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## Adiabatic electron affinities of (AgF)<sub>n</sub> clusters : experiment and DFT calculations

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### **Abstract:**

We present a joint theoretical and experimental investigation of small neutral and anionic silver fluoride clusters (AgF)<sub>n</sub><sup>(-)</sup> with  $n \leq 6$ . We have measured the electron detachment energies of the anions (AgF)<sub>n</sub><sup>-</sup> and determined the adiabatic electron affinities of neutral (AgF)<sub>n</sub> clusters. *Ab initio* calculations in the framework of the density functional theory have been performed to investigate the electronic and structural properties of both neutral and anionic species. The localization of the excess electron in the anion is discussed.

## 1. Introduction

The halides of noble metal have attracted much interest both by experiments and computations, in particular due to many practical applications such as the use of silver bromide in photography [1] and holography [2] or the use of copper halides as catalysts [3]. In a more fundamental point of view, the interactions between halide and noble metal atoms are difficult to characterize. The ionic bonding character is less marked than in alkali halide systems and the presence of *d* electrons of the noble metal makes theoretical investigations very complicated. In previous works[4,5], we have investigated the electronic and structural properties of silver bromide clusters. Our investigations were the first to show that small stoichiometric clusters  $(\text{AgBr})_n$ , with  $n \leq 6$ , adopt cyclic structures and not cubic ones as it was supposed hitherto. These surprising structures were explained by a significant covalent character in the silver bromide bonding with a large mixing between *s-d* hybrid orbitals of silver and *p* orbitals of bromine. More recently, P. Schwerdtfeger et al. [6] have found similar cyclic structures for the noble metal halide tetramers  $(\text{MX})_4$  ( $M = \text{Cu, Ag, or Au}$ ;  $X = \text{F, Cl, Br, or I}$ ).

Here, we present a joint theoretical and experimental investigation of small neutral and anionic silver fluoride clusters  $(\text{AgF})_n^{(-)}$  with  $n \leq 6$ . The clusters are studied in gas phase in a molecular beam. We have measured the electron photodetachment energies of the anions  $(\text{AgF})_n^-$  and determined the adiabatic electron affinities of neutral  $(\text{AgF})_n$  clusters. We also present a theoretical study of the electronic and structural properties in the framework of the density functional theory (DFT). The confrontation between the experimental and theoretical results will allow us to validate the theoretical approach and the reliability of DFT calculations of such anionic systems. Important informations about the bonding in the cluster and also about the localisation of

the charges in anions will be obtained from the calculations.

## 2. Experiment

The experimental setup has already been described elsewhere [7]. The  $(\text{AgF})_n^-$  clusters are produced by laser vaporization of a silver rotating and translating silver rod using a 532 nm Nd:YAG laser in a chamber in which helium gas at about 8 bar is injected. The helium carrier gas contains a small amount of  $\text{SF}_6$  (between 1 and 10%). The fluorine atoms are obtained by decomposition of  $\text{SF}_6$  molecules in the plasma created by the vaporization laser. The gas is then expanded out of the vaporization chamber and the anions are mass selected by a Wiley-Mac-Laren type time of flight mass spectrometer with a reflectron. Photodetachment energies are measured by a two-zone photodepletion technique: In a first experiment, the intensity  $I_{ref}$  of a given mass is recorded. Note that pulsed voltages are applied on the acceleration plates of the TOF mass spectrometer in order to accelerate negatively charged particles. In a second experiment, the anions are photodetached by a pulse optical parametric oscillator (OPO) just before their entrance in the acceleration zone. The duration of the laser pulse is about 10ns, and the laser energy per pulse is about  $0.1 \text{ mJ/cm}^2$ . The diameter of the laser beam in the interaction region is about 5 mm, it is enough to deplete all the clusters which could be detected. The signal  $I_{OPO}$  is recorded as a function of the wavelength of the OPO, which is tunable from 470 to 690 and from 740 to 1250 nm. The depletion signal  $I_{ref} - I_{OPO}$  is proportional to the photodetachment efficiency, since once they have been photodetached, neutral clusters are not any longer accelerated, thus detected. The normalized quantity  $1 - I_{OPO}/I_{ref}$ , plotted in Figure 1 for  $(\text{AgF})_n^-$  with  $n=2-6$ , is proportional to the photodetachment cross section. The laser pulse energy was checked to remain constant during the wavelength scan.

### 3. Calculations

We have used the DFT technique implemented in GAUSSIAN98 [8], combined with relativistic effective core potentials (RECP) to optimize the geometry of several configurations of both neutral  $(\text{AgF})_n$  and anionic  $(\text{AgF})_n^-$  clusters ( $n \leq 6$ ). We have used the hybrid B3LYP functional which involves Becke's three-parameter exchange functional [9-10]. Previous studies [5,11] on the structural and electronic properties of the silver clusters or binary clusters including Ag atoms have shown that explicit treatment of the 4s, 4p and 4d electrons of silver atoms like active valence electrons are necessary to describe in a correct way the electronic structure. Following this, an  $[\text{Ag}^{19+}]$  pseudopotential [12] was used to describe silver core while fluorine was described as  $[\text{F}^{7+}]$  core with 4s and 4p active electrons [13]. The Gaussian basis set on silver was  $8s7p6d$  contracted into  $6s5p3d$ , while that on fluorine was  $4s4p1d$  contracted into  $3s3p1d$ . Pre-and post-processing operations were performed with the graphical interface Gabedit [14].

In the optimization process of cluster geometries, a number of structures were tested for each size. We have initiated the geometry optimization process of  $(\text{AgF})_n^{(-)}$  clusters starting from the known structures of several silver halide clusters ( $(\text{AgBr})_{2-6}$ ,  $(\text{AgF})_4$ , and  $(\text{AgI})_3$ ) already published [4-6,15]. We have tested linear, cyclic and cubic structures. Harmonic frequency analysis was performed to warrant that the optimized structures are local minima. The option GRID=ULTRAFINE was used as requested in GAUSSIAN for computing low frequency modes.

### 4. Results and discussion

#### A. Experimental electron photodetachment energies

Figure 1 shows the electron photodetachment cross sections of  $(\text{AgF})_n^-$  clusters ( $n=2-6$ ) as a function of the energy of the depletion laser. For  $n \geq 7$ , clusters are not in sufficient quantity for a

study. The power of the laser is low enough to avoid two-photon absorptions. The dimension of the laser beam in the interaction region and the delay between the laser pulse and the voltage pulses applied to the acceleration plates are chosen to maximize the depletion. Photodetachment efficiency for  $n = 2$  shows a very steep slope, while the slopes are softer for the other sizes. However all the depletion signals are steep enough to conclude to a resonant process. The energies of about 2 eV seem to be too high to be assigned to electronic excitations. We think that the depletion signal is due to the photodetachment of one electron. Experimental electron detachment energies (aEDE), which are also adiabatic electron affinities (aEA) of neutral  $(\text{AgF})_n$  are given in Table 1. They are taken at the point of inflection at lowest EDE. They are in the 2.1-2.5 eV range with a minimum for  $n=4$ . The cross-section for  $n=5$  seems to decrease after a peak at 2.33 eV. However our signal to noise ratio is not good enough to ensure that this feature is significant.

## B. Geometries and electronic properties

The calculated ground state structures of neutral  $(\text{AgF})_n$  are shown in Figure 2. All the lowest isomers are planar rings with fluorine atoms sitting at the corner and silver atoms in the middle of the edges.  $(\text{AgF})_2$  is a quasi-square of  $D_{2h}$  symmetry with a FAgF angle of 93.4 degree and an Ag-F distance of 2.21 Å. The trimer  $(\text{AgF})_3$  is quasi triangular with fluorine at the apexes. This structure for the trimer is known to be particularly stable in the case of noble metal halides [15-18].  $(\text{AgF})_4$  is found to be a quasi-square with a  $D_{4h}$  symmetry. For this size, Schwerdtfeger and coworkers [6] have found the nonplanar  $D_{2d}$  structure to be more stable than the planar  $D_{4h}$  using the B3LYP functional in combination with LANL2DZ pseudopotential and basis set and also Stuttgart pseudopotential with diffuse and polarization functions. In the present work, the  $D_{2d}$  structure is not a local minimum, the optimization starting from the  $D_{2d}$  structure leading to a  $D_{4h}$  arrangement. However, Schwerdtfeger and coworkers have shown that the  $D_{4h}$  and  $D_{2d}$  structures

are very close in energy (the difference is 0.026 eV) and so the properties computed in the present work will not depend of the considered structure.  $(\text{AgF})_5$  and  $(\text{AgF})_6$  are found to be planar ringlike structures while nonplanar cycles are found not to be local minima and tridimensionnal structures are found to be less stable than planar cycles by more than 1 eV.

Our present results are in line with previous studies [4-5] on the silver bromide clusters for which nonplanar ringlike structures are found to be favored up to the hexamer. The silver-halide interactions are clearly iono-covalent. The atomic charge on silver atoms was found to be in the 0.3-0.5 a.u. range in the case of silver bromide clusters [5], while it is about 0.80 a.u. according to the natural population analysis (NPA) [19] in the case of silver fluoride clusters (the exact values are 0.83, 0.78, 0.77, 0.78, and 0.79 a.u. for  $n=2, 3, 4, 5,$  and  $6$  respectively). Hence, the atomic interactions are more ionic in the presence of fluorine. However the ring structures are also stabilized by additional covalent interactions. Indeed the interactions between the  $d$  orbitals of silver atoms and the  $p$  orbitals of the halide atoms favor halide-silver-halide alignment and silver-halide-silver bent substructures as already explained in Ref [5].

The calculated ground state structures of anionic  $(\text{AgF})_n^-$  are shown in Figure 3. All the lowest-energy isomers are planar except for  $n=6$ .  $(\text{AgF})_2^-$  and  $(\text{AgF})_3^-$  are quasi linear with FAgF linear subunits and bent AgFAg subunits (with an angle of about 150 degrees). The linear structures are found to have imaginary frequencies. The bent character of the AgFAg angles is favored by both the mixing of the  $d$  orbitals of silver with the  $p$  orbitals of fluorine and the polarization of fluorine. One can note that rings are found to lie 0.97 and 0.40 eV above the quasi 1-dimensional structures for  $n = 2$  and  $3$  respectively. For  $n \geq 4$ , the lowest-energy isomer is found to be a cyclic arrangement in which the Ag atoms tend to be gathered, setting a  $\text{Ag}_n$  core, with outer F atoms. For  $n=5$ , the two isomers shown in the figure 3 are quasi-degenerated (the isomer (a) is 0.002 eV below

than isomer (b)).  $(\text{AgF})_6$  presents a dihedral angle of 50 degrees instead of being planar in order to increase the  $\text{F}^-$ - $\text{F}^-$  distance and thus to decrease the  $\text{F}^-$ - $\text{F}^-$  repulsion.

The excess electron in  $(\text{AgF})_n^-$  is localized on silver atoms as shown in figure 4. For  $n=2$  and 3, the electron is localized on the terminal Ag, while it is localized on inner Ag atoms for cyclic structures. We can suppose that for  $n=2$  and 3, the quasi 1-dimensional structures are more stable than cyclic ones for anions because they give more space for the extra electron than the very small ring. The electronic structure of  $(\text{AgF})_2$  can be described as  $\text{F}^- \text{Ag}^+ \text{F}^- \text{Ag}$ . This is confirmed by the NPA population analysis which says  $\text{F}^{-0.80} \text{Ag}^{+0.66} \text{F}^{-0.82} \text{Ag}^{-0.04}$ . Starting from  $n = 4$ , cyclic arrangements are large enough to support one more electron and become more stable than linear structures. The excess electron is shared by inner Ag atoms. The atomic charges on inner silver atoms are about +0.4 a.u. while they are about +0.7 a.u. on outer Ag atoms (Figure 3). In  $(\text{AgF})_6^-$  the electron configuration for inner Ag atoms is found to be  $s^{0.60}d^{9.96}p^{0.07}$  while that of outer Ag atoms is  $s^{0.41}d^{9.83}p^{0.02}$ . In comparison, the electron configuration on silver atoms in the neutral  $(\text{AgF})_6$  cluster is  $s^{0.33}d^{9.86}p^{0.02}$ . The present NPA population analysis shows clearly that the excess electron is located on inner silver atoms in s-type orbitals.

The Ag-Ag distances in the anionic clusters are in the 2.86-3.00 Å range for the cyclic structures. They are longer than the Ag-Ag bond length in the free gaseous  $\text{Ag}_2$  molecule and  $\text{Ag}_2^+$  ion (2.59 Å and 2.78 Å at the B3LYP level, respectively), but much shorter than the Ag-Ag distances in neutral silver fluoride (from 3.04 Å in  $(\text{AgF})_2$  to 3.73 Å in  $(\text{AgF})_6$ ). For each size considered in the present study, the shortest Ag-Ag distances are found to be 2.86 or 2.87 Å and they involve silver atoms sharing the excess electron. Thus the short Ag-Ag distances are due to the sharing of the excess electron.



### C. Adiabatic and vertical electron detachment energies

We now discuss the calculated electron detachment energies of  $(\text{AgF})_n^-$  clusters. We have calculated both the vertical detachment energy vEDE (when the geometry of the neutral cluster is considered as identical to that of the anion) and the adiabatic one aEDE (including the relaxation of the neutral cluster geometry). aEDE is in fact the adiabatic electron affinity (aEA) of the neutral  $(\text{AgF})_n$  clusters. Results are given in Table 1, together with the experimental electron affinity. The calculated aEA (or aEDE) are found in excellent agreement with the experimental data. The calculated values are in the 2.01-2.47 eV range with the larger value for  $n=2$ . This is a rather unexpected finding that the experimental photodetachment energies are found so close to the adiabatic calculated values, rather than the vertical ones. This is related to the behaviour of the cross sections, and then to the vibrational overlap, and continuum wavefunctions. For  $n=5$ , two vEDE values are given in Table 1 corresponding to the two degenerate isomers of  $(\text{AgF})_5^-$ . The large gap between the vEDE and aEDE values for  $n=3, 5$ , and 6 is due to the significant structural reorganization after the detachment of the electron, while the small gap for the tetramer corresponds to small structural changes. For the dimer, a small gap is found while the structural reorganization is similar to that of the trimer which presents on the contrary a large gap. For the dimer and trimer, the vEDE-aEDE gap corresponds to the relative energy for the neutral system between the quasi-linear structure and the cyclic one. For neutral trimer, the cyclic  $D_{3h}$  structure is 1.68 eV below the quasi linear structure, but for the dimer the cyclic  $D_{2h}$  structure is only 0.64 eV below the quasi linear structure. This small value for the dimer can be explained by a large repulsion between  $\text{F}^-$  anions which are close to each other in the  $D_{2h}$  cyclic structure. On the contrary, in the cyclic structure of the trimer the coulombic repulsion are much smaller and so the cyclic structure is more stable.

## 5. Conclusion

We have presented a joint theoretical and experimental investigation of  $(\text{AgF})_n^-$  anions and neutral  $(\text{AgF})_n$  clusters. The adiabatic electron affinities of neutral  $(\text{AgF})_n$  clusters has been measured for  $n \leq 6$ . Electronic and structural properties have been studied in the framework of the density functional theory. The lowest-energy isomers are cyclic structures for neutral species. For anions, the excess electron is located on the terminal silver atom in a quasi 1-dimensional structure for  $n=2$  and 3, while it is shared by several silver atoms which tend to be gathered in a structure formed by a  $\text{Ag}_n$  core with outer fluorine for  $n \geq 4$ . Calculated values in the framework of the DFT for the adiabatic electron affinities of  $(\text{AgF})_n$  are in excellent agreement with the experimental data.

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**Table 1.** Experimental and calculated adiabatic electron detachment energies of  $(\text{AgF})_n^-$  anions for  $n=2-6$ , together with the calculated vertical values.

$n$	<i>EDE expt (eV)</i>	<i>adiabatic EDE (eV)</i>	<i>vertical EDE (eV)</i>
2	$2.50 \pm 0.05$	2.47	3.11
3	$2.28 \pm 0.15$	2.01	3.69
4	$2.1 \pm 0.1$	2.04	3.03
5	$2.25 \pm 0.05$	2.16	3.88 – 3.68
6	$2.2 \pm 0.1$	2.15	3.95

**Figure captions**

**Figure 1.** Electron photodetachment cross sections of  $(\text{AgF})_n^-$  clusters ( $n=2-6$ ) as a function of the energy of the depletion laser.

**Figure 2.** Optimized geometries of the lowest-energy isomers for neutral  $(\text{AgF})_n$  clusters with  $n \leq 6$ . The spatial symmetries are given. Silver atoms are represented by large spheres.

**Figure 3.** Optimized geometries of the lowest-energy isomers for anionic  $(\text{AgF})_n^-$  clusters with  $n \leq 6$ . The spatial symmetries are given. Silver atoms are represented by large spheres. Charges from the natural population analysis are also given in a.u.

**Figure 4.** Excess electron orbitals in  $(\text{AgF})_n^-$ . Iso-value is 0.04 a.u.

Figure 1

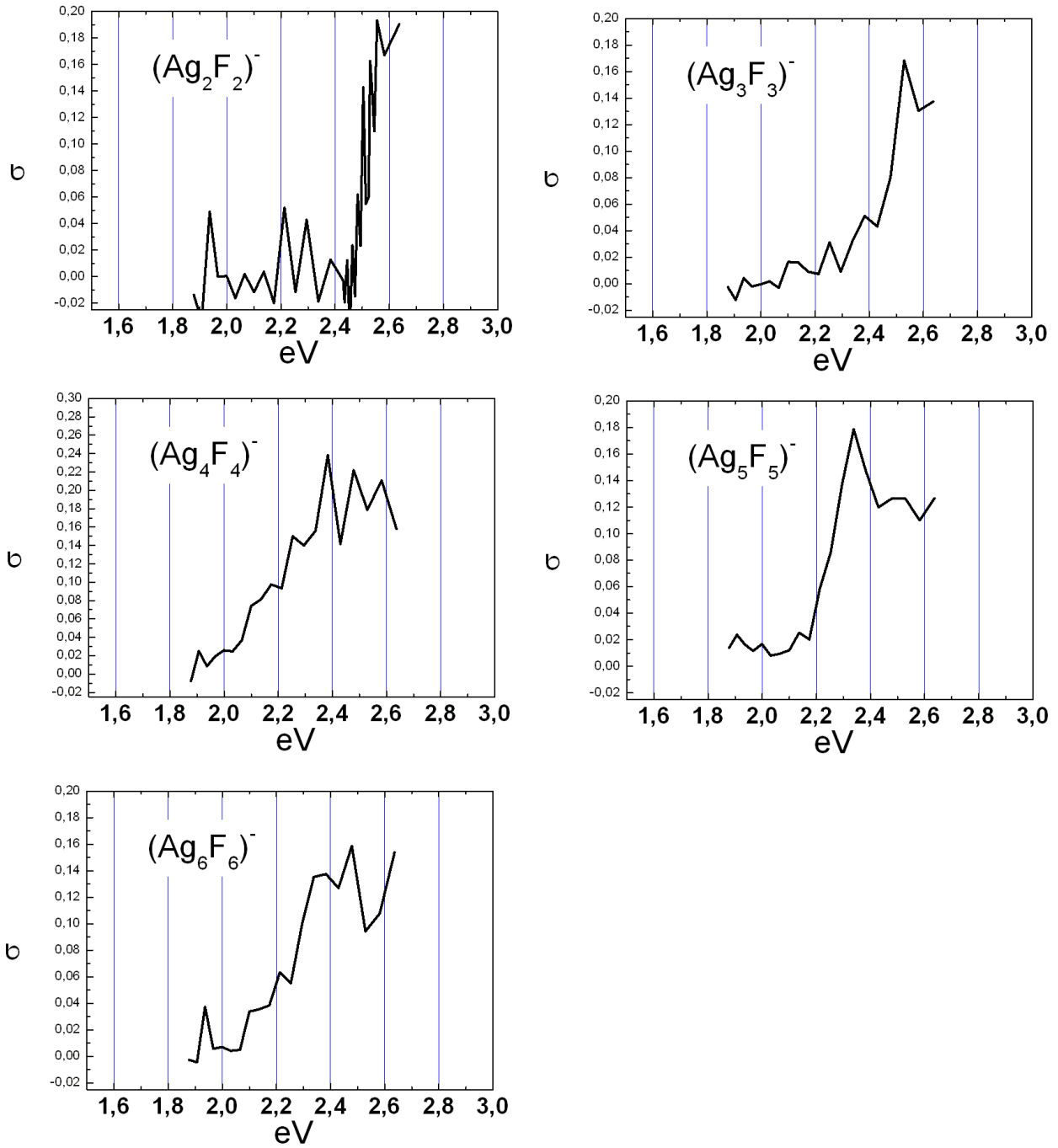


Figure 2.

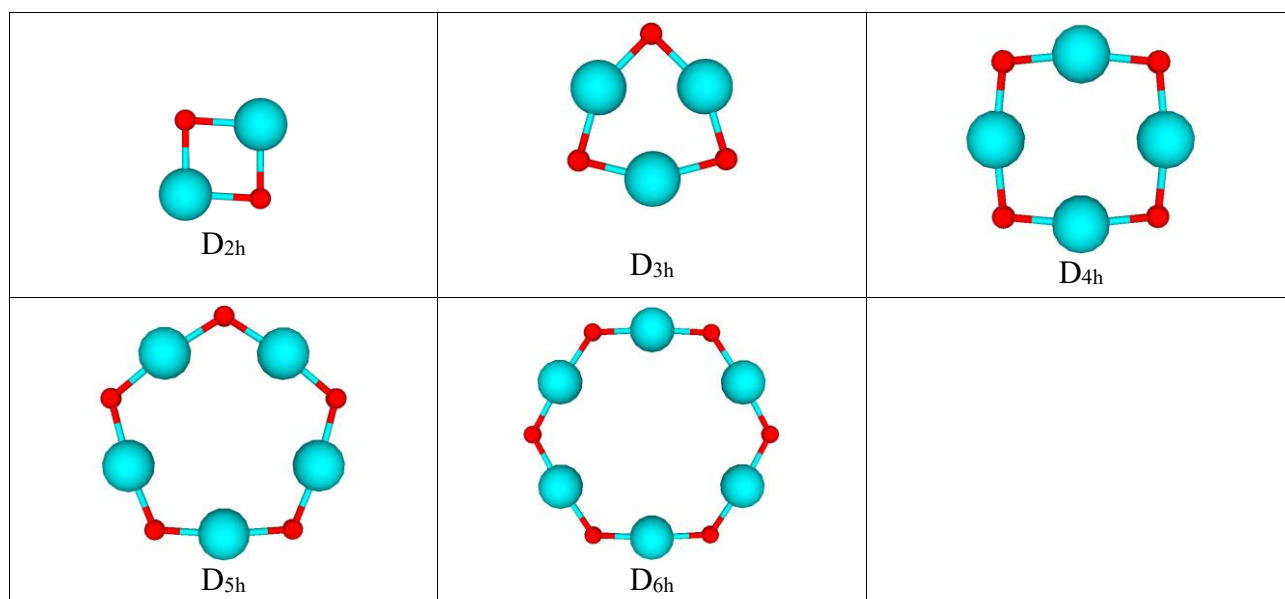


Figure 3.

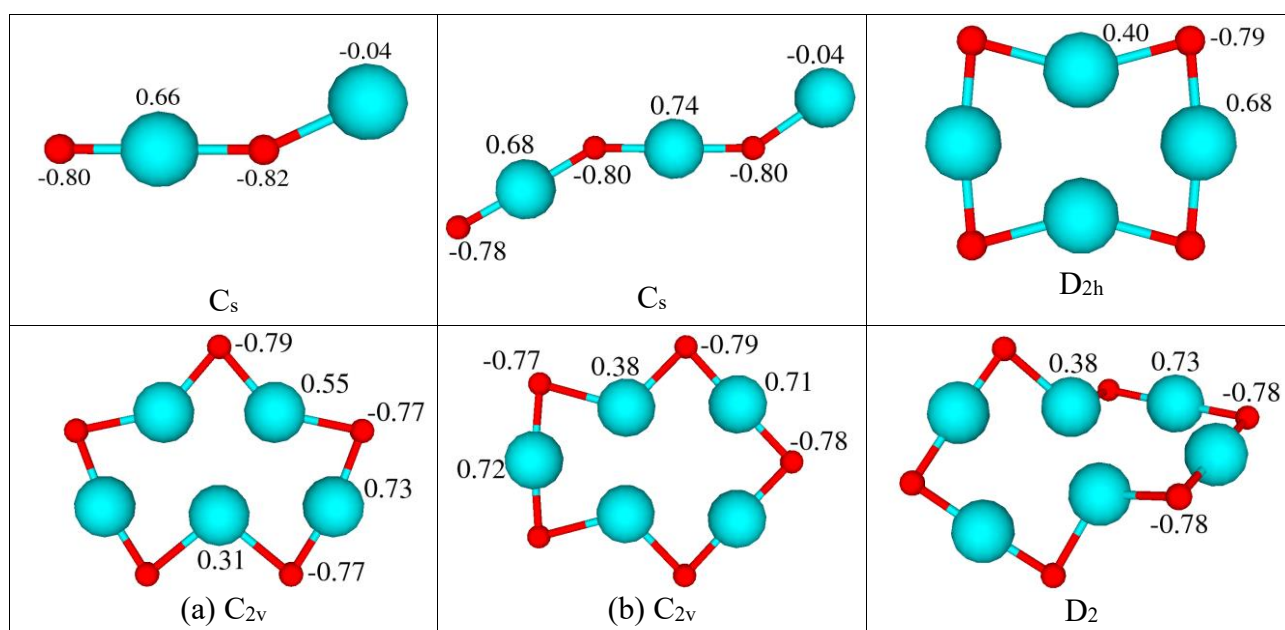




Figure 4.

