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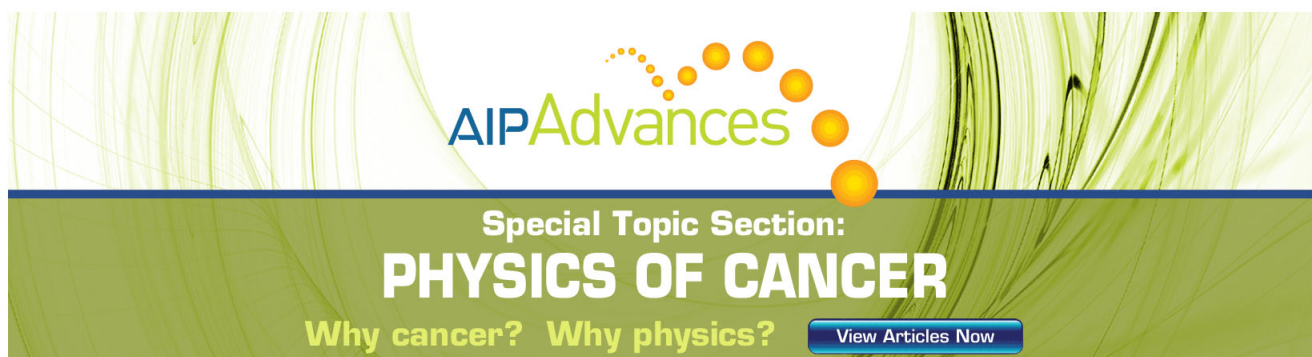
Evolution of superhalogen properties in PtCl$_n$ clusters

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We have systematically calculated the ground state geometries, relative stability, electronic structure, and spectroscopic properties of PtCl$_n$ ($n = 1$–7) clusters. The bonding in these clusters is dominated by covalent interaction. In neutral clusters, chlorine atoms are chemically bound to Pt up to $n = 5$. However, in neutral PtCl$_6$ and PtCl$_7$ clusters, two of the chlorine atoms bind molecularly while the remaining bind as individual atoms. In the negative ions, this happens only in the case of PtCl$_7$ cluster. The geometries of both neutral and anionic clusters can be considered as fragments of an octahedron and are attributed to the stabilization associated with splitting of partially filled d orbitals under the chloride ligand field. The electron affinity of PtCl$_n$ clusters rises steadily with n, reaching a maximum value of 5.81 eV in PtCl$_5$. PtCl$_n$ clusters with $n \geq 3$ are all superhalogens with electron affinities larger than that of chlorine. The accuracy of our results has been verified by carrying out photoelectron spectroscopy experiments on PtCl$_n{}^-$ anion clusters. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4719089]

I. INTRODUCTION

Halogen atoms are among the most electronegative elements in the periodic table. Their high electron affinities (EA) are associated with the electron shell closure rule and it takes only one electron to close their outer most p^5 shell. Consequently, they exist as negative ions and readily form ionic compounds when reacting with electropositive elements, such as Na. Chlorine has the highest electron affinity (3.62 eV) of all elements in the periodic table and NaCl is a well-known salt. However, stabilization of NaCl$_2$ requires the addition of an extra electron. As this extra electron is now redistributed over both the Cl atoms, the electron affinity of NaCl$_2$ is higher than that of the Cl atom. Hence NaCl$_2$ is termed as a *superhalogen*. Gutsev and Boldyrev[1,2] coined this word about 30 years ago to describe an entirely new class of molecules consisting of a central metal atom surrounded by halogen atoms. When the number of the halogen atoms exceeds the maximal valence of the metal atom, the resulting cluster becomes a superhalogen. Superhalogens can thus be described by the formula ML$_{(m+1)/l}$, where m is the maximal valence of the central atom, M, and l is the valence of the electronegative ligand L.[1,2] Thus NaCl$_2$ (Ref. 3), MgCl$_3$ (Ref. 4), and AlCl$_4$ (Ref. 5) are all superhalogens. Numerous superhalogen molecules have been designed and discovered over the past 30 years and these primarily consist of sp metal atoms[1–13] at the core whose maximal valence is easy to determine. However, the maximal valence of transition metal atom is not easy to determine as the extent of the participation of quasi-localized d electrons in chemical bonding is unclear. For example, consider manganese. It has an outer electronic configuration of $3d^5$ $4s^2$. Mn can be considered as having a valence of two when the $4s^2$ electrons participate in chemical bonding. Thus, MnCl$_3$ can be a superhalogen and it is.[14] Similarly, if all seven electrons in $3d^5$ $4s^2$ shells participate in chemical bonding, MnO$_4$ will be a superhalogen and it is.[15] Thus, a systematic study of the onset of superhalogen behavior of transition metal based molecules can be used to determine their maximal valence. There has been considerable interest in recent years in studying transition metal based superhalogens.[16] Vertical electron detachment energy as high as 12.63 eV in Ta$_3$F$_{16}{}^-$ has been predicted[17] and the superhalogen property of this molecule is consistent with the formula ML$_{(m+1)/l}$ where the maximal valence of Ta is 5 ($m = 3 \times 5 = 15$).

In this sense PtF$_6$ is a unique molecule; it is the first molecule which was shown to oxidize O$_2$ and noble gas Xe, both of which have ionization energies slightly above 12 eV.[18,19] Although, only part of the oxidizing ability stemmed from the electron affinity of molecular PtF$_6$, which was estimated to be 6.76 eV,[20] such molecules having high electron affinity became of interest due to various materials applications of oxidizing agents.[21–23] Pt with d^9s^1 is a representative transition metal whose valence is ambiguous. The highest oxidation state of Pt as +6 in PtO$_3$ has been investigated by Andrews and co-workers.[24] A computational study on PtF$_n$ ($n = 2,4,6,8$) showed that PtF$_4$ itself is a superhalogen with an electron affinity of 5.35 eV.[25] This would place the nominal valence of Pt at 3 or lower. Advanced calculations by Riedel[26] show that Pt cannot hold more than six fluorine atoms. In this study we have investigated the interaction of Pt with Cl to see how many Cl atoms can be bound chemically to Pt and how the electron affinities of PtCl$_n$ compare with those of PtF$_n$ clusters. The present work was further motivated by a recent photoelectron spectroscopy work of Wang and Wang[27] who showed that PtCl$_4{}^{2-}$ dianion is unstable against auto ejection of an electron, but the cluster was stable long enough for the authors to measure the negative electron affinity of PtCl$_4{}^-$. Our calculations were carried out using

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density functional theory (DFT) as well as at the coupled cluster with singles and doubles and non-iterative inclusion of triples, CCSD(T), level of theory. Photoelectron spectroscopy experiment on $PtCl_n^-$ anions was performed to validate our theoretical results. In Sec. II we describe the computational and experimental methods. The results are discussed in Sec. III and summarized in Sec. IV.

II. METHODS

A. Computational procedure

Our conformational search was carried out using density functional theory with hybrid B3LYP functional for exchange and correlation potential. Wesendrup and Schwerdtfeger have compared the calculated electron affinities of PtF_n using DFT-B3LYP with those obtained from MP2 and CCSD(T) methods, and concluded that the close agreement of MP2 and CCSD(T) results with less expensive DFT-B3LYP method justifies the use of the latter.[25] Our previous calculations also lend credibility to this choice.[16] Nevertheless, we have repeated our calculations using the CCSD(T) level of theory to examine the accuracy of the DFT results for $PtCl_n$ clusters. For this, we used the geometries obtained at the B3LYP level of theory without further optimization. This approach is justified as the geometries are not very sensitive to approximations in exchange and correlation. All our computations have been performed using GAUSSIAN 03 package.[28] Relativistic effects of Pt were incorporated using the Stuttgart-Dresden-Dunning (SDD) basis set. For Cl we used the all electron 6-311 + G(d) basis set. The structures of neutral and anionic $PtCl_n$ clusters were obtained by optimizing their geometries without any symmetry constraints and with various starting configurations where chlorine binds to Pt both chemically and molecularly. The dynamical stability of the clusters was confirmed by vibrational frequency calculation. We calculated all possible isomers with singlet and triplet spin multiplicities for even electron systems and doublet and quartet spin multiplicities for odd electron systems. States with higher spin multiplicities were also sampled, but they proved to be much higher in energy.

B. Experimental procedure

Anion photoelectron spectroscopy was conducted by crossing a mass-selected negative ion beam with a fixed-energy photon beam and analyzing the energies of the resultant photo-detached electrons. This technique is governed by the well-known energy conserving relationship, $h\nu = EBE + EKE$, where $h\nu$, EBE, and EKE are the photon energy, electron binding energy (transition energy), and the electron kinetic energy, respectively. The details of our apparatus have been described elsewhere.[29,30] Briefly, the photoelectron spectra were collected on an apparatus consisting of an ion source, a linear time-of-flight mass spectrometer for mass analysis and selection, and a magnetic-bottle photoelectron spectrometer for electron energy analysis (resolution ~35 meV at 1 eV EKE). The fourth harmonic (266 nm, 4.66 eV/photon) of a Nd:YAG laser and an ArF eximer laser

(193 nm, 6.42 eV/photon) were used to photo-detach electrons from the cluster anion of interest. Photoelectron spectra were calibrated against the well-known atomic lines of the copper anion.[31]

The $PtCl_n^-$ anions were generated by two different methods. In the first one an infrared desorption/photoemission ionization source, which has been described in detail elsewhere, has been used.[29] In short, low power infrared laser pulses (1064 nm, 1.17 eV/photon) from a Nd:YAG laser were used to desorb neutral molecules from a slowly moving graphite bar which was thinly coated with cisplatin, cis-diaminedichloroplatinum (II), powder (purchased from Alfa Aesar). Almost simultaneously, electrons were generated by visible laser pulses (another Nd:YAG laser operating at 532 nm, 2.33 eV/photon) striking a rotating yttrium oxide disk. $PtCl_n^-$ anions with $n \leq 3$ were formed as a result of cisplatin dissociation upon electron attachment in gas phase. A pulsed gas valve provided a collisionally cooled jet of helium to carry away excess energy and stabilize the resulting anions. In the second method, $PtCl_n$ clusters with $n \geq 2$ were generated using a pulsed arc cluster ionization source, which has been described in detail elsewhere.[32] In brief, a ~30 μs long 150 V electrical pulse applied across anode and platinum cathode of the discharging chamber containing 2 bar of ultrahigh pure chlorine gas partially dissociates the chlorine gas and vaporizes the platinum atoms. About 10 bar of ultrahigh purity helium gas then flushed the chlorine–platinum plasma mix down in a 20 cm flow tube, where it reacts, forms clusters, and cools. Anions generated by both methods were then mass selected for photoelectron spectroscopic studies.

III. RESULTS AND DISCUSSIONS

We begin our discussion with calculations of the equilibrium geometries and relative stabilities of neutral clusters carried out using DFT-B3LYP level of theory. We then focus on the structures and relative stabilities of anionic clusters. Finally, computed results on electron affinities are presented and compared with photoelectron spectroscopy experiments.

A. Neutral clusters

1. Geometries

In Fig. 1 we present the lowest energy isomers of $PtCl_n$ for $n \leq 7$. Two general observations can be immediately made. First, in $PtCl_n$ clusters up to $n = 5$ chlorine molecules dissociate and Cl atoms are chemically bound. However, in neutral $PtCl_6$ and $PtCl_7$ clusters two chlorine atoms bind molecularly. This is in contrast to the geometries of neutral PtF_n clusters where all F atoms are known to bind chemically up to $n = 6$. For $PtCl_6$ the pseudo O_h geometry with triplet and singlet spin multiplicities are, respectively, 0.35 and 0.93 eV higher than the reported molecular complex in Fig. 1. Clearly, the higher electronegativity of fluorine helps to involve more d electrons in bonding and made maximal valence of Pt higher in PtF_n. Second, the configurations of all the clusters can be considered as being part of an octahedron, indicating that

ligand field stabilization dictates the geometry. An additional point is that for all even electron systems ($PtCl_2$, $PtCl_4$, and $PtCl_6$) the preferred spin multiplicity is triplet, while the preferred spin states for all odd electron systems are doublets. We have not considered the effect of spin-orbit coupling on the relative order of various spin states.[33,34]

The bond lengths between Pt and Cl atoms range from 2.21 to 2.44 Å in all clusters where Cl atoms are chemically bound. In neutral $PtCl_6$ and $PtCl_7$ clusters the distances between Pt and Cl atoms forming a molecular complex are 4.84 Å and 2.60 Å, respectively. The distance between the Cl atoms in the Cl_2 molecular complex in these two clusters is 2.06 Å, which is same as the bond length of a free Cl_2 molecule, at this level of computation. We will show in the following that fragmentation pathways of these clusters are consistent with these geometries. It is worth pointing out that in PtF_n clusters the Pt–F bond lengths vary between 1.86 Å to 1.94 Å, which is consistent with the smaller size of the F ion.[25]

To understand the nature of bonding between Pt and Cl atoms we have analyzed the natural bond orbital (NBO) charge distribution. The charge on platinum in PtCl is +0.38 e, indicating that the ionic nature of the bond is low. This is not surprising since the electronegativity of platinum is quite high (2.2 in Pauling's scale). The lowest energy isomer of $PtCl_2$ is linear in accordance with the pure crystal field stabilization energy (CFSE) argument.[35] However, the preferred spin multiplicity of $PtCl_2$ is a triplet while the CFSE argument would suggest a spin singlet state. This difference further points to the fact that the formally d^8 Pt(II) is not ionically bonded to Cl^- anions, and that considerable covalency is involved in the bonding. This is supported by the NBO charge distribution where the charge on the Cl atom is –0.27 e compared to –0.38 e in PtCl. The spin singlet state which is 0.61 eV higher

in energy has a bent geometry. A combined spectroscopic and theoretical analysis had already confirmed the structure of $PtCl_2$ as linear.[36] $PtCl_3$ is T-shaped and has a spin doublet configuration. The NBO charge on one of the Cl atom is –0.18 e while each of the other two Cl atoms has a charge of –0.27 e. The geometry of $PtCl_4$ is square planar and its spin multiplicity is a triplet. However, CFSE argument again suggests a singlet square planar geometry resulting from a d^6 configuration. The NBO charge on the Cl is further reduced to –0.20 e confirming the covalent bonding features. A distorted square pyramid structure is the lowest isomer for $PtCl_5$. CFSE arguments also support a square pyramidal shape for a formal d^5 system over trigonal bipyramid geometry. The two elongated Pt–Cl (2.42 Å) bond and its 70° angle between them are indication of an electron deficient multicenter bonding. That is, chlorine is already facing difficulty in utilizing a fifth electron from Pt. The bonding remains primarily covalent and the charges on the Cl atoms vary from –0.10 e to –0.26 e. The lowest isomer of $PtCl_6$ contains a molecularly bound Cl_2. This is in contrast with the well discussed (distorted) octahedral geometry for PtF_6.[33] A pseudo octahedral geometry for $PtCl_6$ is a minimum at both singlet and triplet states but expulsion of a Cl_2 is exothermic.[37] Even the structure given in Fig. 1 is only 0.04 eV more stable than its dissociated product to $PtCl_4$ + Cl_2. Other halogen bonded and coordinated Cl_2 on $PtCl_4$ clusters exist in the floppy potential energy surface which are all quite close in energy. An analogous situation exists for $PtCl_7$ whose lowest isomer is composed of a Cl_2 molecule bound to the Pt atom of $PtCl_5$. The net charge on Cl_2 is +0.16 e which is lost to the $PtCl_5$ portion of the $PtCl_7$ cluster. In the case of $PtCl_6$, Cl_2 gained 0.01 e as here the Cl_2 is an electron density acceptor. Results of $PtCl_6$ and $PtCl_7$ suggest that there cannot be further addition of atomic Cl on Pt. Consequently, larger clusters were not explored.

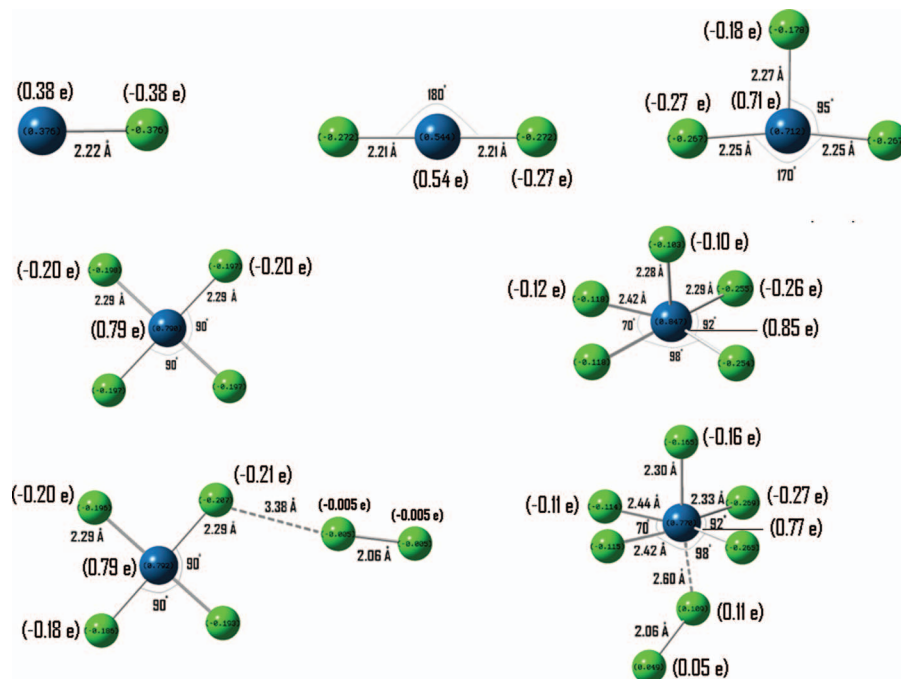
FIG. 1. Geometries of $PtCl_n$ (blue Pt; green Cl). The NBO atomic charges are given on atoms and in parenthesis.

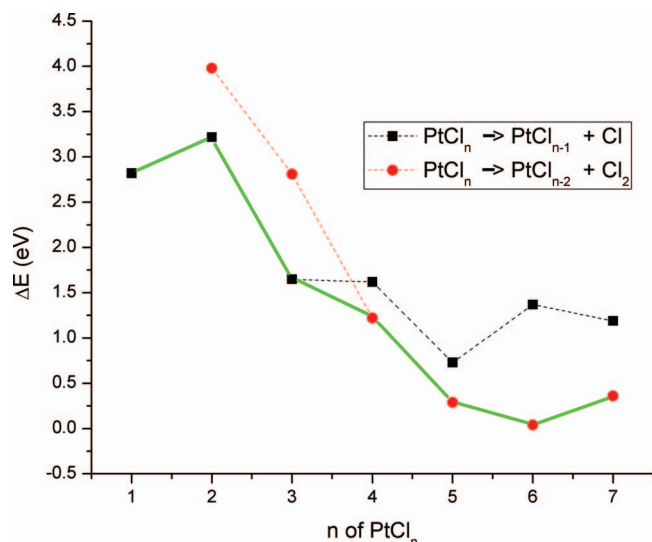FIG. 2. Unimolecular dissociation energies of neutral $PtCl_n$. The lowest energy decomposition channels are joined by a green line.

2. Relative stability

The relative stability of the above clusters against dissociation into Cl atom or Cl_2 molecule was calculated using the following equations:

$$\Delta E_{atomic} = E[PtCl_{n-1}] + E[Cl] - E[PtCl_n]$$

$$\Delta E_{molecular} = E[PtCl_{n-2}] + E[Cl_2] - E[PtCl_n].$$

The lower of these two energies yields the preferred dissociation channel. The dissociation energies are plotted in Fig. 2. As can be seen, the maximum Pt–Cl bond energy (3.22 eV) is present in $PtCl_2$ indicating that the optimal valence of Pt is two. For $PtCl_3$ the bond energy decreases con-

siderably. The lowest decomposition channel for $PtCl_4$ is by an expulsion of Cl_2, which further confirms the stability of $PtCl_2$. $PtCl_n$ clusters dissociate by ejecting a Cl atom for $n \leq 3$ and a Cl_2 molecule for $n \geq 4$. The endothermicity for the Cl_2 dissociation from $PtCl_5$ is 0.29 eV, which is also of similar magnitude as the coordination energy of Cl_2 on $PtCl_5$ in the case of $PtCl_7$ (0.36 eV).

B. Anionic clusters

1. Geometries

The lowest energy structures of anionic $PtCl_n^-$ clusters (Fig. 3) are similar to those of the neutrals for $n \leq 5$ and $PtCl_7^-$, but differ significantly for $PtCl_6^-$. Note that while in neutral $PtCl_6$ two Cl atoms formed a molecular complex, in $PtCl_6^-$ anion they all bind chemically. Two additional geometrical changes may be noted. The additional electron in $PtCl_4^-$ introduces a Jahn-Teller distortion by elongating the trans bonds. The electron deficient characteristics of neutral $PtCl_5$ are now eliminated with the additional electron as they form a square pyramidal structure. As expected from the decreased ionic interaction the bond lengths of anion are longer than those of the neutral. The exception is only for the electron deficient bonds present in neutral $PtCl_5$. Unlike neutral clusters, however, the even electron systems ($PtCl^-$, $PtCl_3^-$, $PtCl_5^-$, $PtCl_7^-$) all have spin singlet states. Though a direct comparison cannot be made because of difference in geometry, the additional electronic repulsive energy appears to override the advantage of exchange stabilization present in neutral clusters. The odd electron systems have all doublet spins.

2. Relative stability

To determine the preferred pathways for fragmentation of the anion clusters we need to calculate energies not only
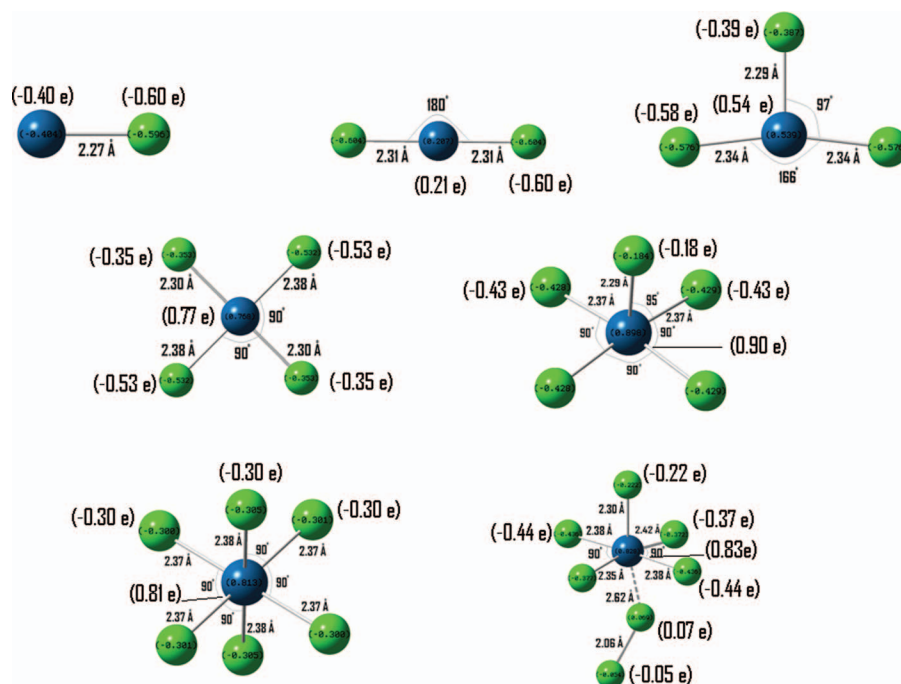

FIG. 3. Geometries of $PtCl_n^-$ anions (blue Pt; green Cl). The NBO atomic charges are given on atoms and in parenthesis.

TABLE I. Electron affinities of $PtCl_n$ clusters calculated at DFT-B3LYP and CCSD(T) levels of theory using different basis functions.

	B3LYP/SDD/ 6-311 + G(d) (eV)	B3LYP/SDD/6-311 + G(3df)//B3LYP/SDD/ 6-311 + G(d) (eV)	CCSD(T)/SDD/6-311 + G(d)//B3LYP/SDD/ 6-311 + G(d) (eV)	CCSD(T)/SDD/6-311 + G(3df)//B3LYP/SDD/ 6-311 + G(d) (eV)
PtCl	2.70	2.67	2.21	2.27
$PtCl_2$	3.68	3.57	3.27	3.31
$PtCl_3$	4.43	4.58	4.46	4.54
$PtCl_4$	5.12	4.99	4.97	5.11
$PtCl_5$	5.81	5.69	5.64	5.84

against dissociation into Cl atoms or Cl_2 molecules as has been done for the neutral clusters, but also against the charge carried by the fragments. This is achieved by calculating the following three different dissociation energies:

$$\Delta E_{atomic} = E[PtCl_{n-1}] + E[Cl^-] - E[PtCl_n^-],$$

$$\Delta E_{atomic} = E[PtCl_{n-1}^-] + E[Cl] - E[PtCl_n^-],$$

$$\Delta E_{molecular} = E[PtCl_{n-2}^-] + E[Cl_2] - E[PtCl_n^-].$$

These energies are plotted in Fig. 4 as a function of cluster size. As in the neutral, the highest endothermic decomposition energy is for $PtCl_2^-$. The lowest decomposition channel from $PtCl_4^-$ onward is via having the cluster retain the negative charge. This indicates that $PtCl_n$ ($n \geq 3$) clusters have higher electron affinities than Cl, and hence they are all superhalogens (see below for further discussion). The lowest decomposition channel for $PtCl_6^-$ and $PtCl_7^-$ is by ejecting a Cl_2 molecule. The dissociation energy of 0.29 eV for $PtCl_7^-$ is nothing but the coordination energy of Cl_2 to $PtCl_5^-$. This value is lower than the corresponding value for the neutral (0.36 eV) since the negative charge makes the coordination weak. This conclusion is supported by longer Pt–Cl_2 bond

(2.62 Å vs. 2.60 Å) as well as lesser charge transfer (0.02 e vs. 0.16 e) from Cl_2 in the anion.

C. Electron affinities

The electron affinities of $PtCl_n$ clusters were calculated by taking the energy difference between the lowest energy structures of neutral and anionic clusters. Vertical detachment energy (VDE), on the other hand, measures the energy difference between the ground state of the anion and its neutral cluster at the anion ground state geometry.

To examine the accuracy of the DFT based results we have repeated the calculations on stable $PtCl_n$ using coupled cluster, CCSD(T), level of theory. Calculations were also repeated with a more extended basis set, namely, 6-311G + (3df). The computed electron affinities at both levels of theory are compared in Table I. We note that with the exception of PtCl and $PtCl_2$, the results agree with each other within 0.2 eV, which is typically the accuracy attributed to the DFT based results.

The EA and VDE values for $PtCl_n$ ($n = 1$–7) are plotted in Fig. 5 and discussed below. There is a steady increase in electron affinity till $n = 5$. Note that the electron affinity of Pt atom is 2.07 eV at this computational level, which agrees
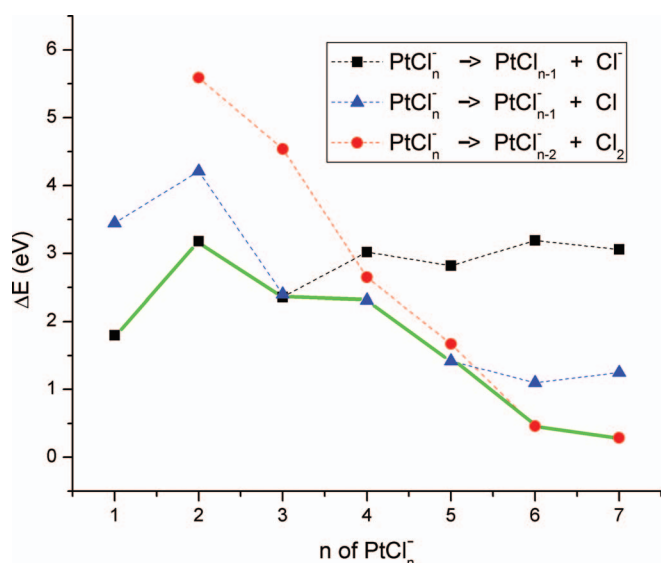

FIG. 4. Unimolecular dissociation energies of $PtCl_n^-$ anions. The lowest energy decomposition channels are joined by a green line.
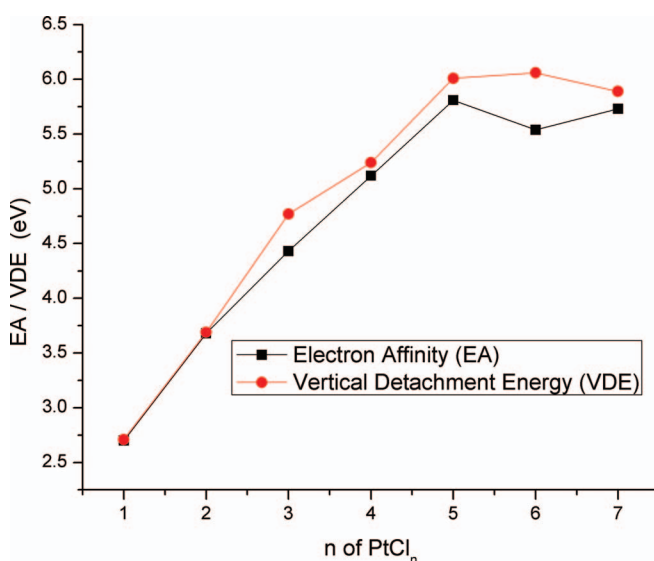

FIG. 5. Electron affinities of $PtCl_n$ and vertical detachment energies of $PtCl_n^-$ anions at B3LYP/SDD/6-311 + G(d).
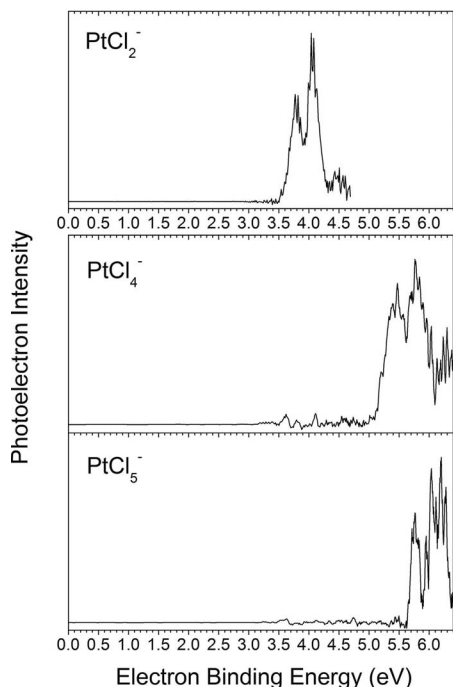
FIG. 6. Photoelectron spectra (PES) of $PtCl_2^-$, $PtCl_4^-$, and $PtCl_5^-$. The spectra were measured at photon energies of 4.66 eV (for $PtCl_2^-$) and 6.42 eV (for $PtCl_4^-$ and $PtCl_5^-$).

displays an onset at $\sim$3.5 eV and a peak maximum at 3.83 eV. The onset provides an approximate value of the EA and the peak maximum is a measurement of the VDE. The calculated result at the B3LYP level of theory agrees well with experiment.

An additional Cl atom further raises the electron affinity to 4.43 eV, making $PtCl_3$ a super halogen. Though the rise in electron affinity is not very dramatic, it may be noted that $PtCl_3$ fits the formula suggested for the super halogen, with the valence of Pt as two. We were unable to measure the EA and VDE of $PtCl_3$ due to its poor intensity. The electron affinity of $PtCl_4$ is 5.12 eV and that of $PtCl_5$ is 5.81 eV, the highest among $PtCl_n$ series. Considering the nature of atomic binding of Cl as the measure of the maximum valence of Pt, $PtCl_5$ also fits the formula of a superhalogen ($m = 4$). We succeeded in measuring the PES of both these anions (Fig. 6). The experimental EA's of 5.1 eV for $PtCl_4$ and 5.6 eV for $PtCl_5$ agree well with our calculated results in Table I.

The relative stability of anionic $PtCl_6^-$ makes the electron affinity of $PtCl_6$ (5.54 eV) higher that that of $PtCl_4$. The noticeable difference in VDE and EA for $PtCl_6$ (cf. Fig. 5) also comes from the difference in structure between the anion and the neutral. While neutral $PtCl_6$ consists of a molecular Cl_2, its anionic counterpart has all Cl atoms bound chemically. $PtCl_7$ has similar electron affinity (5.73 eV) as that of $PtCl_5$ which can be expected from their structures.

Since the high electron affinity is dictated by the stability of the anion, and consequently the distribution of the additional electron, we examined how the atomic charges on anionic clusters vary with respect to neutral clusters. In Fig. 7(a) we plot the NBO atomic charges on neutral and anionic $PtCl_n$ clusters. Due to high electronegativity of Pt, the positive charge on Pt is low and increases only marginally with each additional chlorine atom. In the anion, as the number of Cl atoms increase, the additional electron is almost fully distributed over chlorine atoms as evidenced by the narrowing of the gap between the two curves and merging at around
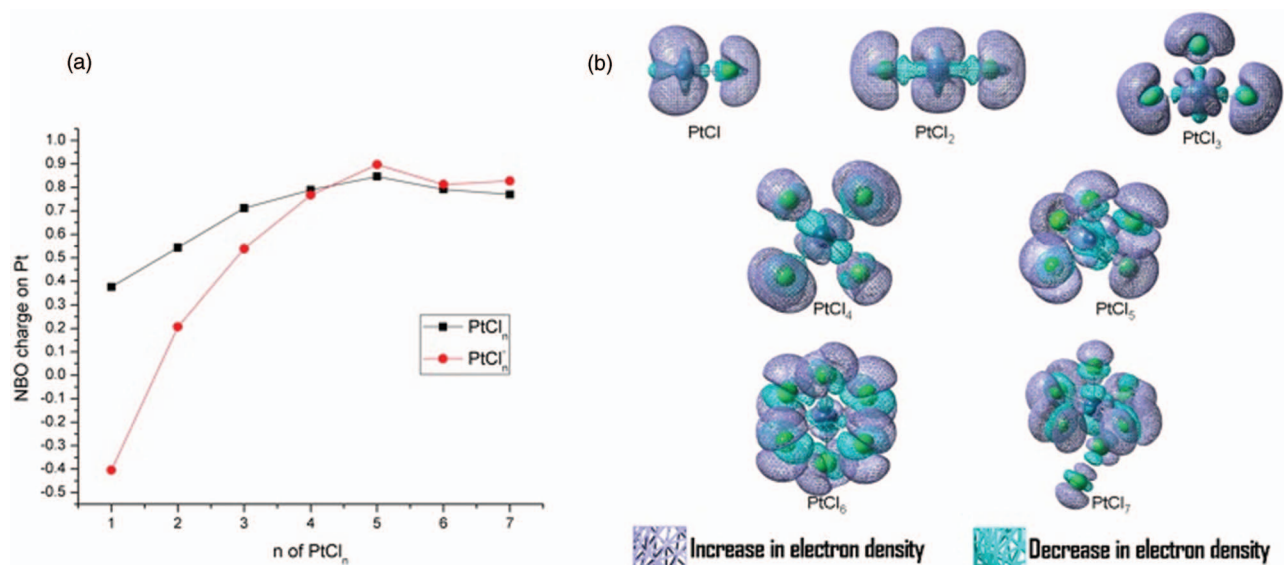
well with the experimental value of 2.13 eV.[38] Attaching a highly electronegative Cl atom only marginally increases the electron affinity of PtCl to 2.70 eV. An additional Cl raises the electron affinity to 3.68 eV, which is comparable to the electron affinity of Cl, namely, 3.62 eV. We should point out that our calculated value for the EA of Cl atom is 3.72 eV. As discussed earlier, the optimal valence of Pt is two. Thus, an electron affinity of 3.68 eV for $PtCl_2$ is indeed surprising. To verify the accuracy of our prediction, we carried out photoelectron spectroscopy experiment. The experimental result is given in Fig. 6. The photoelectron spectrum of $PtCl_2^-$

FIG. 7. (a) NBO charges on Pt for neutral and anionic $PtCl_n$. (b) Electron density difference plot (anion–neutral) of the $PtCl_n$ clusters in the anion geometry. The iso-surface value is 0.001 e/bohr^3.

$n = 4$ in Fig. 7(a). Thus, the favorable delocalization of the extra electron over all the electronegative chlorine atoms makes the anion lower in energy and the neutral cluster a superhalogen. The distribution of the extra electron is explicitly analyzed by subtracting the electron density of the neutral clusters from anions. Figure 7(b) shows the iso-surface (0.001 e/bohr^3) of the electron density difference. This complements the results obtained from the NBO analysis and shows that the added electron in the anion is distributed over all the Cl atoms.

IV. CONCLUSION

In summary, a systematic study of PtCl$_n$ ($n \leq 7$) clusters revealed that tethering of three Cl atoms are sufficient to increase the electron affinity of PtCl$_3$ to 4.43 eV, making it a superhalogen. This indicates that the nominal valence of Pt is two. However, continued increase in electron affinity, the dissociative binding of Cl in PtCl$_n$ clusters, the nature of Pt–Cl bond, and the dissociation energies of the clusters all point to the fact that the maximal valence of Pt is four. Thus, PtCl$_5$ has the highest electron affinity (5.81 eV) in this series. These results differ from those of PtF$_n$ clusters where the electron affinities continue to increase even up to $n = 6$. This shows that the oxidation state of Pt depends upon the element it is interacting with. We have validated our theoretical results with photoelectron spectroscopy experiment on PtCl$_2^-$, PtCl$_4^-$, and PtCl$_5^-$.

ACKNOWLEDGMENTS

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