Physica E: Low-dimensional Systems and Nanostructures 97 (2018) 368–374

Contents lists available at ScienceDirect

Physica E: Low-dimensional Systems and Nanostructures

journal homepage: www.elsevier.com/locate/physe

Wobbled electronic properties of lithium clusters: Deterministic approach through first principles

Anoop Kumar Kushwaha [a,*], Saroj Kumar Nayak [a,b]

[a] School of Basic Sciences, Indian Institute of Technology, Bhubaneswar, 751007, India
[b] Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute Troy, NY, 12180, United States

ARTICLE INFO

Keywords:
Lithium clusters
Binding energy
Polarizability
Li_n-MeCN electrostatic interaction

ABSTRACT

The innate tendency to form dendritic growth promoted through cluster formation leading to the failure of a Li-ion battery system have drawn significant attention of the researchers towards the effective destabilization of the cluster growth through selective implementation of electrolytic media such as acetonitrile (MeCN). In the present work, using first principles density functional theory and continuum dielectric model, we have investigated the origin of oscillatory nature of binding energy per atom of Li_n ($n \leq 8$) under the influence of MeCN. In the gas phase, we found that static mean polarizability is strongly correlated with binding energy and shows oscillatory nature with cluster size due to the open shell of Li_n cluster. However, in acetonitrile medium, the binding energy has been correlated with electrostatic $Li_n - $MeCN interaction and it has been found that both of them possess wobbled behavior characterized by the cluster size.

1. Introduction

Studying the variation of electronic properties of metallic clusters and their causal factors has great importance from both academic and practical point of view. Being the lightest of all metals, lithium clusters (Li_n) are the most theoretically investigated clusters to date due to the exceptionally strong correlation between their electronic structure and size as well as geometry. Interestingly, for the past few years, small Li_n have received considerable attention due primarily to their innate property to form clusters at normal condition which leads to the dendrite formation in lithium battery. Recently, Singh et al. and his group have found that, at low concentrations, lithium ions tend to spread out on graphene (for anode in Li-ion battery) and with increase in the Li content, small Li_n clusters have been identified which can potentially nucleate to form Li dendrite, leading to device failure [1]. In 2014, Pokorney et al. reported the novel mechanism behind the premature and accelerated battery failure in St. Jude Medical Fortify Assura implantable cardioverter defibrillators (ICDs) [2]. The apparent reason being the lithium cluster formation between the battery electrodes, which resulted in a short circuit and triggered a subsequent catastrophic battery depletion [2–4]. Stability and optimization of the current Li-ion technology, thus, require further in-depth analyses, which is why the study of lithium clusters appears to be of immense importance from a practical point of view.

Lithium clusters are potential contenders for prototype systems because of the unique size dependent electronic properties (i.e. ionization potential, electron affinity, polarizability, binding energy, etc.) they possess, which have been well investigated implementing both theoretical and experimental methods [5–10]. However, though seemingly simple, there are stiff challenges for theorists and experimentalists when it comes to Li clusters solvated in dielectric polar/nonpolar solvents. The solvent environment plays a decisive role in many molecular processes [11,12] further affecting the electronic structure of the metallic clusters [13,14]. Interaction between the solvent and the metal atoms (on the surface of the cluster) has been known to bring significant change to the electronic structure of the metallic cluster. To account for the electrostatic interaction (solvation energy), it is desirable to include explicit solvent molecules [12,15,16]. However, such calculation could be computationally expensive due to large size of the system, therefore implicit solvent models offer an efficient alternative [17,18]. The basis of the implicit continuum model is the sharp boundary between the solute and the bulk of the solvent, represented as a structureless polarizable medium, characterized by its dielectric constant. In these models, the molecule/cluster under investigation is located inside a cavity surrounded by a homogeneous dielectric medium of the solvent.

Acetonitrile (MeCN) is a dipolar aprotic solvent having dipole moment and polarizability of the order of 3.93 D and 4.48 $/^3$ (for MeCN monomer), respectively, which are very much close to those of water

---

* Corresponding author.
E-mail address: ak20@iitbbs.ac.in (A.K. Kushwaha).

https://doi.org/10.1016/j.physe.2017.12.009
Received 12 June 2017; Received in revised form 3 October 2017; Accepted 1 December 2017
Available online 5 December 2017
1386-9477/© 2017 Elsevier B.V. All rights reserved.

[19]. MeCN shows excellent stability towards reduced O_2 species and has great importance in Li-air battery technology [20]. There are a number of theoretical calculations that have focused on the structure of lithium cluster [8,10,21–25]. Further investigations have also been done for systems containing lithium ion/salt solvated in various organic solvents (i.e. ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, acetonitrile etc.) [11,12,16,20,26–29]. However, most of the computational analyses have focused on either structural/electronic properties of lithium cluster in gas phase or lithium ion solvation properties in solvent phase. Although Hou et al. reported that the dielectric continuum solvent affects the electronic properties i.e. binding energy, HOMO-LUMO gap, polarizability of metallic cluster of different size [14], further reports on such systems involving metallic clusters and organic solvents is rather scarce.

Binding energy is a fundamental property of molecule/cluster which could help predict the relative stability. There are several experimental and theoretical reports which suggest that BE/n of Li_n in the gas phase shows a monotonous increment with the addition of a single atom to the cluster [8,10,14,24,30]. In the present study, it is observed that the BE/n of Li_n in the gas phase shows monotonous increment. However, inside a continuum dielectric medium like acetonitrile, the BE/n of Li_n shows oscillatory variation with increasing number of atoms in the cluster. To get more insight, we have implemented ab-initio molecular orbital formalism [31,32] based on density functional theory [33,34] to calculate natural population analysis (NPA) charge, static mean polarizability and Li_n-MeCN electrostatic interaction which would unravel the origin of odd-even oscillation of BE/n of Li_n in the acetonitrile phase. Furthermore, we describe, details of our methodology and theoretical scheme followed by results and relevant discussions.

2. Theoretical method and computational details

2.1. Normalized binding energy

The normalized binding energy of Li_n in gas phase and in acetonitrile phase can be defined by the following formula;

$$\mathrm{E_b}(Li_n, GP) = \frac{nE(Li, GP) - E(Li_n, GP)}{n} \tag{1}$$

$$\mathrm{E_b}(Li_n, MeCN) = \frac{nE(Li, MeCN) - E(Li_n, MeCN)}{n} \tag{2}$$

where $E(Li_n, GP)$ and $E(Li_n, MeCN)$ are the total energy of a lithium cluster having n lithium atoms in GP and after solvation of Li_n cluster in acetonitrile phase, respectively. Whereas, $E(Li, GP)$ and $E(Li, MeCN)$ are the total energy of single lithium atom in GP and after solvated in acetonitrile phase, respectively.

2.2. Polarizability

We have investigated the polarizabilities of the optimized neutral Li_n cluster as a function of the cluster size. Polarizability is a static response property of the atomic/molecular/cluster based system which can be correlated to the perturbation due to an external electric field. The polarizability of a molecule/cluster can be obtained by the expansion of the field–dependent energy $(E(\vec{F}))$. The $E(\vec{F})$ can be expanded in a series of components of the uniform electric field $\vec{F}$,

$$E(\vec{F}) = E(0) + \sum_i \mu_i F_i + \frac{1}{2}\sum_{ij}^{n} \alpha_{ij} F_i F_j + \cdots\cdots \tag{3}$$

where $E(0)$ is the energy of the molecule/cluster in the absence of the electric field. $\mathrm{F_i}$ and $\mathrm{F_j}$ are the components of applied electric field whereas μ_i is the component of static dipole moment tensor. The quantity α_{ij} is the components of the static dipole polarizability tensor and can be calculated by considering the second-order derivative (with respect to components of the electric field) of the energy i.e.

$$\alpha_{ij} = \left(\frac{\partial^2 E}{\partial F_i \partial F_j}\right) \quad F = 0 \tag{4}$$

The equal value to the components of dipole polarizability (i.e. $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$) shows the spherical symmetric nature of the molecule/cluster. The static mean polarizability is computed through the trace of polarizability tensor as;

$$\langle\alpha\rangle = \frac{1}{3} tr(\alpha_{ij}) = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{5}$$

2.3. Li_n–MeCN electrostatic interaction term

The binding energy of a lithium cluster can be calculated by taking the consideration of difference between the energy of a lithium atom with concerned lithium cluster. The calculation of solvent effects on the energies is straight-forward in case of molecular mechanics, while in the case of quantum calculation, it is required a correction in the molecular Hamiltonian with a suitable solute solvent interaction operator (in general PCM operator), which is defined as;

$$\hat{V}^R = \sum_i q\left(\vec{s_i}\right)\hat{V}\left(\vec{s_i}\right). \tag{6}$$

where $\hat{V}(\vec{s_i})$ indicates the electrostatic potential operator calculated on the surface tesserae. The operator $\hat{V}^R$ modifies the solute molecule Hamiltonian and also polarizes the solute electronic wavefunction.

$$\hat{\mathscr{H}}^0(in\ \ GP) \rightarrow \hat{\mathscr{H}}^{eff}\left(= \hat{\mathscr{H}}^0 + \hat{V}^R\right)(in\ \ solution)$$

$$\Psi^0(GP) \rightarrow \Psi(in\ \ solution)$$

Thus, due to the presence of the solution, the electronic Schrodinger equation transforms to,

$$\hat{\mathscr{H}}^{eff}|\Psi\rangle = \left[\hat{\mathscr{H}}^0 + \frac{1}{2}\hat{V}^R\right]|\Psi\rangle = E|\Psi\rangle \tag{7}$$

where $\hat{\mathscr{H}}^{eff}$ is the effective Hamiltonian of Li_n cluster and $|\Psi\rangle$ is the corresponding polarized/perturbed wave function in the presence of a dielectric medium. The effective Hamiltonian assumes a nonlinear characteristic as the solvent-induced operator which depends on the solute charge distribution through the PCM charges. The electrostatic interaction energy between polarized solute and the solvent, which corresponds to the integral $\langle\Psi|\hat{V}^R|\Psi\rangle$, predicts the total energy incorporating all PCM corrections. One-half of this energy corresponds to the polarization work spent to create the charge density inside the dielectric.

2.4. Computational details

The most stable isomer of each Li_n cluster has been selected for our study on the basis of earlier reports. For the optimization and single point energy calculation of the stable isomers, we apply the density functional theory (DFT) based calculation. In the DFT, different approximations are used to define the exchange correlation function. For our calculation, we have considered local density approximation (LDA) and hybrid functional. We separately employ the Slater-Vosko-Wilk-Nusair (SVWN) and B3LYP functionals to confirm variation in the binding energy of the lithium cluster. The functional B3LYP consists of Becke's 1988 gradient corrected exchange functional and Lee, Yang, and Parr (LYP)'s correlation functional [35,36]. In the gas phase, the stable geometry of Li_n clusters are optimized separately with both B3LYP and SVWN functional having the same basis set 6-31 + G(d). During optimization of the Li_n

Download English Version:

https://daneshyari.com/en/article/7933903

Download Persian Version:

https://daneshyari.com/article/7933903

Daneshyari.com