\mathrm{Li}_8\mathrm{O}_2$ isomer with a single $\mathrm{Li}^{(0)}$ is the most stable, because of its magnetic ground state [4]. Also, a $\mathrm{Li}^{(0)}$ could in principle be expected in $\mathrm{Li}_6\mathrm{O}_2$, but the number of $\mathrm{Li}^{(0)}$–Li bonds would likely be insufficient to stabilize the cluster. As far as the species bearing an odd number of electrons are concerned, their stability is less obviously driven by the number of $\mathrm{Li}^{(0)}$. Indeed, the energy gain obtained when the highest occupied molecular orbital (HOMO) is accomodated on a $\mathrm{Li}^{(0)}$ rather than on a $\mathrm{Li}^{(1)}$ gets reduced because of the lack of the electron pairing, so that more subtle factors may compete to determine the geometry of the most stable isomers.

Table 1. Excess binding energies $\Delta E_{\mathrm{b}}^{(0)}$, $\Delta E_{\mathrm{b}}^{(+)}$ and Li detachment energies $D_{\mathrm{Li}}^{(0)}$, $D_{\mathrm{Li}}^{(+)}$ for the most stable neutral $\mathrm{Li}_{4+p}\mathrm{O}_2$ and cationic $\mathrm{Li}_{5+p}\mathrm{O}_2^+$ clusters, respectively, as a function of the number of excess electrons p (see text for definition). All energies are in eV.

p	$\Delta E_{\mathrm{b}}^{(0)}$	$\Delta E_{\mathrm{b}}^{(+)}$	$D_{\mathrm{Li}}^{(0)}$	$D_{\mathrm{Li}}^{(+)}$
1	2.58	1.53	2.58	1.53
2	2.23	1.54	1.88	1.54
3	1.94	1.48	1.37	1.38
4	1.83	1.54	1.49	1.72
5	1.77	1.485	1.54	1.25
6	1.73		1.50	

Table 2. Vertical [4] (adiabatic) ionization potential I_{v} (I_{a}) of neutral $\mathrm{Li}_{4+p}\mathrm{O}_2$ most stable isomers (second and third column). Their difference is given in fourth column. Columns 5 to 7: I_{v}, I_{a}, and $I_{\mathrm{v}}-I_{\mathrm{a}}$ for elemental Li_p clusters, from [10]. All the values are in eV.

p	I_{v}	I_{a}	$I_{\mathrm{v}}-I_{\mathrm{a}}$	I_{v}	I_{a}	$I_{\mathrm{v}}-I_{\mathrm{a}}$
1	3.46	3.45	0.01			
2	3.79	3.78	0.01			
3	3.84	3.62	0.22	4.18	3.95	0.23
4	3.82	3.72	0.10	4.61	4.55	0.06
5	3.63	3.55	0.12	4.48	4.15	0.33
6	3.95	3.79	0.16	4.53	4.32	0.21

3.2 Binding energy and ionization potentials

In Table 1 we report the excess binding energy, defined as $\Delta E_{\mathrm{b}}^{(0)}(p)=\frac{E(\mathrm{Li}_4\mathrm{O}_2)+pE(\mathrm{Li})-E(\mathrm{Li}_{4+p}\mathrm{O}_2)}{p}$ and $\Delta E_{\mathrm{b}}^{(+)}(p)=\frac{E(\mathrm{Li}_5\mathrm{O}_2^+)+pE(\mathrm{Li})-E(\mathrm{Li}_{5+p}\mathrm{O}_2^+)}{p}$ for the neutral and the cationic nonstoichiometric clusters, respectively. Note that the reference clusters are $\mathrm{Li}_4\mathrm{O}_2$ for the neutral and $\mathrm{Li}_5\mathrm{O}_2^+$ for the cationic series, which both have the exact number of electrons necessary to fill all the valence states (no excess electrons). $\Delta E_{\mathrm{b}}^{(0)}(p)$ and $\Delta E_{\mathrm{b}}^{(+)}(p)$ are both a measure of the average excess binding energy related to the Li enrichment of the clusters. $\Delta E_{\mathrm{b}}^{(0)}(p)$ and $\Delta E_{\mathrm{b}}^{(+)}(p)$ give an indication of their overall stability and may be compared with the binding energy per valence electron of pure Li_p and Li_{p+1}^+ clusters.

A complementary quantity, also given in Table 1, is the energy gain due to the detachment of a Li atom, defined as $D_{\mathrm{Li}}^{(0)}(p)=E(\mathrm{Li}_{4+p-1}\mathrm{O}_2)+E(\mathrm{Li})-E(\mathrm{Li}_{4+p}\mathrm{O}_2)$ and $D_{\mathrm{Li}}^{(+)}(p)=E(\mathrm{Li}_{5+p-1}\mathrm{O}_2^+)+E(\mathrm{Li})-E(\mathrm{Li}_{5+p}\mathrm{O}_2^+)$ for the neutral and cationic series, respectively. These energies are relevant in the process of evaporation of a single Li atom from the clusters. One should note that our computed $D_{\mathrm{Li}}^{(+)}(p)$ are in satisfactory agreement with the value of 1.3 eV derived from experiments on $\mathrm{Li}_{2m+p}\mathrm{O}_m^+$ clusters [6], given that temperature effects are not taken into account in the present calculation.

In the neutral $\mathrm{Li}_{4+p}\mathrm{O}_2$ series, the rapid decrease of $\Delta E_{\mathrm{b}}^{(0)}(p)$ at the beginning of the series correlates with a strong reduction of $D_{\mathrm{Li}}^{(0)}(p)$. It is a signature of the progressive weakening of the Li–O ionic bond [4], which opens the way to the mechanism of Li enrichment by formation of $\mathrm{Li}^{(0)}$–Li bonds. This second stage in the growth is characterized by $D_{\mathrm{Li}}^{(0)}(p)\simeq 1.5$ eV, close to the experimental value of Li binding energy in bulk Li (1.63 eV)

In the cationic series, $\Delta E_{\mathrm{b}}^{(+)}(p)$ shows a rather different behavior. Firstly, it is systematically lower ($\simeq 1.5$ eV) than $\Delta E_{\mathrm{b}}^{(0)}(p)$, and secondly, it shows odd–even oscillations as a function of the number of excess electrons. The first result is not unexpected, since the lack of one electron appreciably decreases the screening of the electrostatic repulsion between the ions. The difference between $\Delta E_{\mathrm{b}}^{(+)}(p)$ and $\Delta E_{\mathrm{b}}^{(0)}(p)$ would likely decrease at larger sizes than those considered here. Odd–even oscillations of $\Delta E_{\mathrm{b}}^{(+)}(p)$ and $D_{\mathrm{Li}}^{(+)}(p)$ as functions of p are more evident than in their counterparts for neutral clusters ($\Delta E_{\mathrm{b}}^{(0)}$ and $D_{\mathrm{Li}}^{(0)}$, respectively). They present an analogy with the findings for pure lithium clusters [10,19]. This reveals the enhanced stability of cationic clusters with an even number of excess electrons ($p=2n$) with respect to the evaporation of a Li monomer. In this respect, the cationic $\mathrm{Li}_{5+p}\mathrm{O}_2^+$ series is more akin to pure lithium clusters than the neutral $\mathrm{Li}_{4+p}\mathrm{O}_2$. We also note that the odd–even oscillations are less evident at the very beginning of the series, in agreement with recent experiments [11].

The different stability of neutral and cationic clusters has implications for the behavior of the ionization potential as a function of p. The vertical and adiabatic ionization potentials (I_v and I_a respectively) of the most stable $\mathrm{Li}_{4+p}\mathrm{O}_2$ isomers, computed by means of total-energy differences, are collected in Table 2 (left part) and compared to those of elemental Li_p clusters (right part). Our computed I_a are in good agreement with the ionization potentials recently measured for lithium oxide clusters [20]. Not surprisingly, the largest $I_\mathrm{v} - I_\mathrm{a}$ differences are found for the clusters whose topology changes upon ionization ($p = 3, 6$). This is also true for elemental clusters [10], whose shapes are more sensitive to the overall charge than are those of the oxide clusters considered here.

The adiabatic ionization potentials I_a of the oxide clusters show also odd–even oscillations. In a previous work [17] we found that, for particular cluster families with the same inner core and without $\mathrm{Li}^{(0)}$, the excess electron levels are almost equally spaced, and are smoothly decreasing functions of the cluster size, a fact which can account for the odd–even staggering [21]. Moreover, the HOMO level can be lowered by means of structural deformations; this favors the appearance of $\mathrm{Li}^{(0)}$ in the oxide clusters. This is the case, in particular, for $\mathrm{Li}_7\mathrm{O}_2^+$, $\mathrm{Li}_9\mathrm{O}_2^+$, and $\mathrm{Li}_{10}\mathrm{O}_2$, and the magnetic $\mathrm{Li}_8\mathrm{O}_2$ isomer [4], which show an enhanced stability. Accordingly, the odd–even oscillations are more evident in I_a than in I_v, for both $\mathrm{Li}_{4+p}\mathrm{O}_2$ and Li_p. In addition, we note that at low p, $I_\mathrm{a}(\mathrm{Li}_p)$ shows more marked odd–even oscillations than $I_\mathrm{a}(\mathrm{Li}_{4+p}\mathrm{O}_2)$. This may be due to the less flexible topologies of the oxide clusters, which have a more rigid ionic core with only two possible conformations (two or three $\mathrm{Li}^{(2)}$; see Fig. 1 and [4,16]). Indeed, the stiffer the system, the weaker the odd–even staggering [21,22].

4 Conclusions

We have studied the atomic and electronic structure and the energetics of cationic $\mathrm{Li}_{5+p}\mathrm{O}_2^+$ clusters, as issued from Car–Parrinello simulations, and we have compared their characteristics to those found previously for their neutral counterparts. The influence of the charge state on the cluster topology happens to be crucial for $\mathrm{Li}_7\mathrm{O}_2$ and $\mathrm{Li}_{10}\mathrm{O}_2$. We have stressed the role played by lithium atoms unbound to oxygens ($\mathrm{Li}^{(0)}$). These $\mathrm{Li}^{(0)}$ atoms can accomodate the excess electrons in low-lying electronic levels. Cluster stability thus results from an interplay between the number of available $\mathrm{Li}^{(0)}$ and the number p of excess electrons to be accomodated. This interpretative framework accounts for the large stability of $\mathrm{Li}_7\mathrm{O}_2^+$, $\mathrm{Li}_9\mathrm{O}_2^+$, and $\mathrm{Li}_{10}\mathrm{O}_2$, which have an even number of excess electrons p – making possible the electron pairing – and exactly $p/2$ $\mathrm{Li}^{(0)}$ atoms, coordinated with a large number of other lithiums.

We have discussed the implications of these results on measurable quantities, such as the Li detachment energy and the adiabatic ionization potential. We have shown that the latter displays odd–even oscillations as a function of the number of excess electrons. They result from the interplay of the electronic, geometric, and magnetic effects which drive the cluster topologies, and not solely from the electron pairing. A systematic study of larger $\mathrm{Li}_{5+p}\mathrm{O}_2^+$ clusters is currently in progress, in order to investigate the possible occurrence of electronic shells.

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