

A theoretical analysis of bi-metallic $(\text{Cu-Ag})_{n=1-7}$ nano alloy clusters invoking DFT based descriptors

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Due to its large scale applications in the real field, the study of bi-metallic nano-alloy clusters is an active field of research. Though a number of experimental reports are available in this domain, a deep theoretical insight is yet to receive. Among several nano-clusters, the compound formed between Cu-Ag has gained a large importance due to its remarkable optical property. Density Functional Theory (DFT) is one of the most popular approaches of quantum mechanics to study the electronic properties of materials. Conceptually, DFT based descriptors have turned to be indispensable tools for analyzing and correlating the experimental properties of compounds. In this venture, we have analyzed the experimental properties of the $(\text{Cu-Ag})_{n=1-7}$ nano-alloy clusters invoking DFT methodology. A nice correlation has been found between optical properties of the aforesaid nano-clusters with our evaluated theoretical descriptors. The similar agreement between experimental bond length and computed data is also reflected in this analysis. Beside these, the effect of even-odd alternation behavior of nano compounds on the HOMO-LUMO gap is very important in our computation. It is probably the first attempt to establish such type of correlation.

Keywords: *Density Functional Theory; bi-metallic nano-alloy; hardness; softness; electrophilicity index*

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1. Introduction

Due to existence of a large number of quantum mechanical and electronic effects, nanoparticles possess unique physicochemical properties [1–4]. The classification of nanoparticles is done in terms of size ranging from 1 to 100 nm. That particular size range exists between the level of atomic/molecular and bulk material [5]. However, there are still some instances of nonlinear transition of certain physical properties, which may vary depending on the size, shape and composition [6, 7]. A large number of available scientific reports describe the effects of size and structure which change the optical, electronic, magnetic, chemical and other physical properties of nanoparticles [1, 3, 4]. The outstanding work reported by Dawid and Gburski [8] nicely explained the dynamical behavior of argon-krypton clusters and also made a comparison with monoatomic

Ar₁₃ cluster. A deep insight into the research of nanoparticles with well-defined size and structure may lead to some other alternatives for better performance [9]. The nanoparticles, due to their vast applications in the areas, such as biological labeling, photochemistry, catalysis, information storage, magnetic device, optics, sensors, photonics, optoelectronics, nanoelectronics, etc., are of immense importance [1, 3, 10–12].

Noble metals can be extensively applied in several technological areas due to their superior catalytic, magnetic and electronic properties [13–19]. In a number of papers, the positive conjoint effects of two or more noble metals on the above mentioned properties have been lucidly explained [14, 20, 21]. In present days, different compositions of nano-alloys are utilized for advancement of methodologies and characterization techniques [14, 20, 22]. A thorough study of core-shell structures of nano-compounds is very popular because their properties can be tuned by a proper control of other structural and chemical

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parameters. Group 11 metal (Cu, Ag and Au) clusters exhibit the filled inner d-orbitals with one unpaired electron in the valence s-shell [23]. This electronic arrangement is responsible for reproduction of exactly similar shell effects [24–28] which are experimentally observed in the alkali metal clusters [29–31]. Among the nano-clusters of group 11 elements, the compound formed between Cu–Ag is very much popular due to its large scale applications. The exact position of silver within the copper-silver core-shell structure is highly important to tune the physicochemical properties. The location of silver has a controlling effect on the optical properties of such particles as the optical properties are governed by plasmon resonance frequency of silver, which is also dependent on its structural environment [32]. It has been already established that copper-silver bi-metallic nano-clusters, such as catalysts can enhance the reaction efficiency and selectivity [33, 34]. Though a number of experimental studies have been done on this particular type of compounds, a theoretical analysis invoking Density Functional Theory (DFT) is still unexplored in this domain.

Since the last couple of years Density Functional Theory has been dominant method for the quantum mechanical computation of periodic systems. Due to its computational friendly behavior, DFT is very much popular to study the many-body systems [9]. Super conductivity of metal based alloys [35], magnetic properties of nano-alloy clusters [36, 37] quantum fluid dynamics [38], molecular dynamics [39], nuclear physics [40, 41] can be extensively studied invoking DFT methodology. Recently, we have established the importance of density functional based global and local descriptors in the domain of drug designing process [42, 43]. The study of density functional theory is broadly classified into three sub-categories viz. theoretical, conceptual, and computational [44–47]. Conceptual density functional theory gives a new insight into the study of chemical reactivity [48–50]. The conceptual density functional theory is highlighted following Parr's dictum "Accurate calculation is not synonymous with useful interpretation. To calculate a molecule is not to understand it" [51].

In this venture, we have successfully studied some bi-metallic nano-clusters containing Cu and Ag, invoking DFT based global descriptors viz. hardness, HOMO-LUMO gap, softness, electrophilicity index. An attempt has been made to correlate the properties of the real compounds with their computational counterparts.

2. Computation details

In this study, we have made an analysis of the bi-metallic nano-alloy clusters of $(\text{Cu-Ag})_n$, where $n = 1 - 7$. 3D modeling and structural optimization of all the compounds have been performed using ADF software package [52] within Density Functional Theory framework. For optimization purpose, the Local Density Approximation (LDA) has been adopted. Although LDA functionals are not so much complex but their effectiveness has already been established in many-fold applications, particularly for solid state physics [53], where accurate phase transitions in solids [54] and liquid metals [55, 56] are predicted, and for lattice crystals, in which 1 % precision is successfully achieved [57]. Energy minimization of all the mentioned alloys has been performed without imposing any restrictions on the molecular spin, and z-axis has been chosen as the spin polarization axis. In this computation process, the Symmetrized Fragment Orbitals (SFOs) are combined with auxiliary Core Functions (CFs) to ensure orthogonalization on the (frozen) Core Orbitals (COs). For the optimization of the structures, double zeta basis sets (DZ) have been used along with frozen core approximation. The quadrupole moment of a molecule was calculated in terms of analytical integration methodology.

The calculation of ionization energy (I) and electron affinity (A) have been performed invoking Koopmans' approximation [48] based on the following ansatz:

$$I = -\epsilon_{\text{HOMO}} \quad (1)$$

$$A = -\epsilon_{\text{LUMO}} \quad (2)$$

Thereafter, using I and A, the conceptual DFT based descriptors viz. electronegativity (χ), global

hardness (η), molecular softness (S) and electrophilicity index (ω) have been computed. The equations used for such calculations are as follows:

$$\chi = -\mu = (I + A)/2 \quad (3)$$

where μ represents the chemical potential of the system.

$$\eta = 1/2(I - A) \quad (4)$$

$$S = [1/(2 \cdot \eta)] \quad (5)$$

$$\omega = (\mu)^2/(2\eta) \quad (6)$$

3. Results and discussion

In this study, computational analysis of Cu-Ag bi-metallic nano-clusters invoking electronic structure theory has been performed. The orbital energies in form of HOMO (Highest Occupied Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbital) gap along with computed DFT based descriptors for mentioned nano-clusters viz. molecular electronegativity, global hardness, global softness and global electrophilicity index, have been reported in the Table 1. The molecular dipole moment in debye unit is also presented in the Table 1. The quadrupole moments of the same nano-clusters along different axes are reported in the Table 2. From the Table 1, a direct relationship between HOMO-LUMO gaps of the nano-clusters and their evaluated global hardness values is revealed. As the frontier orbital energy gap increases, the hardness value increases. From experimental point of view, it is an expected trend. The molecule possessing the highest HOMO-LUMO gap is the least prone to response against any external perturbation. From the Table 1, it is clear that Cu₃Ag₃ is the least reactive species, whereas Cu₇Ag₇ exhibits the maximum response. Though there is no such available quantitative data for optical properties of aforesaid clusters, we can tacitly assume that there must be a direct qualitative relationship between optical properties of Cu-Ag nano-clusters

with their computed HOMO-LUMO gap. The assumption is based on the fact that optical properties of materials are interrelated with flow of electrons within the systems, which in turn depends on the difference between the distance of valence and conduction band. There is a linear relationship between HOMO-LUMO gap with the difference in the energy of valence-conduction band [58]. On that basis, we may conclude that optical properties of the bi-metallic nano-clusters improve with an increase in their hardness values. Similarly, the softness data exhibits an inverse relationship towards the experimental optical properties. Although the same type of direct relationships is observed in case of computed electronegativity, electrophilicity index and dipole moment along with their HOMO-LUMO gap, but for Cu₃Ag₃ cluster an exception is marked. The linear correlation between HOMO-LUMO gap along with the computed hardness is lucidly plotted in Fig. 1. The high value of regression coefficient ($R^2 = 0.999$) observed in Fig. 1, validates our predicted model. From the obtained correlation coefficients of several DFT based descriptors and their HOMO-LUMO gaps, it can be concluded that the best linear relationship is observed in case of hardness and the least one for dipole moment ($R^2 = 0.034$) of these nano-clusters. The electron density distributions of HOMO and LUMO of Cu₂Ag₂ exhibiting the highest reactivity among the mentioned nano-clusters, are plotted in Fig. 2 and Fig. 3, respectively.

The quadrupole charge separation is represented in a form of quadrupole moment according to Buckingham convention in the Table 2. The quadrupole moment values in different axes are represented in atomic units (a.u.).

As per the cluster physics, dissociation energy and second difference of total energy have a marked influence on the relative stability of a particular system. These two energies are highly sensitive quantities and they exhibit a pronounced even-odd alternation behavior for neutral and charged clusters, as a function of cluster size [59]. A similar type of alternation behavior is also exhibited by the HOMO-LUMO gap of any particular compound. It has already been reported that

Table 1. Computed DFT based descriptors of $(\text{Cu-Ag})_{n=1-7}$ nano-clusters.

| Species name | HUMO-LUMO gap (eV) | Electronegativity (eV) | Hardness (eV) | Softness (eV) | Electrophilicity index (eV) | Dipole moment (debye) |
|---------------------------------|--------------------|------------------------|---------------|---------------|-----------------------------|-----------------------|
| CuAg | 2.022 | 4.216 | 1.011 | 0.494 | 2.108 | 0.723 |
| Cu ₂ Ag ₂ | 0.765 | 4.154 | 0.383 | 1.307 | 2.076 | 0.003 |
| Cu ₃ Ag ₃ | 2.501 | 4.209 | 1.251 | 0.400 | 2.105 | 0.016 |
| Cu ₄ Ag ₄ | 0.788 | 4.163 | 0.422 | 1.186 | 2.081 | 0.007 |
| Cu ₅ Ag ₅ | 0.435 | 4.871 | 0.217 | 2.297 | 2.435 | 0.647 |
| Cu ₆ Ag ₆ | 0.653 | 4.789 | 0.326 | 1.531 | 2.395 | 0.411 |
| Cu ₇ Ag ₇ | 0.245 | 5.021 | 0.122 | 4.083 | 2.511 | 0.554 |

Table 2. Computed quadrupole moment in a.u. of $(\text{Cu-Ag})_{n=1-7}$ nano-clusters.

| Species name | Quad-xx | Quad-xy | Quad-xz | Quad-yy | Quad-yz | Quad-zz |
|---------------------------------|---------|---------|---------|---------|---------|---------|
| CuAg | −0.234 | 0.000 | 0.000 | −0.234 | 0.000 | 0.468 |
| Cu ₂ Ag ₂ | 0.286 | −2.834 | 0.000 | 2.975 | 0.000 | −3.262 |
| Cu ₃ Ag ₃ | 2.928 | 0.005 | 0.000 | 2.926 | 0.000 | −5.855 |
| Cu ₄ Ag ₄ | 4.906 | 3.713 | 0.000 | 6.773 | 0.000 | −11.678 |
| Cu ₅ Ag ₅ | −58.230 | 1.115 | 0.000 | −62.346 | 0.000 | −66.445 |
| Cu ₆ Ag ₆ | −71.863 | 1.257 | 0.000 | −74.764 | 0.000 | −79.662 |
| Cu ₇ Ag ₇ | −84.497 | 2.638 | 0.000 | −85.217 | 0.000 | −92.968 |

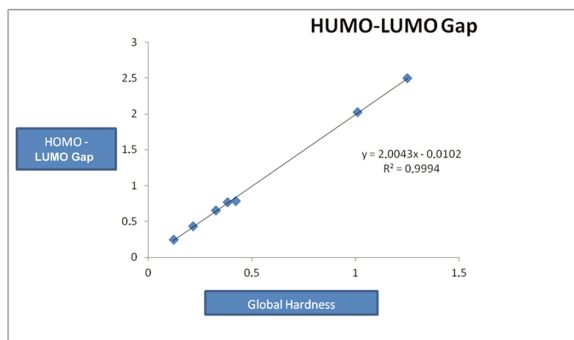


Fig. 1. A linear correlation plot between HUMO-LUMO gap and global hardness.

the cluster with an even number of total atoms exhibits less reactivity and possesses larger HUMO-LUMO gap, whereas the reverse trend is observed for the clusters containing a total odd number of the atoms [57]. The stability of the even number electronic cluster is actually an outcome of their closed electronic configuration which always produces extra stability. We have reported HUMO-LUMO gap as a function of cluster size in Table 3. It is distinct from the Table 3 that the bi-metallic clusters containing even number of total atoms possess higher

HUMO-LUMO gap as compared to the clusters having odd number of total atoms. The only exception is observed in the case of Cu₇Ag₇. Thus, our computed data supports the experimental odd-even alternation behavior of bi-metallic nano-clusters.

A comparative analysis has been made between experimental bond length [60–62] and our computed data of the species, namely Ag₂, Cu₂ and CuAg. The result is reported in Table 4. A close agreement between experimental data and our computed bond length is reflected in Table 4. It supports and validates our computational analysis.

4. Conclusions

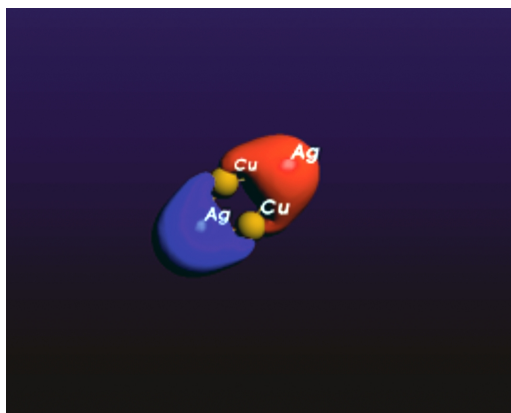
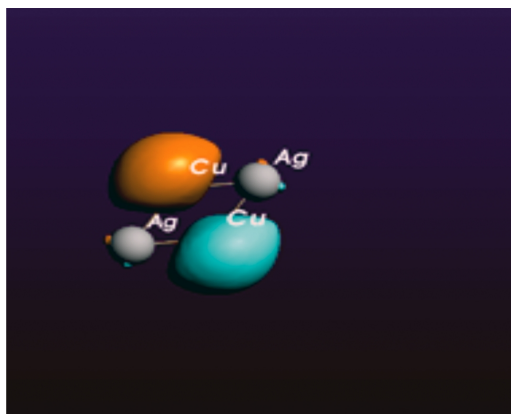
Due to diverse nature of applications, bi-metallic nano-alloy clusters have gained immense importance. Nano-clusters containing group 11 metals, namely copper and silver, exhibit a remarkable optical property. In this paper, we have theoretically analyzed the optical property of $(\text{CuAg})_{n=1-7}$, in terms of conceptual DFT based descriptors viz. global hardness, electronegativity, softness, electrophilicity index and dipole moment.

Table 3. A comparative study between odd and even pair of atoms of bi-metallic nano-clusters along with their HOMO-LUMO energy gap.

| Species name (even pair) | HUMO-LUMO gap (eV) | Species name (odd pair) | HUMO-LUMO gap (eV) |
|---------------------------------|-----------------------|---------------------------------|-----------------------|
| CuAg | 2.022 | CuAg ₂ | 0.328 |
| Cu ₂ Ag ₂ | 0.765 | CuAg ₄ | 0.301 |
| Cu ₃ Ag ₃ | 2.501 | Cu ₄ Ag | 0.316 |
| Cu ₄ Ag ₄ | 0.788 | Cu ₃ Ag ₂ | 0.341 |
| Cu ₅ Ag ₅ | 0.435 | Cu ₂ Ag | 0.041 |
| Cu ₆ Ag ₆ | 0.653 | | |
| Cu ₇ Ag ₇ | 0.245 | | |

Table 4. The calculated bond lengths (Å) for the Ag₂, Cu₂, CuAg species.

| Species | Theoretical bond length | Experimental bond length |
|-----------------|----------------------------|-----------------------------|
| Ag ₂ | 2.61 | 2.53 ⁵⁹ |
| Cu ₂ | 2.16 | 2.22 ⁶⁰ |
| CuAg | 2.33 | 2.37 ⁶¹ |

Fig. 2. Contour plot of HOMO of Cu₂Ag₂.Fig. 3. Contour plot of LUMO of Cu₂Ag₂.

Our computed result reveals that HOMO-LUMO gap runs hand in hand along with global hardness data. Due to the absence of any quantitative benchmark, optical property of Cu–Ag nano-cluster has been tacitly assumed to be exactly equivalent to its HOMO-LUMO gap. Here, the computed data indicates a direct relationship between optical property of the mentioned bi-metallic nano-alloys and global hardness values. This trend is consistent with other experimental facts. The high value of regression coefficient between hardness and HOMO-LUMO gap supports our approach pertaining to modeling. Our computed bond lengths for the species, like Cu₂, Ag₂ and CuAg, are numerically very close to the experimental values. In this report, the effect of even-odd alternation behavior on HOMO-LUMO gap is also reflected distinctly.

References

- [1] ZABET-KHOSOUSI A., DHIRANI A.-A., *Chem. Rev.*, 108 (2008), 4072.
- [2] DANIEL M.C., ASTRUC D., *Chem. Rev.*, 104 (2004), 293.
- [3] GHOSH S.K., PAL T., *Chem. Rev.*, 107 (2007), 4797.
- [4] CHAUDHURI R. G., PARIA S., *Chem. Rev.*, 112 (2012), 2373.
- [5] ALIVISATOS A.P., *Science*, 271 (1996), 933.
- [6] KASTNER M.A., *Phys. Today*, 46 (1993), 24.
- [7] HARUTA M., *Cattech*, 6 (2002), 102.
- [8] DAWID A., GBURSKI Z., *J. Molec. Struct.*, 410 (1997), 507.
- [9] ISMAIL R., *Theoretical studies of free and supported nanoalloy clusters*, Ph.D. Thesis (2012), 20.
- [10] ROUCOUX A., SCHULZ J., PATIN H., *Chem. Rev.*, 102 (2002), 3757.
- [11] MUNOZ-FLORES B.M., KHARISOV B.I., JIMENEZ-PEREZ V.M., MARTINEZ P.E., LOPEZ S.T., *Ind. Eng. Chem. Res.*, 50 (2011), 7705.
- [12] MURRAY R.W., *Chem. Rev.*, 108 (2008), 2688.

- [13] TENG X., WANG Q., LIU P., HAN W., FRENKEL A.I., WEN, MARINKOVIC N., HANSON J.C., RODRIGUEZ J.A., *J. Am. Chem. Soc.*, 130 (2008), 1093.
- [14] FERRANDO R., JELLINEK J., JOHNSTON R.L., *Chem. Rev.*, 108 (2008), 845.
- [15] HENGLEIN A., *J. Phys. Chem.*, 97 (1993), 5457.
- [16] DAVIS S.C., KLABUNDE K.J., *Chem. Rev.*, 82 (1982), 153.
- [17] LEWIS L.N., *Chem. Rev.*, 93 (1993), 2693.
- [18] SCHMID G., *Chem. Rev.*, 92 (1992), 1709.
- [19] SCHON G., SIMON U., *Colloid. Polym. Sci.*, 273 (1995), 101.
- [20] ODERJI H.Y., DING H., *Chem. Phys.*, 388 (2011), 23.
- [21] LIU H.B., PAL U., MEDINA A., MALDONADO C., ASCENCIO J.A., *Phys. Rev. B*, 71 (2005), 075403.
- [22] BALETTO F., FERRANDO R., *Rev. Mod. Phys.* 77 (2005), 371.
- [23] ALONSO J.A., *Chem. Rev.*, 100 (2000), 637.
- [24] KATAKUSE I., ICHIHARA T., FUJITA Y., MATSUO T., SAKURAI T., MATSUDA H., *Int. J. Mass Spectrom. Ion Processes*, 67 (1985), 229.
- [25] KATAKUSE I., ICHIHARA T., FUJITA Y., MATSUO T., SAKURAI T., MATSUDA H., *Int. J. Mass Spectrom.*, 74 (1986), 33.
- [26] HEER W.A.D., *Rev. Mod. Phys.*, 65 (1993), 611.
- [27] GANTEFOR G., GAUSA M., MEIWES-BROER K.-H., LUTZ H.O., *J. Chem. Soc., Faraday Trans.*, 86 (1990), 2483.
- [28] LEOPOLD D.G., HO J., LINEBERGER W.C., *J. Chem. Phys.*, 86 (1987), 1715.
- [29] LATTES A., RICO I., SAVIGNAC A.D., SAMII A.A.Z., *Tetrahedron*, 43 (1987), 1725.
- [30] CHEN F., XU G.-Q., HOR T.S.A., *Mater. Lett.*, 57 (2003), 3282.
- [31] TALEB A., PETIT C., PILENI M.P., *J. Phys. Chem. B*, 102 (1998), 2214.
- [32] LANGLOIS C., WANG Z.W., PEARMAIN D., RICOLEAU C., LI Z.Y., *J. Phys.*, 241 (2010), 012043.
- [33] JANKOWIAK J.T.A., BARTEAU M.A., *J. Catal.*, 236 (2005), 366.
- [34] PICCININ S., ZAFEIRATOS S., STAMPFL C., HANSEN T.W., HÄVECKER M., TESCHNER D., *Phys. Rev. Lett.*, 104 (2010), 035503-1.
- [35] WACKER O.J., KUMMEL R., GROSS E.K.U., *Phys. Rev. Lett.*, 73 (1994), 2915.
- [36] ILLAS F., MARTIN R.L., *J. Chem. Phys.*, 108 (1998), 2519.
- [37] GYORFFY B., STAUNTON J., STOCKS G., in: GROSS E., DREIZLER R. (Eds.), *Fluctuations in density functional theory: random metallic alloys and itinerant paramagnets*, Plenum, NY, 1995, p. 461.
- [38] KÜMMEL S., BRACK M., *Phys. Rev. A*, 64 (2001), 022506.
- [39] CAR R., PARRINELLO M., *Phys. Rev. Lett.*, 55 (1985), 2471.
- [40] KOSKINEN M., LIPAS P., MANNINEN M., *Nucl. Phys. A*, 591 (1995), 421.
- [41] SCHMID R.N., ENGEL E., DREIZLER R.M., *Phys. Rev. C*, 52 (1995), 164.
- [42] CHAKRABORTY T., GHOSH D.C., *Int. J. Chemoinf. Chem. Eng.*, 1 (2011), 53.
- [43] CHAKRABORTY T., GHOSH D.C., *Int. J. Chem. Model.*, 4 (2012), 413.
- [44] PARR R.G., YANG W., *Annu. Rev. Phys. Chem.*, 46 (1995), 701.
- [45] KOHN W., BECKE A.D., PARR R.G., *J. Phys. Chem.*, 100 (1996), 12974.
- [46] LIU S., PARR R.G., *J. Chem. Phys.*, 106 (1997), 5578.
- [47] ZIEGLER T., *Chem. Rev.*, 91 (1991), 651.
- [48] PARR R.G., YANG W., *Density functional theory of atoms and molecules*, Oxford University Press, Oxford, 1989.
- [49] CHERMETTE H., *J. Comp. Chem.*, 20 (1999), 129.
- [50] GEERLINGS P., PROFT F.D., LANGENAEKER W., *Chem. Rev.*, 103 (2003), 1793.
- [51] GEERLINGS P., PROFT F.D., *Int. J. Mol. Sci.*, 3 (2002), 276.
- [52] ADF2013, SCM, *Theoretical chemistry*, Vrije Universiteit, Amsterdam, 2013.
- [53] JONES R.O., GUNNARSSON O., *Rev. Mod. Phys.*, 61 (1989), 689.
- [54] ZUPAN A., BLAHA P., SCHWARZ K., PERDEW J.P., *Phys. Rev. B*, 58 (1998), 11266.
- [55] THEILHABER J., *Phys. Fluids B*, 4 (1992), 2044.
- [56] STADLER R., GILLAN M.J., *J. Phys.-Condens. Mat.*, 12 (2000), 6053.
- [57] ARGAMAN N., MAKOV G., *J. Phys.-Condens. Mat.*, 68 (2000), 69.
- [58] XIAO H., KHELI J.T., GODDARD III W.A., *J. Phys. Chem. Lett.*, 2 (2011), 212.
- [59] WANG H.Q., KUANG X.Y., LI H.F., *Phys. Chem. Chem. Phys.*, 12 (2010), 5156.
- [60] BEUTEL V., KRAMER H.G., BHALE G.L., KUHN M., WEYERS K., DENTRODER W., *J. Chem. Phys.*, 98 (1993), 2699.
- [61] BALBUENA P.B., DEROSA P.A., SEMINARIO J.M., *J. Phys. Chem. B*, 103 (1999), 2830.
- [62] BISHEA G.A., MARAK N., MORSE M.D., *J. Chem. Phys.*, 95 (1991), 5618.

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