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Quantum chemical investigation on structures and energetics of Tungsten Fluoride (WF_n^q) species ($q = 0, \pm1; n < 6$)

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Abstract. The present work deals with a systematic study on WF_n species using *ab initio* density functional method. The geometrical features related to the equilibrium structures of WF_n species up to $n = 5$ are highlighted and the effect of addition as well as removal of an electron is discussed. The chemical stability of these species is discussed by calculating their HOMO-LUMO energy gap and binding energy per atom. The frontier molecular orbital surfaces are also analyzed. The energy based electronic properties such as ionization potential, electron affinity, absolute electronegativity and chemical hardness are also evaluated which provide insights into chemical reactivity of these species.

Keywords. Tungsten fluorides; structure; HOMO-LUMO gap; molecular property; DFT.

1. Introduction

Transition metal elements are well known to bind with a number of atoms due to their variable oxidation states. This feature can be attributed to the participation of inner shell d electrons in bonding. Transition metal fluorides (MF_n) have been popular due to their extremely high electron affinities (EAs) with increasing number of fluorine atoms (n) on the periphery of M. This eventually happens due to the electron delocalization over several F atoms. As noticed by Gutsev and Boldyrev for the first time in 1981, the EAs of such species can exceed the maximum possible EA of halogen atom which is 3.62 eV for Cl, and therefore, such species are classified as superhalogens.[1–3] There exist a number of theoretical and experimental evidences for superhalogen behavior of transition metal fluorides.[4–8] Superhalogen property of molecular species is not only restricted to transition metal fluorides but also reported for a number of transition metal oxides.[9–13]

Tungsten (W) belongs to 5d series of transition metal group with outer electron distribution of $5d^46s^2$. Its hexafluoride (WF_6) is widely employed in the manufacture of semiconductor devices. It is used for the deposition of tungsten metal to form interconnects due to its high conductivity and compatibility with the silicon substrate. As compared to other hexafluorides of the same series, its EA is very low (3.5 eV) and so, it

does not belong to the class of superhalogens.[3] Furthermore, there exists no systematic study on WF_n species for $n < 6$. The corresponding experimental data are neither accurate nor reliable. In order to present a systematic understanding of WF_n ($n < 6$) species, we have performed a density functional survey. We have also included their mono ionized counterparts in order to get further insights into these species.

The present paper is organized as follows. First, we have discussed structures of all WF_n^q species for $q = 0, \pm1$. The HOMO-LUMO surfaces and energy gaps are calculated to discuss their stability. Ionization potentials and electron affinities of these species are also calculated and discussed. Finally, we have calculated some parameters describing chemical reactivity of these species.

2. Computational methods

The geometry optimization of all initial structures is carried out without any symmetry constraint by self consistent field iterations within density functional scheme using a hybrid exchange-correlation functional B3LYP[14,15] in conjunction with SDD basis set for all atoms. The present computational scheme has already been employed in some previous studies on transition metal fluorides.[5–8] Furthermore, this computational procedure yields IPs of WF_4 and WF_5, 9.53 eV and 10.16 eV, respectively which agree with the values of 9.89 eV and 10.03 eV (±0.10) reported by Hildenbrand.[16] Similarly, our calculated EAs of WF_4

and WF_5, 2.16 eV and 3.09 eV, respectively, are consistent with the results of De Wall and Neuert,[17] Thynne and Harland,[18] George and Beauchamp[19] and Compton *et al.*[20] The available experimental data are rather old but sufficient to suggest the reliability of our results and validity of the present scheme.

Normal mode frequencies are also calculated for all structures in order to ensure that they belong to at least a minimum in the potential energy surface. The same calculations are repeated for higher spin states to determine the preferred spin multiplicity of the neutral and monoionic species. The most popular Gaussian 09 program is used to perform all computations.[21] It is widely accepted that the natural bonding orbital (NBO) analysis gives insights into chemical bonding and NBO based partial atomic charges are more reliable due to its low basis set dependency.[22] In a recent study, we have also demonstrated the reliablity of NBO charges over the partial charges obtained by various other schemes.[23] NBO analyses are performed with the help of NBO 3.1 program[24] as implemented in Gaussian 09 package.

3. Results and Discussion

3.1 *Structural properties*

In order to obtain the lowest energy structures of neutral and singly charged WF_n species, we have considered various possible structures in which all F atoms interact simulatneously to central W atom as shown in figure 1. For $n = 2$, linear (1b) and bent (1c) structures, T-shaped (1d) and trigonal planar (1e) for $n = 3$, and tetrhedral (1f) and square planar (1g) structures for $n = 4$ are considered as initial geometries for optimization. It needs to be emphasized that we have considered only those structures in which F atoms bind dissociatively with W. Therefore, optimized structures do not necessarily correspond to global minima but at least to some local minima. To obtain the ground state of these species with respect to spin, we have also optimized these structures for higher spin states. The ground state spins of these species are idenfied as the structures with the lowest possible energies.

The ground state equilibrium geometries of WF_n species are displayed in figure 2 for $n = 1$ to 5. The symmetry and spin multiplicity (in brackets) of each species are also given. All neutral WF_n species assume the lowest spin in their ground states. In case of WF_n^- species, ground states correspond to the higher spin states. The singlet and triplet states of WF^- are found to be 2.33 and 0.87 eV higher in energy than the ground state. For WF_2^-, doublet and quartet states exceed 0.43 eV and 4.64 eV in energy to the sextet state. Furthermore, lower spin states of WF_n^- are 0.61, 0.58 and 0.30 eV higher in energy than our calculated ground state for $n = 3$, 4 and 5, respectively. For WF_n^+ species, the ground states correspond to the higher spin only up to $n = 2$ but take the lowest spin states for $n \geq 3$. The singlet and triplet spin states of WF^+ are 8.31 and 0.26 eV higher in energy than its ground (quintet) state. Similarly, the lowest (doublet) spin is 0.57 eV higher in energy than the ground state of WF_2^+.

From figure 2, it is apparent that all WF_n species closely mimic their structures irrespective of their charges expect for $n = 2$. For $n = 2$, the neutral (C_{2v}) geometry is almost linear which is bent appreciably with the removal of an electron (in its cationic state) whereas, WF_2 anion takes a linear $D_{\infty h}$ structure. Figure 3 shows plot of the average bond-length, W-F, in WF_n neutral species and their mono ionic counterparts up to $n = 5$. The average bond-lengths of 1.86–1.90 Å in neutral WF_n species are higher than their cations but smaller than their anionic counterparts, in general. For $n = 1$, however, addition or removal of electron results in the increase in the bond-length. Moreover, the bond-length of WF_3, 1.90 Å is the highest among all neutral species, while its ionic counterparts possess the smaller bond-length values (figure 3).
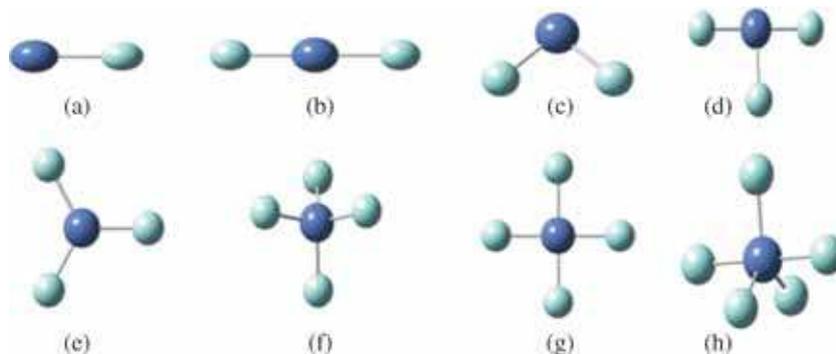

Figure 1. Initial geometries of WF_n^q species considered for $q = 0, \pm 1$ and $n = 1 - 5$.
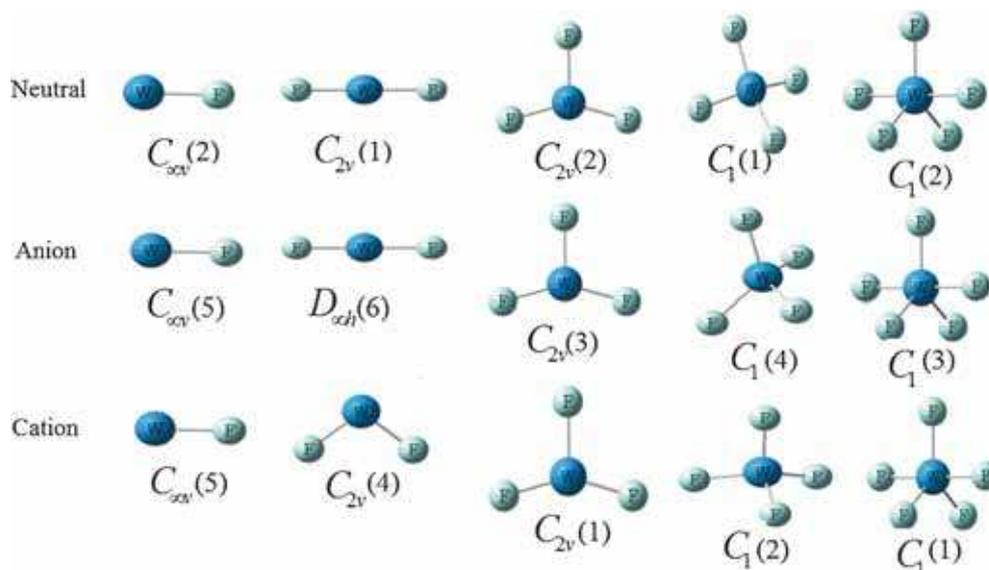
Figure 2. Equilibrium geometries of WF_n^q species for $q = 0, \pm 1$ and $n = 1 - 5$.

3.2 *HOMO-LUMO surfaces, energy gap and binding energies per atom*

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) surfaces of neutral, anionic and cationic WF_n species are plotted in figure 4. These orbitals are mainly responsible for chemical reaction or interaction with other species. One can note that the HOMOs of WF_n species are mainly localized on W atom which show a resemblance to those of their cations and anions consistent with their similar structures described above. However, the HOMO of WF_2 consists of mainly s atomic orbital

Figure 3. Average bond-length of W−F in WF_n^q species for $q = 0, \pm 1$ and $n = 1 - 5$.

of W atom in contrast to WF_2^+ and WF_2^- which are composed by p atomic orbitals. This can be expected due to the fact that the electronic configuration of W becomes $5d^5 6s^1$ in WF_2, $5d^5 6s^0$ in WF_2^+ and $5d^5 6s^2$ in WF_2^-. Furthermore, the LUMOs of WF_n species are delocalized over whole molecules unlike their anions. Therefore, the transitions from HOMO to LUMO in WF_n species represent the charge transfer to F atoms.

In order to analyze the stability of WF_n species, we have calculated the energy gap between their HOMO and LUMO which are also given in figure 4. This energy gap can be used to compare thermodynamic stability and/or chemical reactivity of WF_n species. In order to discuss the effect of addition or removal of an electron on the stability, we have also calculated the same energy gap for all ionic species as given in figure 4. From figure 4, one can see that the smallest energy gap, 0.65 eV of WF_3 suggest its more reactive or less stable nature. However, WF_3 is significantly stabilized by addition or removal of an electron. Figure 5 is a plot of the NBO charges on W atom vs n in WF_n neutral as well as ionic species. One can note that the addition of electron to WF_3 increases the electronic localization on W whereas removal of electron decreases it. One can see that the difference in NBO charges of W in WF_3 and WF_3^- is 0.75 e whereas the same for WF_4 and WF_4^- is only 0.40 e. Unlike WF_3, extra electron in WF_4 prefers to be delocalized over F atoms such that the difference in NBO charges on W is significantly reduced. In case of removal of an electron, on the contrary, the difference in NBO charges in WF_3 is smaller than that in WF_4. This fact is also reflected in their
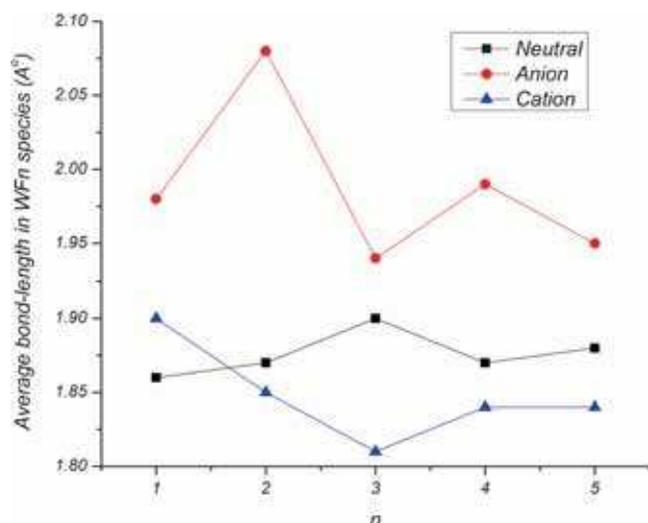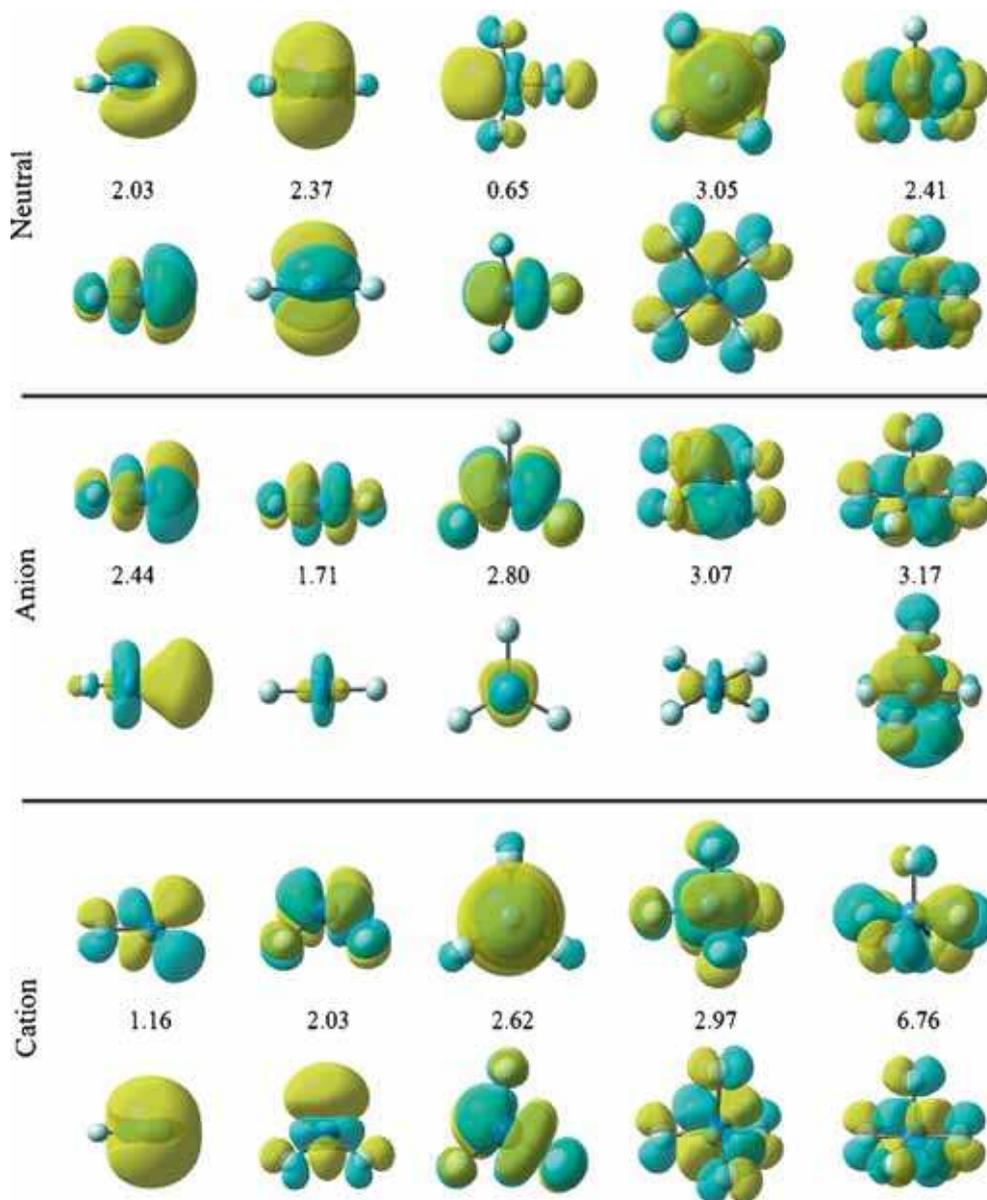
Figure 4. HOMO (upper set) and LUMO (lower set) surfaces of neutral, anionic and cationic WF_n species for $n = 1 - 5$. The energy gaps are given in eV.

molecular orbital sufaces. The HOMO surface of WF_3 shows delocalization of electrons whereas the HOMOs of its ionic counterparts are localized in nature. This may explain the reduced stability of WF_3 and enhanced stability of its ions. Furthermore, the highest energy gap of 3.05 eV corresponds to WF_4 which is unaffected by addition or removal of electron. More interestingly, the removal of an electron from WF_5 provides an enormous stabilization by increasing its energy gap from 2.41 eV to 6.76 eV. In general, the HOMO-LUMO gap of WF_n species ranges approximately between 2 to 3 eV except for $n = 3$. Note the energy gap of C_{60}, which is only 1.6 eV.

The trend of stability of WF_n is further analyzed by calculating their binding energies per atom (ΔE) as follows,

$$\Delta E = E[W] + n \times E[F] - E[WF_n]/(n + 1) \quad (1)$$

and listed in table 1. Here, $E[..]$ represents total electronic energy of respective species including zero point correction. One can see that ΔE increases with the increase in n, in general. However, for $n = 3$, ΔE decreases which is consistent with the reduced HOMO-LUMO gap of WF_3. The ΔE of WF_4 further suggests its enhanced stability due to it being larger among all WF_n species.
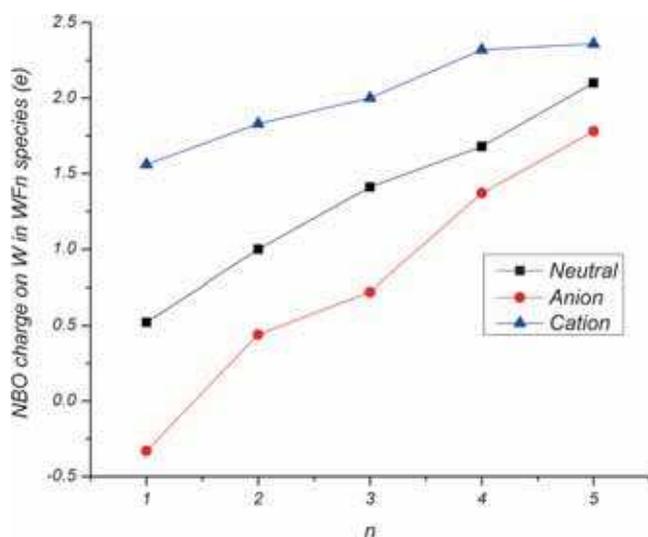
Figure 5. Partial NBO charges (in e) on W in WF_n^q species for $q = 0, \pm 1$ and $n = 1 - 5$.

3.3 *IP, EA and related parameters*

The effect of addition or removal of an electron from neutral WF_n species can be further analysed by their IP and EA values. IP and EA are calculated by the difference of energies between neutral species and their cations and anions, respectively in their ground state configurations. The calculated IP and EA values of WF_n species are collected in table 1. The lower IP and higher EA of WF_3 further establish its stabilization either by removal or by addition of an electron as mentioned earlier.

In general, the IP of WF_n increases with the increase in number of peripheral F atoms except for $n = 3$. This may imply that electron releasing tendency of WF_n decreases successively with the increase in n. In order to explain this fact, we have analyzed the charge distribution in WF_n species. In figure 5, one can see that the charges concentrated on W in WF and WF^+ are 0.52 e and 1.56 e, respectively. This implies that the ionization of WF removes an electron completely from W atom. However, in the case of $n = 5$, only about 25% of electron is contributed by W during ionization and 75%

comes from 2p orbital of F atoms. This happens due to delocalization of electrons over several F atoms as the successive F atoms are attached to W.

On the other hand, EA of WF_n species follows a dramatic trend, that is, it decreases with even number of F atoms ($n = 2, 4$). This may be explained on the basis of antibonding character of the HOMOs of WF_2 and WF_4 which is also reflected in their surface plots (figure 4). An addition of extra electron to WF_2 or WF_4 results in the decrease in EA of these species. This fact can be better understood on the basis of the HOMO-LUMO gap. The extra electron added to WF_n species increases the energy gap for $n = 1, 3$ or 5 but decreases in case of $n = 2$ or 4 (figure 4).

In order to compare the chemical reactivity of WF_n species, we have calculated absolute electronegativity (χ) and chemical hardness (η) as follows[25,26] which are also listed in table 1.

$$\chi = 1/2 \ (IP + EA) \tag{2}$$

and

$$\eta = 1/2 \ (IP - EA) \tag{3}$$

Absolute electronegativity measures the ability of species to attract electron and correlates inversely with the proton affinity. The increase in χ of WF_n species with the increase in n suggests the corresponding decrease in their proton affinities. This is consistent with the calculated IPs of WF_n species. Chemical hardness provides a quantitative measurement of the chemical stability of a system. The variation in η value follows the same trend as that of the HOMO-LUMO energy gap in WF_n species, as usual.

3.4 *Vibrational properties*

In this section, we disscuss significant vibrational modes of WF_n species. Vibrational frequencies are calculated to ensure the kinetic stability of optimized structures as all frequencies are found to be real. Table 1 also lists the frequency of selected vibrational modes. We have considered only stretching vibrations as they

Table 1. Various electronic parameters of WF_n species. All values are given in eV. Vibrational streching frequencies (in cm^{-1}) and intensities (in a.u.) are also listed.

n	ΔE	IP	EA	Absolute electronegativity	Chemical hardness	Frequency (intensity)
1	2.89	7.39	3.12	5.26	2.14	682.2 (52.6)
2	4.08	8.73	1.86	5.30	3.44	707.3 (164.5)
3	4.05	7.61	3.72	5.67	1.95	576.2 (129), 739.1 (107.7)
4	4.58	9.53	2.16	5.85	3.69	700 (181.8)
5	4.54	10.16	3.09	6.63	3.54	629.8 (137.2), 654.9 (231.1), 711.5 (142)

are the modes with the highest intensity. Out of all WF_n species ($n \leq 5$), single stretching mode of WF ($682\,cm^{-1}$) has the lowest intensity. On the other hand, most intense vibrations belong to WF_5 ($661\,cm^{-1}$), corresponding to antisymmetric stretching. Two more WF_5 stretching modes can be seen at 630 and $712\,cm^{-1}$, having equal intensities. Similarly, antisymmetric and symmetric stretchings of WF_3 are found at 739 and $575\,cm^{-1}$, respectively. The significant modes of WF_2 ($743\,cm^{-1}$) and WF_4 ($700\,cm^{-1}$) correspond to antisymmetric stretreching.

4. Conclusions

In summary, we have performed a systematic study on the structures of WF_n ($n = 1$ to 5) species in their neutral, anionic and cationic states. The ground states of all these species are identified with respect to their spins. WF_3 is found to be less stable among all WF_n species due to its lesser HOMO-LUMO gap. Using ground state energies of WF_n species, we have calculated the ionization potential and electron affinity of the neutral species and discussed the observed trend. Unlike other members of this family which shows higher EAs with successive F atoms,[5–8] a critical behavior of WF_n has been established. The chemical reactivity of these species is analyzed by their absolute electronegativity and chemical hardness.

Acknowledgement

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