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THEORETICAL STUDY OF THE INTERACTION OF TRANSITION METALS WITH SILICA

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The interesting applications of ultrathin silica films on transition metals drove us to analyze the interactions between them. We selected only sixteen transition metals to observe a pattern and started at a molecular level to understand the principal interactions involved between them. A conformational search and a subsequent optimization of the structures, together with frequency calculations at the MP2/LANL2DZ level of theory for the metals and MP2/6-31G* for the rest of the atoms. The results show that the interactions are favorable with the transition metals we selected.

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1. Introduction

Silicon dioxide (SiO_2) is one of the most abundant materials of the earth. It is a key material in several aplications of the modern technology [1]. The importance of this material lies in the important role it plays in materials science, microelectronics [2], geology, catalysis and photonics [1].

The growth of silica on metal substrates has been of interest for the past few years due to the fact that this technique produces ultrathin oxide films of a well-defined thickness. The thinnest silicon oxide films are made of monolayers [1]. It can be expected that these oxide films find applications as insulating layers in nanoelectronic devices or as tunneling barriers [2]. Ultrathin silica films use silica as gate dielectric transistors for the new generation of metal-oxide-semiconductor transistors [1]. There is special interest in their miniaturization [2]. This strongly depends on the knowledge of the transition region of sub-stoichiometric SiO_X at the SiO_2/Si interface [1].

Experimental studies that have been able to grow ultrathin silica films on metals reveal that the film structure strongly depends on the metal substrate used (Mo, Ni, Pd, Ru, Pt) [1]. However, only a handful of the interactions with metals have been studied theoretically. Therefore, this study focuses on studying the interactions between silica and the transition metals with atomic numbers 23-30 (V-Zn) and 41-48 (Nb-Cd) [3].

It is interesting to note that although the net chemical formula of silica is SiO_2, the Si atom shows a tetrahedral coordination with 4 oxygen atoms surrounding a central Si atom [4]. When a ultrathin SiO_2 film is formed on the metals [1], not all of the oxygens are shared with the central Si atom, as it is shown in Figure 1 [4]. In this study we focus the interaction of one molecule of SiO_2 with one atom of different transition metals. Therefore, SiO_2 is represented by SiO_4 [4]. To understand the basic interactions involved between metals and silica, we studied only one charged atom of the metal (M^{2+}) and one molecule of $(SiO_4)^{4-}$.

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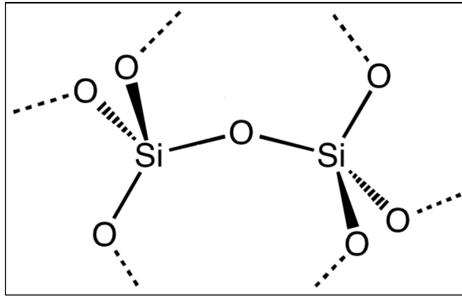


Fig. 1. Schematic representation of SiO_2.

2. Computational methods

The systems composed of SiO_2 and the transition metals were minimized with quantum mechanical computations using Gaussian 09 software [5]. Optimization and frequency calculations were performed with the Møller Plesset MP2 method together with the LANL2DZ basis set for the Si and O atoms; and the 6-31G* basis set for the metal atoms [6]. Zero point energies were used to correct the values of energy. The Hessian matrix elements were analyzed to select energy minima species. Transition states were distinguished from energy minima structures. Positive frequencies denoted energy minima systems while negative frequencies were transition states [6]. Global orbital cutoffs and fine convergence criteria were used on basis set definitions to confirm precision.

We consider the internal thermal energy (E) as a sum of the translational (E_t), rotational (E_r), vibrational (E_v) and electronic (E_e) energies, where E_e is the sum of the total electronic energy and the zero-point energy [7].

$$E = E_t + E_r + E_v + E_e \tag{1}$$

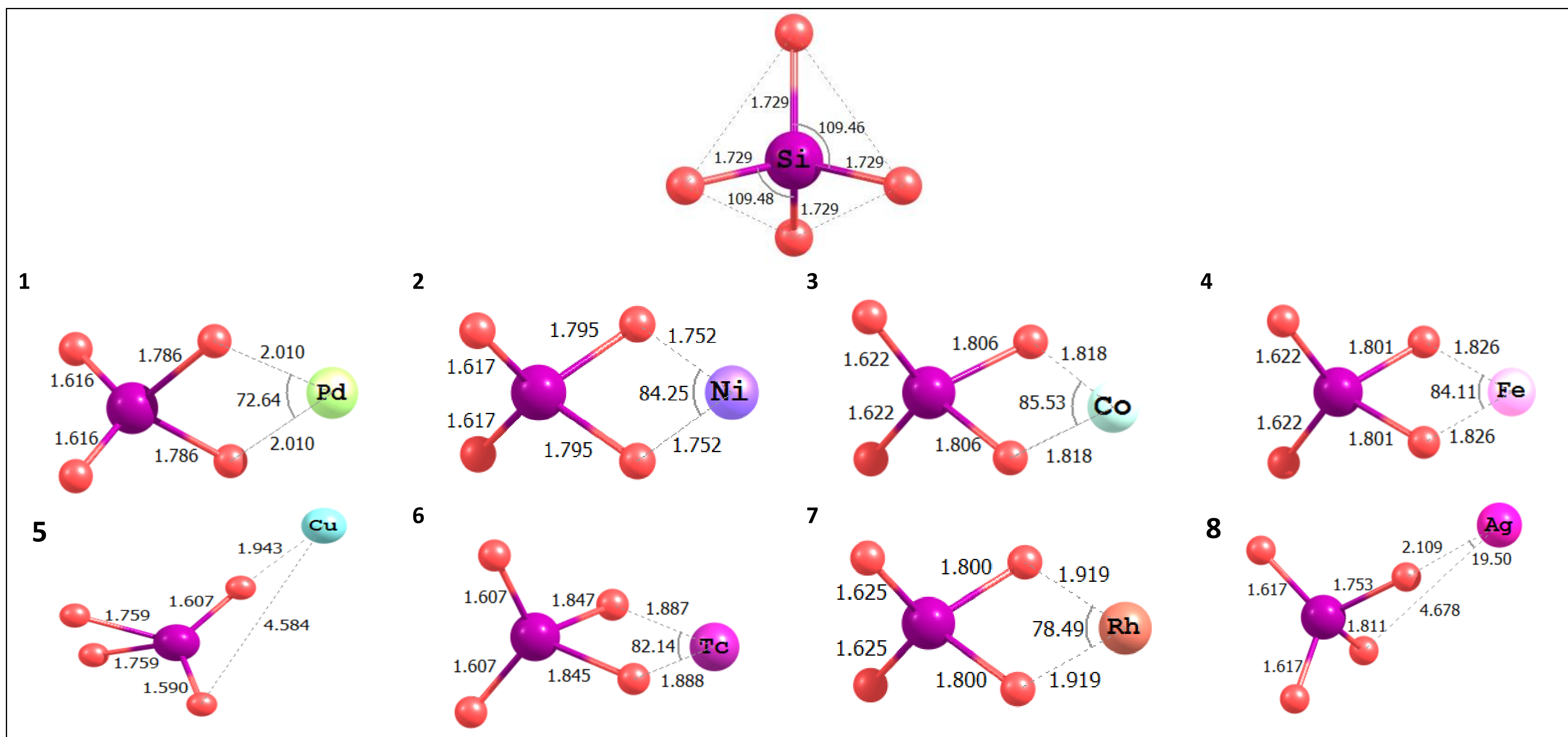
Dissociation energies (ΔE) for the systems were calculated as follows:

$$\Delta E = E_{M^{2+}(SiO_4)^{4-}} - E_{(SiO_4)^{4-}} - E_{M^{2+}} \tag{2}$$

Where E_{SiO_4-M} represents the energy of the system formed by the interaction between the charged $(SiO4)^{4-}$ and the charged metal M^{2+}, while $E_{(SiO_4)^{4-}}$ and $E_{M^{2+}}$ are for the $(SiO4)^{4-}$ and the M^{2+} , respectively. All of our systems yielded negative dissociation energies, but we report only relative dissociation energies were calculated to compare their stability. The reference geometry is the one with lowest dissociation energy such that its relative dissociation energy is exactly 0.00 kcal/mol (In this case, Pd(SiO4) was the most stable system with a dissociation energy of -1131.78 kcal/mol) whereas the rest of the systems show positive values of relative dissociation energies although their dissociation energies are negative. For the sake of space, in this manuscript we only show the systems with the lowest energy, however several geometrical configurations were obtained.

3. Results and discussion

The optimized structures of the systems formed by the transition metals (M^{2+}) with atomic numbers 23-30 (V-Zn) and 41-48 (Nb-Cd) and silica $(SiO_4)^{4-}$ are shown on Figure 2. The values of relative dissociation energy and HOMO/LUMO gaps are listed on Table 1.



Si
1.729
109.46
1.729
1.729
109.48
1.729
1
1.786
2.010
1.616
72.64
Pd
1.616
1.786
2.010
2
1.795
1.752
1.617
84.25
Ni
1.617
1.795
1.752
3
1.806
1.818
1.622
85.53
Co
1.622
1.806
1.818
4
1.801
1.826
1.622
84.11
Fe
1.622
1.801
1.826
5
Cu
1.943
1.607
1.759
4.584
1.759
1.590
6
1.607
1.847
1.887
82.14
Tc
1.607
1.845
1.888
7
1.800
1.919
1.625
78.49
Rh
1.625
1.800
1.919
8
Ag
2.109
19.50
1.617
1.753
1.811
4.678
1.617

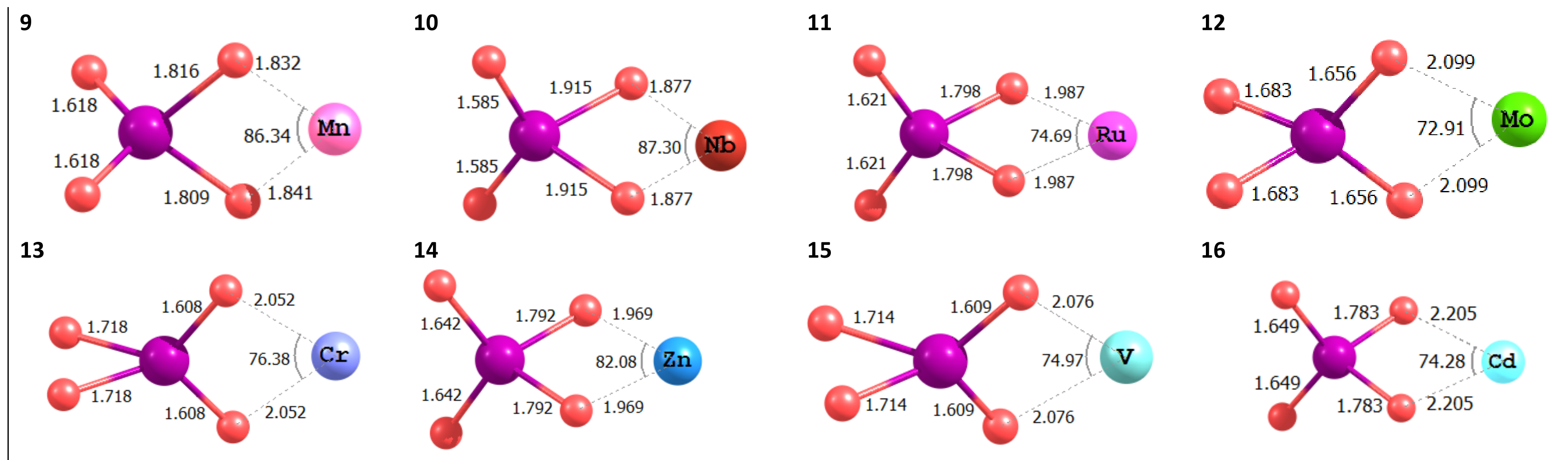


Fig. 2. Selected geometrical parameters of the systems formed by the transition metals (M^{2+}) with atomic numbers 23-30 (V-Zn) and 41-48 (Nb-Cd) and silica ($(SiO_4)^{4-}$) whereby bond distances and angles are measured in Å and °, respectively.

Table 1. List of the group and period of the transition metal cations involved in the interaction with SiO_4, together with relative dissociation energies with zero point corrections, $\Delta E_{rel}(0)$ in kcal/mol and HOMO/LUMO gaps in eV of the systems.

	System	Group	Period	$\Delta E_{rel}(0)$	GAP
1	$Pd(SiO_4)$	VIII B	5	0.00	3.59
2	$Ni(SiO_4)$	VIII B	4	16.47	3.49
3	$Co(SiO_4)$	VIII B	4	27.31	3.43
4	$Fe(SiO_4)$	VIII B	4	35.14	3.28
5	$Cu(SiO_4)$	I B	4	35.15	3.01
6	$Tc(SiO_4)$	VII B	5	37.98	3.18
7	$Rh(SiO_4)$	VIII B	5	38.34	2.76
8	$Ag(SiO_4)$	I B	5	40.09	3.03
9	$Mn(SiO_4)$	VII B	4	45.38	3.16
10	$Nb(SiO_4)$	V B	5	47.91	3.00
11	$Ru(SiO_4)$	VIII B	5	70.31	3.53
12	$Mo(SiO_4)$	VI B	5	105.97	3.03
13	$Cr(SiO_4)$	VI B	4	110.23	2.37
14	$Zn(SiO_4)$	II B	4	111.62	5.01
15	$V(SiO_4)$	V B	4	113.72	2.33
16	$Cd(SiO_4)$	II B	5	142.42	5.79

The most stable system, silica-Pd shows that Pd interacts with two equidistant oxygens at 2.01 Å and foms an angle of 72.6°. This interaction modifies the Si-O distances, yielding two Si-O distances of 1.62 Å and the other two of 1.79 Å. This can be explained by the fact that Pd^{2+}, with a configuration of $[Kr]4d^8$ can readily accept two electrons to fill its valence d shell and stabilize. This can be observed on the HOMO/LUMO plots, where the LUMO plot is more prominent than the HOMO plot.

The next system is the one formed with Ni, which has a relative dissociation energy of 15.99 kcal/mol and a HOMO/LUMO gap of 3.49 eV. This structure also shows an interaction between Ni and two equidistant oxygens but at a different distance of 1.75 Å. This modifies the structure of the silica molecule to a structure with the same parameters as in structure 1. In general, the frequencies of the slica-Pd system are smaller than those of silica-Ni. Using the Planck-Einstein relation [8], we conclude that this could account for the higher stability of the Pd system because the translational, rotational and electronic energies were very similar and the variation was mostly on the vibrational energy.

System 3 has a relative dissociation energy of 27.31 kcal/mol with a HOMO/LUMO gap of 3.43 eV. The O-Co-O angle is of 85.5° with bond distances of 1.82 Å each one. In this case, Co has a greater oxygen-metal distance than in structure 3, yielding a higher dissociation energy. For structure 4, Fe forms a O-Fe-O angle of 84.1° with Fe-O distances of 1.83 Å. The longer Fe-O distance compared to that of Co-O causes the system to be less stable, with a relative dissociation energy of 35.14 kcal/mol. Structure 5 shows that Copper prefers interacting with only one oxygen instead of two, with distances of 1.94 Å and 4.58 Å forming a Si-Cu-Si angle of 18.9°. Its HOMO/LUMO gap is of 3.01 eV. The interaction of Cu with only one oxygen and at a longer distance causes the relative dissociation energy to rise to a value of 35.15 kcal/mol.

System 6 has a HOMO/LUMO gap of 3.18 eV and forms a Si-Tc-Si angle of 82.1° with Tc-O distances of 1.89 Å. In this case, although the Tc-O distances are shorter than for the case of Cu, the vibrational energy was noticeably higher for Tc. This can also be confirmed by the fact that Tc 9 out of 12 frequencies of the system with Tc were higher than those of Cu. System 7 interacts with SiO_4 with two oxygens at a distance of 1.92 Å with a O-Rh-O angle of 78.5°. In this case, the Rh-O distances are higher than those of Tc. In addition, 11 out of 12 frequencies of the $Rh(SiO_4)$ system are higher than those of $Tc(SiO_4)$. Thus, system 7 is less stable than system 6, with a relative dissociation energy of 38.34 kcal/mol.

Table 2. Frequencies of the systems formed by the transition metals (M^{2+}) with atomic numbers 23-30 (V-Zn) and 41-48 (Nb-Cd) and silica ($(SiO_4)^{4-}$).

	System	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
freq	SiO_4	Pd	Ni	Co	Fe	Cu	Tc	Rh	Ag	Mn	Nb	Ru	Mo	Cr	Zn	V	Cd
1	328.27	102.85	106.75	116.32	73.12	66.92	142.44	94.41	32.11	103.71	259.89	167.08	143.28	135.93	113.82	113.22	98.18
2	328.27	212.42	252.26	258.55	265.08	78.55	225.35	255.93	51.08	258.53	129.17	241.81	190.58	212.19	260.61	213.99	223.22
3	467.75	236.83	289.39	271.03	272.2	235.77	268.15	294.26	90.23	266.29	207.54	244.34	211.05	229.69	276.79	235.81	271.43
4	467.75	319.27	371.55	356.9	377.75	244..56	365.31	381.04	163.9	367.28	239.55	342.67	286.7	318.2	319.13	322.89	279..60
5	467.75	390.81	407.84	412.26	418.04	353.28	378.37	425.18	255.28	406.53	343.31	367.9	343.78	404.99	430.36	403.58	421.27
6	664.21	428.45	463.76	435.18	449.88	408.03	423.96	505.74	344.15	415.03	353.71	447.69	450.07	434.87	443.o4	457.92	422.35
7	771.98	483.04	470.38	453.97	449.9	440.61	461.09	595.3	410.91	447.41	410.57	454.64	500.49	492.07	462.92	501.01	465.59
8	771.99	515.74	656.09	622.29	644.02	630.77	587.97	668.58	441.72	595.19	501.3	592.64	584.2	620.08	549.21	625.74	512.28
9	771.99	558.8	672.38	623.53	649.71	651.19	761.6	884.1	578.21	633.98	716.84	595.08	708.08	695.77	553.62	705.57	538.9
10		655.57	750.53	637.87	698.11	839.04	884.04	1006.17	708.53	647.26	787	659.38	849.1	818.92	653.29	822.58	656.36
11		927.25	916.78	901.62	892.47	1023.05	987.59	1031.21	877.83	899.43	963.95	899.76	907.88	1042.05	866.99	1045.49	857.67
12		1061.56	1053.43	1041.95	1029.27	1141.77	1093.74	1344.58	1062.86	1042.4	1169.73	987.09	1805.76	1089.18	984.41	1091.06	967.8

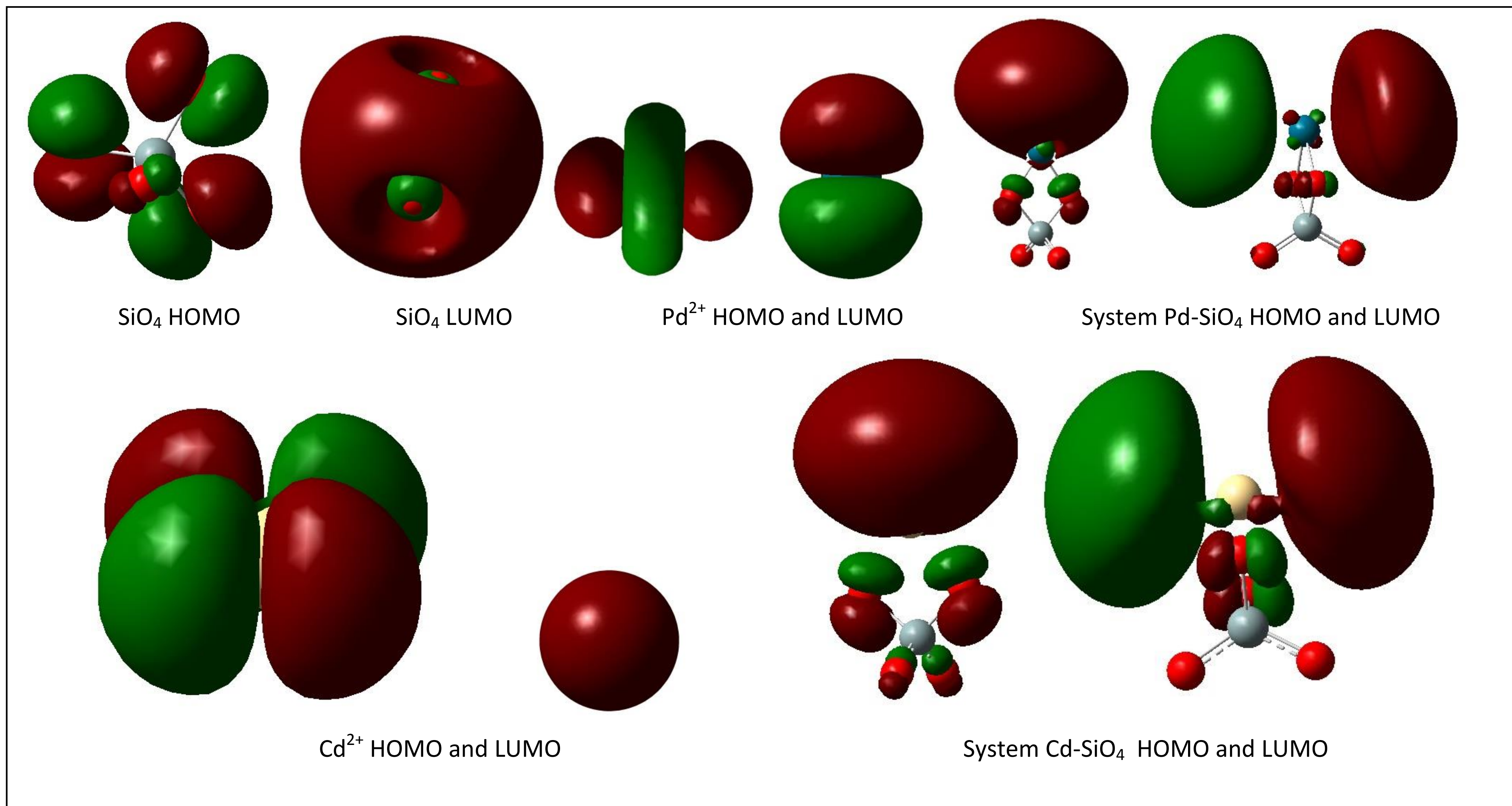


Fig. 3. HOMO/LUMO plots of SiO_4, Pd^{2+}, $Pd(SiO_4)$, Cd^{2+}, $Cd(SiO_4)$.

System 8 shows that Ag interacts mainly with one oxygen at a distance of 2.11 Å. This causes the interaction to be less stable than with Rh. This was expected, since Ag is more frequent with an oxidation state of +1 than with an oxidation state of +2 [9]. Its relative dissociation energy is of 40.09 kcal/mol and its HOMO/LUMO gap is of 3.03 eV. The next case is system 9, where the O-Mn-O angle is of 86.3° with Mn-O distances of 1.83 Å and 1.84 Å. Although these distances are smaller than those of Ag, 10 out of 12 frequencies of the Mn(SiO_4) system are higher than those of Ag(SiO_4). This destabilizes system 9 to 45.38 kcal/mol with a HOMO/LUMO gap of 3.16 eV.

System 10 shows a higher Nb-O distance of 1.88 Å compared to the Mn-O distance in system 9. The O-Nb-O angle is of 87.3° and its HOMO/LUMO gap is of 3.00 eV. Therefore, the dissociation energy is higher with a value of 47.91 kcal/mol. System 11 has a O-Ru-O angle of 74.7° and a Ru-O distance of 1.99 Å. Besides, most of its frequencies are higher in value than for system 10, yielding a less stable system with a dissociation energy of 70.31 kcal/mol and a HOMO/LUMO gap of 3.53 eV.

System 12 has a HOMO/LUMO gap of 3.03 eV, a O-Mo-O angle of 72.9° and a Mo-O distance of 2.10 Å. In this case, both the frequencies and the Mo-O distace are higher than for the system 11, causing the dissociation energy to elevate to 105.97 kcal/mol. For system 13, the Cr-O distance is higher than for system 12, with a value of 2.05 Å. The O-Cr-O angle is of 76.3°. Furthermore, the two oxygens not bonded to the metal are too close to each other, causing tension and thus rising the relative dissociation energy. Therefore, it is higher, with a value of 110.23 kcal/mol and its HOMO/LUMO gap is of 2.37 eV.

System 14 has a HOMO/LUMO gap of 5.01 eV and a slightly higher relative dissociation energy with a value of 111.63 kcal/mol. The Zn-O distance is of 1.97 Å and the O-Zn-O angle is of 82.0°. In spite of the fact that the distance Zn-O is higher than for system 13, half of the frequencies of system 14 are higher than that of system 13 which could account for the small rise in relative dissociation energy. System 15 has a HOMO/LUMO gap of 2.33 eV with a O-V-O angle of 75.0° and a V-O distance of 2.08 Å. In this case, both the metal-oxygen distance and most of the frequencies are higher than for system 14. Also, the two oxygens not bonded to a metal in system 15 are too close, causing tension and rising the relative dissociation energy. Thus, its value is higher than for system 14 with a value of 113.72 kcal/mol. Finally, Cd(SiO_4) forms a O-Cd-O angle of 74.3° with a Cd-O distance of 2.21 Å. This is the highest distance at which any of the metals studied interacted with SiO_4 and could be the reason why it is the less stable with a relative dissociation energy of 142.42 kcal/mol and a HOMO/LUMO gap of 5.79 eV.

The HOMO/LUMO gaps of the structures are listed on Table 1. Their values do not fully explain the contribution of the HOMO and LUMO orbitals to the stability of each system. Normally, a small gap implies that less energy is required to excite electrons from the HOMO to the LUMO. Anyhow, the degree to which molecular orbitals mix is proportional to $S^2/\Delta\varepsilon$, where S is the overlap and $\Delta\varepsilon$ is the difference in molecular energies on two species [10]. If S is not too different for the orbitals considered then $\Delta\varepsilon$ dominates and the smaller energy gap would take precedence. Figure 3 shows the HOMO and LUMO plots of SiO4, Pd^{2+}, Pd(SiO_4), Cd^{2+}, Cd(SiO_4). We chose Pd(SiO_4) and Cd(SiO_4) because these are the most and least stable systems, respectively. It can be seen that the metal Pd^{2+} has a higher LUMO since it is an ion initially and can readily accept electrons to neutralize its charge. When it interacts with SiO_4, the HOMO is based on Pd, which has already accepted the electrons. On the other hand, Cd^{2+} shows a greater HOMO than LUMO, since its electronic configuration is [Kr]$4d^{10}$. Since the d subshell is full, it is not as prone to donate any more electrons or accept them as Pd. Thus, it shows a lower stability. In addition to this, the longest metal-oxygen distance is present on the Cd(SiO_4), lowering its stability even more.

4. Conclusions

The Pd(SiO4) system is the most stable due to the fact that Pd^{2+} can accept electrons and fill its valence d subshell to stabilize. It can be seen that the most stable systems pertained to Groups IB and VIIIB. This could be due to the high number of electrons in the d subshell of each element. The least stable was Cd(SiO_4) since the Cd^{2+} d valence subshell is full and does not

accept electrons as easily as Pd^{2+}. The HOMO and LUMO plots helped understand the behavior of the systems, in conjunction with the dissociation energies and the frequencies.

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