Does spin–orbit coupling effect favor planar structures for small platinum clusters?†

Ali Sebetci‡

We have performed relativistic effective core potential calculations with and without spin–orbit coupling term in the framework of the density functional theory and investigated the geometry and binding energy of different isomers of free platinum clusters Pt_n (n = 4–6) for the spin multiplicities from singlet to nonet. The spin–orbit coupling effect has been discussed for the minimum-energy structures, relative stabilities, vibrational frequencies, magnetic moments, and the highest occupied and lowest unoccupied molecular-orbital gaps. It is found in contrast to some of the previous calculations that 3-D configurations are still lowest energy structures of these clusters, although spin–orbit effect makes some planar or quasi-planar geometries more stable than some other 3-D isomers. Spin–orbit coupling effects change the relative stability of various isomers.

I. Introduction

Small transition metal clusters have been attracting wide interest due to their potential applications as building blocks of functional nanostructured materials, electronic devices, and nanocatalysts.[1] In particular, platinum is one of the most important ingredients in the heterogeneous catalysis of hydrogenation as well as in the catalysis of the CO, NO_x, and hydrocarbons. It is currently the preferred oxidation and reduction catalyst for low-temperature polymer electrolyte membrane (PEM) fuel cells.[2] As the sizes of the Pt particles decrease, their catalytic activities tend to increase because of the increased surface areas of smaller particles and the structural sensitivity of some reactions.[3]

Lineberger and co-workers have investigated the electronic spectra of small platinum and palladium (n = 2,3) clusters by the negative ion photodetachment spectroscopic method[4,5] and Eberhardt and co-workers have obtained the valence and core-level photoemission spectra of mass selected monodispersed Pt_n (n = 1–6) clusters.[6] In a recent theoretical calculation, we have studied bare and hydrogenated Pt_nH_m (n = 1–5 m = 0–2) clusters in the scalar-relativistic density functional theory (DFT) formalism.[7] Relevant literature can be found in ref. 7 for previous experimental and theoretical investigations. In addition to them, Saenz *et al.*[8] have worked on the interaction of Pt clusters with molecular oxygen. Futschek *et al.*[9] have presented *ab initio* density functional studies of structural and magnetic isomers of Ni_n and Pt_n

clusters with up to 13 atoms. Seivane and Ferrer[10] have analyzed the impact of the magnetic anisotropy on the geometric structure and magnetic ordering of small atomic clusters of palladium, iridium, platinum, and gold from two to five, six, or seven atoms, depending on the element. Bhattacharyya and Majumder[11] have reported the growth pattern and bonding trends in Pt_n (n = 2–13) clusters and concluded in their first principles study that small Pt_n clusters have planar geometries and a structural transition to non-planar geometries occurs at n = 10. Similarly, Huda *et al.*[12] predicted that spin–orbit (SO) coupling effect favors planar structures for small Pt clusters.

In the present work, we discuss the effect of SO coupling on the structural, electronic and magnetic properties of small Pt_n (n = 4–6) clusters by employing Gaussian atomic-orbital methods in the relativistic effective core potential (ECP) DFT calculations. The possible local minima and ground state isomers, binding energies (BE), relative stabilities, magnetic moments, and the highest occupied and the lowest unoccupied molecular-orbital (HOMO-LUMO) energy gaps have been calculated with and without SO coupling to compare the results for both cases. Vibrational frequency calculations for each optimized structure have been carried out to differentiate local minima from transition states.

II. Computational method

NWChem 5.0 program package[13] has been used to perform geometry optimizations and total energy calculations by DFT. CRENBL[14] basis set, ECP, and SO operator for Pt have been employed where the outermost 18 electrons of free Pt atom ($5s^2 5p^6 5d^9 6s^1$) are treated as valence electrons. The generalized gradient approximation of Becke's exchange functional[15] and Lee–Yang–Parr correlation functional[16] (B3LYP) has been chosen as the hybrid exchange–correlation (xc) functional. The default convergence criteria, which are 1 μE_h for energy, and 0.5 $mE_h \, a_0^{-1}$ for the geometry optimization, are used.

IFW Dresden, Helmholtzstrasse, 20, 01069 Dresden, Germany.
E-mail: sebetci@ucr.edu

The geometries have been relaxed without imposing any symmetry constraints. Spin-polarized calculations have been done for the first five spin multiplicities (from singlet to nonet). The SO coupling DFT calculations have been done in a Kramers-unrestricted approach. Figures were produced by ChemCraft graphics program.[17]

III.   Results and discussion

A   Pt and Pt$_2$

First, we discuss the properties of Pt and Pt$_2$ to assess the accuracy of our theoretical method. The ground-state Pt atom was found in the triplet state $(5d^9 6s^1)$ for the non-SO coupling case in agreement with the experimental results.[18] The excitation energy of the singlet $5d^{10}6s^0$ state has been calculated as 0.510 eV (neglecting SO coupling) which can be compared with a spin-averaged experimental value of 0.478 eV.[18] This excitation energy has previously been calculated by Cui et al.[19] as 0.481 eV. By including SO effects, the excitation energy of the closed-shell configuration is 0.881 eV to be compared with the experimental value of 0.761 eV.[18] Both of these calculated excitation energies are much better than the ones obtained by Fortunelli in 1999,[20] which is the only one, to our knowledge, in an equivalent level of the theory to compare our results. We have calculated the SO splitting in the 5d orbital of Pt atom in its singlet state $(5d^{10}6s^0)$ for simplicity and obtained as 1.131 eV, which is in reasonable agreement with the value of 1.256 eV calculated by the all-electron full-relativistic DFT code FPLO[21] by employing Perdew–Wang[22] local xc functional in both programs. The ionization potential (IP) of Pt has been calculated as 9.319 eV in the SO term included case where the experimental value is 8.958 eV.[23] Huda et al. has calculated IP of Pt as 9.381 eV in their DFT study with the projected augmented wave (PAW) method.[12] The calculated electron affinity (EA) is 1.853 eV (non-SO) which is comparable to the experimental value of 2.123 ± 0.001 eV.[24] The discrepancy between the calculated and experimental values of the EA may be reduced when the experimental value is adjusted to remove SO effects which can be estimated to decrease it by about 0.2 eV.[25]

The ground state spin multiplicity of the Pt$_2$ dimer is found to be triplet for the non-SO coupling case. The bond lengths for the Pt dimer were calculated as 2.373 and 2.406 Å for non-SO and SO calculations, respectively, while the experimental value[26] is 2.333 Å. The corresponding binding energies are 2.708 eV (non-SO) and 2.476 eV (SO), where they are calculated with respect to the atomic ground state. The experimental BE is 3.14 ± 0.02 eV.[27] Cui et al.[19] has obtained the bond length and the binding energy in their scalar-relativistic calculations as 2.388 Å and 2.437 eV, respectively, which are comparable to our results. The present method with SO effects slightly overestimates the Pt dimer bond length and therefore underestimates the binding energy. However, the main aim of the present work is to investigate the effect of the SO term on the relative stability of the isomers, rather than providing very accurate quantitative results. Both of the calculated vibrational frequencies of 237 cm^{-1} (non-SO) and 219 cm^{-1} (SO) agree pretty well with the measured value of 223 cm^{-1}.[28]

Table 1   Relative stability of Pt$_4$ isomers predicted by non-SO and SO DFT calculations

| Isomer | Structure | non-SO | | SO | |
		Spin moment/μ_B	ΔE/eV	Spin moment/μ_B	ΔE/eV
(4-1)	Tetrahedron	2	0.000	1.84	0.026
		4	0.109[a]	3.64	0.000
		6	1.110		
		8	2.239		
(4-2)	Rhombus	0	0.576	2.10	0.133
		2	0.471		
		4	0.206		
		6	0.945		
(4-3)	Square	0	0.232	0.00	0.357
		2	0.321	1.77	0.493
(4-4)	Y-like	0	1.410	0.54	0.410
		2	0.892	1.50	0.458
		4	0.551	3.51	0.354
		6	1.134	3.47	0.337

[a] Saddle point.

3.2   Pt$_4$

We report the relative stability of Pt$_4$ isomers with and without SO coupling for different spin multiplicities in Table 1. Each SO calculation was performed after a non-SO one starting from the charge and spin densities obtained by the non-SO calculation. Sometimes, different non-SO spin multiplicities converge to the same SO electronic state in the relaxation process. Since the SO energies could depend on the direction of the magnetization of the non-SO starting orbitals, and since some of the SO energy differences reported in the present work are in the range of the so-called magnetization anisotropy energy, it is not always guaranteed that the magnetic ground state has been obtained.

In the SO coupling included calculations, since the spin (S) and orbital angular momenta (L) interact, they are not separately conserved but the total angular momentum $J = L + S$ is conserved. When the relativistic effects are considered as a perturbation then one can consider $L^2 = L(L + 1)$ and $S^2 = S(S + 1)$ as being conserved.[29] We use the term spin moment in Tables 1, 2 for SO cases in that sense. The geometric structures and bond lengths of each isomer of Pt$_4$ for their most stable spin multiplicities are given in Fig. 1.

Similar to the results in our previous study on bare and hydrogenated small Pt clusters[7] where we did not employ SO coupling effects and similar to ref. 9 and 30, the calculated lowest energy structure of Pt tetramer is a tetrahedron for both cases of non-SO and SO. When SO effects are not considered, the ground state spin multiplicity of the tetrahedron is 3 and it has the point group symmetry C_{3v}. On the other hand, when SO effects are taken into account, quintet, septet, and nonet initial spin multiplicities converge to the same spin moment of 3.64 μ_B and this state has 26 meV lower energy than the one with 1.84 μ_B spin moment. In addition, the point group symmetry of the optimized structure in this case is D_{2d}. Our prediction of tetrahedron as the ground state geometry is in contrast with some of the previous results.[11,12,31] A common

922 | Phys. Chem. Chem. Phys., 2009, 11, 921–925

This journal is © the Owner Societies 2009

Table 2 Isomeric structure properties of Pt_n (n = 4–6) clusters with and without SO coupling

Isomer	Structure	Symmetry non-SO	SO	Spin moment/μ_B non-SO	SO	Total BE/eV atom^{-1} non-SO	SO	SO Energy/eV atom^{-1}	HOMO–LUMO gap/eV non-SO[b]	SO	ω_l and $\omega_h{}^a$/cm^{-1} non-SO	SO
(4-1)	Tetrahedron	C_{3v}	D_{2d}	2	3.64	2.122	1.914	0.208	1.603	1.162	80, 215	99, 215
(4-2)	Rhombus	C_{2v}	C_{2v}	4	2.10	2.071	1.882	0.190	1.890	1.433	50, 213	44, 206
(4-3)	Square	D_{4h}	D_{4h}	0	0.00	2.064	1.825	0.239	1.577	1.487	9, 198	41, 187
(4-4)	Y-like	C_s	C_1	4	3.49	1.985	1.830	0.155	2.316	1.903	42, 234	48, 241
(5-1)	Pyramid	C_{2v}	C_{2v}	6	5.58	2.319	2.126	0.193	1.584	1.629	47, 209	51, 197
(5-2)	Capped tetra.	C_{2v}	C_s	4	3.67	2.321	2.090	0.231	1.656	1.403	39, 212	46, 198
(5-3)	W-like	C_1	C_1	4	3.58	2.288	2.087	0.201	1.780	1.563	41, 229	46, 230
(5-4)	Bipyramid	D_3	C_1	4	3.56	2.284	2.077	0.207	1.807	1.236	71, 223	69, 210
(5-5)	Capped square	C_1	C_1	2	2.43	2.187	2.053	0.134	1.946	1.296	50, 229	50, 228
(5-6)	X-like	C_1	C_1	2	3.39	2.135	2.028	0.107	2.063	1.754	30, 269	34, 246
(6-1)	Trigonal prism	C_{2v}	C_1	6	5.42	2.483	2.286	0.196	1.000	1.173	19, 197	11, 184
(6-2)	Triangle	C_1	C_1	6	3.44	2.418	2.267	0.151	3.081	1.392	37, 239	26, 242
(6-3)	Face capped pyr.	C_1	C_2	6	4.75	2.458	2.260	0.198	1.339	1.319	39, 206	38, 201
(6-4)	Double square	C_{2v}	C_1	6	0.74	2.369	2.230	0.139	1.958	1.343	31, 230	34, 245
(6-5)	Bridge capped pyr.	C_1	C_1	6	5.42	2.376	2.227	0.147	1.662	1.592	32, 216	22, 204
(6-6)	Face capped bipyr.	C_1	C_1	8	7.01	2.421	2.226	0.195	2.579	1.325	35, 200	^{c}
(6-7)	Octahedron	C_1	C_2	6	4.83	2.309	2.201	0.108	0.870	1.304	72, 209	49, 194
(6-8)	W-like	C_1	C_s	6	4.04	2.395	2.199	0.196	2.444	1.384	36, 238	47, 226
(6-9)	Double capped tetra.	D_{2d}	D_{2d}	4	3.66	2.417	2.177	0.240	1.824	1.265	28, 192	27, 196
(6-10)	Bridge capped bipyr.	C_1	C_1	4	0.00	2.425	2.175	0.250	1.625	1.326	41, 217	48, 217
(6-11)	Double capped square	C_2	C_1	2	3.22	2.371	2.170	0.202	1.511	1.279	30, 216	30, 229

^{a} Lowest and highest vibrational frequencies. ^{b} α Spin. ^{c} Convergence cannot be achieved.

feature of these studies is that they have been done by employing plane wave codes (ref. 11 and 12 are by PAW method of VASP,[32] ref. 31 is by CPMD [33]) and predict that the rhombus isomer is the lowest energy structure with a spin multiplicity of 5 despite the fact that Futschek et al.[9] have employed the code VASP too and obtained a distorted tetrahedron similar to our results. According to the present calculations of non-SO case, the quintet state is the ground magnetic state of the rhombus, but its total energy is 0.206 eV higher than that of the tetrahedron. For the SO case, the rhombus whose singlet, triplet, quintet, and septet initial spin multiplicities converge to a spin moment between 2.08 and 2.11 μ_B has 0.133 eV higher energy than the tetrahedron. The optimized structures of the rhombus in both non-SO and SO cases have the same point group symmetry C_{2v}. As in the case of the dimer, SO effects slightly stretch the bond lengths. Both of these structures are out of plane where the angles between the triangular planes are 113° (non-SO) and 105° (SO). Thus, the SO effect strengthens the non-planarity of the rhombus in contrast to the findings of Huda et al.[12] The third, and fourth lowest energy isomers of Pt tetramer are the square and Y-like (see Fig. 1) planar structures, respectively. The total energy of the singlet square (non-SO) is 0.232 eV higher than that of the global minimum. SO effect increases this energy difference to a value of 0.357 eV which is dissimilar to the general trend that SO effects decrease the energy differences between the isomers. For the Y-like isomer, the energy separations from the lowest energy structure are 0.551 eV (non-SO quintet) and 0.337 eV (SO 3.47 μ_B).

3.3 Pt$_5$

We have identified six different stable isomers of Pt$_5$ clusters and reported their relative stabilities, structures and bond lengths in

the ESI.† Although a bridge side capped tetrahedron with a spin multiplicity of 5 has been obtained as the lowest energy structure for the non-SO case which agrees with our previous calculations,[7] SO coupling effects favor a pyramid with 5.58 μ_B spin moment. The energy separation between the capped tetrahedron and the pyramid in the former case is only 11 meV which may be considered within the accuracy of the calculations. On the other hand, SO effects favor a pyramidal structure to the tetrahedral one as much as 167 meV. While the obtained pyramidal isomer as the lowest energy structure contradicts the findings of Bhattacharyya and Majumder,[11] Huda et al.,[12] Grönbeck and Andreoni,[31] Xiao and Wang,[34] Saenz et al.,[8] and Futschek et al.,[9] it agrees with the predictions of Balasubramanian et al.,[30] Yang et al.,[35] and Seivane and Ferrer.[10] Bhattacharyya and Majumder,[11] and Huda et al.[12] have predicted planar bridge side capped structure, Grönbeck and Andreoni,[31] and Saenz et al.[8] have predicted planar W-like structure, Xiao and Wang,[34] and Futschek et al.[9] have predicted trigonal bipyramid as the global minimum configuration.

The third low lying isomer is an out of plane W-like structure with a spin moment of 3.58 μ_B having 173 meV higher energy than the global minimum. Previously we have identified this trapezoidal-type structure as the fifth low lying isomer.[7] However, in that study we have considered only its singlet and triplet states. Thus, the discrepancy can be attributed to the limitation of the previous calculations for the first two spin multiplicities. The fourth energetically favorable structure is a bipyramid with 3.57 μ_B spin moment. The planar, bridge side capped square structure which has been predicted as the global minimum of Pt$_5$ clusters[11,12] by a plane wave code, has been obtained as the fifth isomer in our calculations. It has 0.674 eV (non-SO) and 0.373 eV (SO) higher energies than the lowest energy structures. Finally, a
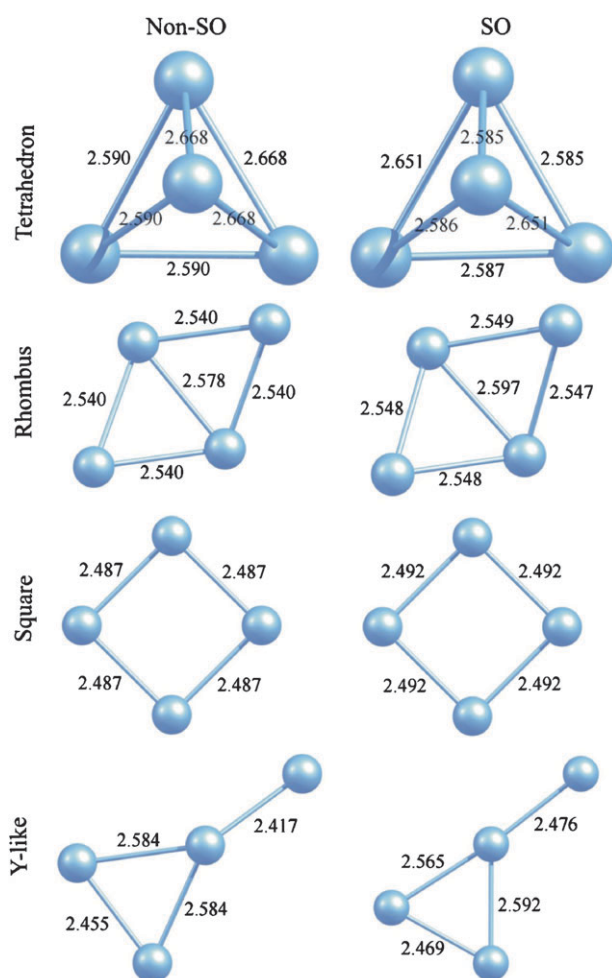
Fig. 1 Relaxed geometries of Pt_4 isomers for the most stable spin multiplicity of each isomer with and without SO coupling effects (distances are in Å).

non-planar X-like geometry has been identified as a stable isomer with the highest total energy. Unlike most of the other isomers, the most stable magnetic state of the X-like structure for SO case could be obtained from an initial nonet state which gives very high relative energy (2.859 eV) in non-SO calculations.

The effect of SO coupling on the bond lengths of Pt_5 clusters is not monotonic. For the pyramidal structure, while the interatomic distances between the apex atom and the atoms on the squared plane are stretched, the distances between the atoms on the squared plane are diminished. For the capped tetrahedron, as SO effects make the triangle constructed by the capping atom and the two atoms bonded to the capping atom a bit larger, all other bond lengths are kept nearly the same. All bond lengths of W-like structure and most of them in X-like structure are stretched by SO coupling, on the contrary, it does not have a significant effect on the bond length of the bipyramid, and even causes contractions in the bond length of the capped square isomer.

3.4 Pt_6

The relative stabilities of eleven different isomer of Pt_6 and their bond lengths and structures can be found in the ESI.†

The most stable structure of Pt_6 has been obtained as a trigonal prism in the septet state for non-SO case and a state with 5.43 μ_B spin moment for SO case. Xiao and Wang[34] have predicted a planar double capped square, Bhattacharyya and Majumder[11] have identified a planar triangular structure, Futschek et al.[9] have obtained a face capped pyramid as the lowest energy isomer of Pt_6. In our calculations, the triangle is the second lowest energy structure having 0.113 eV high energy (SO case) than the prism, the face capped pyramid is the third isomer with 0.154 eV higher energy, while an out-off plane double capped square has been obtained as the last isomer with 0.696 eV relative energy to the lowest one. Dissimilar to Pt_4 and Pt_5 clusters, SO coupling effect changes the order of the most Pt_6 isomers. When SO effects are not included in the calculations, the second and the third isomers are predicted as the face capped pyramid and the bridge capped bipyramid, respectively. Similarly, the double capped tetrahedron has less relative energy for non-SO case than SO case. On the other hand, SO effect decreases significantly the relative energies of planar or quasi-planar structures. For instance, 0.390 eV of septet triangle becomes 0.113 eV, 2.031 eV nonet double square becomes 0.334 eV, 0.880 eV of double capped square becomes 0.696 eV due to SO mixing. The big difference between the relative energies of double square in the nonet state (2.031 eV for non-SO case and 0.334 eV for SO case) can be explained by the fact that SO effect highly changes the initial spin multiplicity and converges to a spin moment of 0.74 μ_B. Thus, we agree with Huda et al.[12] that SO coupling does have a considerable effect on these clusters, and it increases the stability of planar structures. However, we do not agree with neither Huda et al.[12] nor Bhattacharyya and Majumder[11] that the planar structures are the most stable isomers of small Pt_n (n = 4–6) clusters. This conclusion is supported not only by the results of Futschek et al.[9] but also by the findings of Tian et al.,[36] who have calculated the structural properties of Pt_7 cluster by using DFT with both Gaussian and plane wave basis sets and obtained a 3-D capped trigonal prism as the global minimum, which can be constructed by adding an atom on the center of one of the rectangular faces of the triangular prism. As in the case of Pt_5, while SO effect increases some of the bond lengths of Pt_6 clusters, it decreases some others.

3.5 Most stable isomers of Pt_4-Pt_6

Point group symmetries, spin magnetic moments, total binding energies per atom, SO energies per atom (binding energy difference between non-SO and SO cases), HOMO–LUMO gaps, and lowest and highest vibrational frequencies for the most stable spin states of each isomers of all Pt clusters studied in this work can be found in Table 2. SO coupling effects always reduce binding energy since they make larger contributions to the atomic energy than to the cluster energy. As the cluster size increases from 4 to 6, the binding energy per atom increases as well (from 2.122 to 2.483 eV for non-SO case, from 1.914 to 2.286 eV for SO case). In contrast to the results of Huda et al.,[12] SO energy per atom decreases from 0.208 to 0.193 eV when the size of the clusters changes from 4 to 5. For the lowest energy structure of Pt_6, SO energy per atom is

0.196 eV. Except for the first isomers of Pt_5 and Pt_6 and the seventh isomer of Pt_6, HOMO–LUMO gaps are reduced due to SO mixing. For the non-SO case, planar or quasi-planar (4–4), (5–5), (5–6), (6–2), (6–4), (6–8) structures have significantly large HOMO–LUMO gaps. SO effects reduce these large gaps. In general, SO coupling effect does not change the vibrational frequencies considerably. The distorted structures may arise merely due to the one-determinant wavefunction instead of a "state-average" over the components in degenerate cases.

4. Summary

In conclusion, we have studied the effect of SO coupling on small Pt clusters, Pt_n (n = 4–6). Four isomers of Pt_4, six isomers of Pt_5, and eleven isomers of Pt_6 were calculated with and without SO effects. It is found that SO coupling effects have a considerable effect on these clusters which can change the order of isomers. Although it increases the stability of planar structures, it cannot make these planar structures the most stable isomers. The lowest energy structures of Pt_4, Pt_5, and Pt_6 clusters are predicted as a tetrahedron, pyramid, and trigonal prism, respectively. In general, SO mixing reduces both total binding energies and HOMO–LUMO gaps.

Acknowledgements

References

1 G. Schmid, *Adv. Eng. Mater.*, 2001, **3**, 737.
2 W. Vielstich, A. Lamm and H. A. Gasteiger, *Handbook of Fuel Cells: Fundamentals, Technology, Applications*, Wiley, West Sussex, 2003.
3 Y. Xu, W. A. Shelton and W. F. Schneider, *J. Phys. Chem. A*, 2006, **110**, 5839.
4 J. Ho, M. L. Polak, K. M. Ervin and W. C. Lineberger, *J. Chem. Phys.*, 1993, **99**, 8542.
5 K. M. Ervin, J. Ho and W. C. Lineberger, *J. Chem. Phys.*, 1988, **89**, 4514.
6 W. Eberhardt, P. Fayet, D. M. Cox, Z. Fu, A. Kaldor, R. Sherwood and D. Sondericker, *Phys. Rev. Lett.*, 1990, **64**, 780.
7 A. Sebetci, *Chem. Phys.*, 2006, **331**, 9.
8 L. R. Saenz, P. B. Balbuena and J. M. Seminario, *J. Phys. Chem. A*, 2006, **110**, 11968.
9 T. Futschek, J. Hafner and M. Marsman, *J. Phys.: Condens. Matter*, 2006, **18**, 9703.
10 L. F. Seivane and J. Ferrer, *Phys. Rev. Lett.*, 2007, **99**, 183401.
11 K. Bhattacharyya and C. Majumder, *Chem. Phys. Lett.*, 2007, **446**, 374.
12 M. N. Huda, M. K. Niranjan, B. R. Sahu and L. Kleinman, *Phys. Rev. A*, 2006, **73**, 053201.
13 E. J. Bylaska, W. A. de Jong, K. Kowalski, T. P. Straatsma, M. Valiev, D. Wang, E. Apra, T. L. Windus and S. Hirata *et al.*, "NWChem, A Computational Chemistry Package for Parallel Computers, Version 5.0" (2006), USA, *Pacific Northwest National Laboratory*, Richland, Washington, 99352-0999, USA.
14 R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. LaJohn and P. A. Christiansen, *J. Chem. Phys.*, 1990, **93**, 6654.
15 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
16 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
17 http://www.chemcraftprog.com.
18 C. E. Moore, *Natl Bur. Stand. (US) Circ.*, 1971, **467**.
19 Q. Cui, D. G. Musaev and K. Morokuma, *J. Chem. Phys.*, 1998, **108**, 8418.
20 A. Fortunelli, *THEOCHEM*, 1999, **493**, 233.
21 K. Koepernik and H. Eschrig, *Phys. Rev. B*, 1999, **59**, 1743.
22 J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.
23 A. Marijnissen, T. T. ter Meulen, P. A. Hackett and B. Simard, *Phys. Rev. A*, 1995, **52**, 2606.
24 N. D. Gibson, B. J. Davies and D. J. Larson, *J. Chem. Phys.*, 1993, **98**, 5104.
25 H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, 1985, **14**, 731.
26 M. B. Airola and M. D. Morse, *J. Chem. Phys.*, 2002, **116**, 1313.
27 S. Taylor, G. W. Lemire, Y. M. Hamrick, Z. Fu and M. D. Morse, *J. Chem. Phys.*, 1988, **89**, 5517.
28 J. C. Fabbi, J. D. Langenberg, Q. D. Costello, M. D. Morse and L. Karlsson, *J. Chem. Phys.*, 2001, **115**, 7543.
29 S. Blundell, *Magnetism in Condensed Matter*, Oxford Universty Press, New York, 2001.
30 K. Balasubramanian, *J. Chem. Phys.*, 1987, **87**, 6573; D. Dai and K. Balasubramanian, *J. Chem. Phys.*, 1995, **103**, 648; D. Majumdar, D. Dai and K. Balasubramanian, *J. Chem. Phys.*, 2000, **113**, 7919; D. Majumdar, D. Dai and K. Balasubramanian, *J. Chem. Phys.*, 2000, **113**, 7928.
31 H. Grönbeck and W. Andreoni, *Chem. Phys.*, 2000, **262**, 1.
32 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.
33 R. Car and M. Parrinello, *Phys. Rev. Lett.*, 1985, **55**, 2471.
34 L. Xiao and L. Wang, *J. Phys. Chem. A*, 2004, **108**, 8605.
35 S. H. Yang, D. A. Drabold, J. B. Adams, P. Ordejón and K. Glassford, *J. Phys.: Condens. Matter*, 1997, **9**, L39.
36 W. Q. Tian, M. Ge, B. R. Sahu, D. Wang, T. Yamada and S. Mashiko, *J. Phys. Chem. A*, 2004, **108**, 3806.

This journal is © the Owner Societies 2009

Phys. Chem. Chem. Phys., 2009, **11**, 921–925 | 925