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FIRST-PRINCIPLES STUDY OF STABILITY OF OZONE CLUSTERS $(O_3)_n$, n=1-6

N.P. Adhikari[1]
Central Department of Physics, Tribhuvan University, Kirtipur, Kathmandu, Nepal
and
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy.

MIRAMARE – TRIESTE

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[1] Regular Associate of ICTP. npadhikari@gmail.com

Abstract

The present work describes the equilibrium configuration for ozone molecule, its dimer, trimer, tetramer, pentamer and hexamer obtained with the first-principles calculations implemented by the Gaussian 03W set of programs in the DFT(MPW1PW91) and DFT(B3LYP) levels of approximation. The consistency of the results has been tested by their convergence with respect to the use of basis sets with increasing size and complexity. With the DFT(MPW1PW91) level of approximation, we have estimated the bond distance and the bond angle of ozone molecule to be 1.24 Å and 118.3º, which agree well with the previously reported values 1.272 Å and 116.8º, respectively. With DFT(MPW1PW91), we have estimated the binding energy of ozone molecule to be 5.79 eV which also agrees well with the previously reported value 6.17 eV within 6%. The distance between the two nearest oxygen atoms of the dimer of ozone $(O_3)_2$ is estimated to be 1.42 Å. The binding energy of $(O_3)_2$ is estimated to be 0.0403 eV in the DFT(B3LYP) level of approximation, which agrees to the previously reported value of 0.0415eV within 1%. The distance between the two nearest oxygen atoms of the trimer of ozone $(O_3)_3$ is estimated to be 2.9 Å and the binding energy of $(O_3)_3$ has been calculated to 0.1075 eV in the DFT(MPW1PW91) level of approximation, which agrees with the previously reported value of 0.1037eV within 1%. We have also estimated the binding energy of ozone tetramer, pentamer and hexamer which turns out to be 0.52 eV, 0.61 eV and 2.79 eV respectively, indicating the stability of ozone tetramer, pentamer and hexamer.

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I. Introduction

Ozone is used in the purification of water. It has been studied by many authors because of its important photochemical and photo-physical roles in the atmospheric ozone layer surrounding the earth. The molecule ozone has been studied experimentally and theoretically [1-25] by many authors. In many cases, theoretical results do not agree with the experiments. Musial et al. have studied excited and ionized states of ozone molecule with coupled cluster methods [1]. Similarly, the excited and ionized states of ozone have been studied by Ohtsuka et al. using the MEG/EX–MEG method [26]. By studying the singlet and triplet excited states and the ionized states of ozone, they have discussed the accuracy of applicability of the MEG4/EX-MEG method. They have shown that this method can describe well quasi-degenerate electronic structures and give good agreements with the experimental data. Banichevich et al. [27] studied potential energy surfaces of ozone in its ground state and in the lowest-lying eight excited states employing multireference configuration interaction treatment in a Gaussian AO basis. They found that ozone has a number of singlet and triplet electronic states which are weakly bound towards O2 and O dissociation. Similarly, Grein [28] applied DFT [29] to study geometries and energies of excited states of ozone. The author showed that DFT is useful in finding geometries and energies of ozone molecules in excited states. DFT is easy to use, however, it has limitations to be applicable to symmetric molecules only. It is a useful tool for a symmetric molecule like ozone. Further, the DFT has the advantage of ready convergence to a stationary geometry, the common availability of computer programs and computationally very cheap in comparison to calculation methods like Møller-Plesset perturbation theory(MP), configuration interaction (CI) etc., which also take into account electron-electron correlation energy.

The study of ozone cluster has attracted a great deal of attention. Murai et al. [30] studied the ozone storing process in silica gel. They found that it is possible to detach ozone from silica gel under the same temperature and same pressure conditions with which ozone is adsorbed. Further, they also verified ozone clusters of O6 and O9, i.e., the dimer and trimer of ozone clusters using MOPAC program. However, using the MOPAC they were unable to conclude whether the ozone cluster of sizes four or more molecules exist. The purpose of this paper is to confirm the stability of tetramer, pentamer and hexamer of ozone clusters.

Section II describes the computational details. We use DFT to study the stability of ozone clusters. Section III focuses on results and discussion. Finally, in section IV, we close this paper with conclusions and outlook.

II. Computational details

We have used density functional theory (DFT) to study the stability of ozone clusters. We performed density functional theory calculations taking into account of the electron-electron correlation. For smaller cluster sizes we have tested our results by Mφller-Plesset perturbation of second order calculation. In the present work, we mostly focus on the results obtained by DFT using the above mentioned basis sets. All the calculations described in this report have been performed using the Gaussian 2003 set of programs.

We have employed MPW1PW91 and B3LYP as exchange correlation functionals implemented in Gaussian 2003. In their formulation, these energy functionals include a linear combination of a small amount (20%) of exact exchange with Becke 88 gradient corrected exchange [31] and with a correlation energy functional (PW91) [32], and LYP [33]

$$E_{xc} = a\ E_{HF} + bE_{X(LSD)} + cE_{X(GGA)} + eE_C \tag{1}$$

Standard parameterization has been retained (a=0.20, b=1-a, c=0.72 for Becke's exchange, e=0.81 for the gradient corrected correction energy functional).

To get the equilibrium structure the geometry was optimized, at first, with different spin multiplicity. After obtaining the equilibrium structure, we focus on the spin multiplicity, which gives the lowest energy. For ozone clusters of sizes more than two, we tried many different configurations of inputs to get global minima which was confirmed through vibrational analysis. The binding energies are calculated by the following expression:

$$B.E.[(O_3)_n] = E[(O_3)_n] - n*E(O_3) \tag{2}$$

where $B.E.[(O_3)_n]$ is the binding energy of ozone cluster of n molecules, $E[(O_3)_n]$ is the energy of ozone cluster of n molecules and $E(O_3)$ is the energy of an ozone molecule.

We have performed a systematic calculation with different basis sets like, 3-21G, 3-21G*, 6-31G, 6-31G*, 6-311G, 6-311G(3df), 6-311++G(3df). The results are tested for basis set convergence.

III. Results and discussion

We have performed the first-principles calculations to find the ground state energy of the oxygen atom. The calculations have been performed in the DFT level of approximation with B3LYP and MPW1PW91 exchange correlation functionals. It is found that the triplet state is more stable than the singlet state of

oxygen. Similar calculations for oxygen molecule show that the singlet state of oxygen molecule is more stable than the triplet state.

Ozone molecule: Calculations have been performed to obtain the equilibrium geometry and ground state energy of ozone molecule. Figure 1 presents the equilibrium configuration of ozone molecule. The singlet state of ozone molecule is more stable than the triplet state. In the equilibrium structure of an ozone molecule, the distance between atoms (1O-2O) and (2O-3O) is 1.24 Å and the value of the bond angle (1O-2O-3O) is 118.4º. The previously reported values of the bond distance and bond angles are 1.272 Å and 116.8º [34], respectively. The bond distances and bond angles agree within 2% with the previously reported data [34].
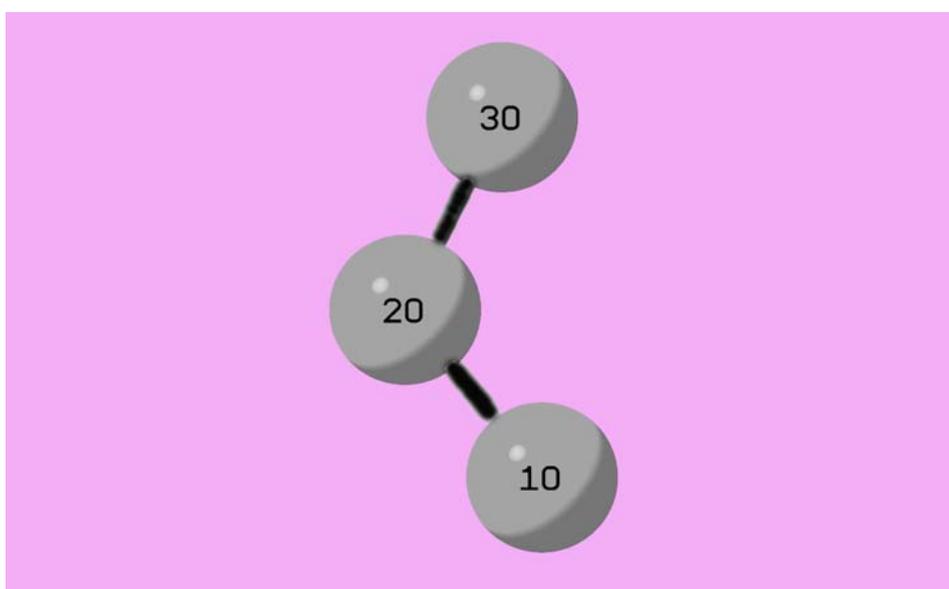

Figure 1: Equilibrium geometry of the singlet state of ozone molecule obtained in the DFT(MP1PW91) level of approximation using the basis set 6-311++G(3df).

Our calculations of energy of ozone molecule show that the exchange-correlation functional B3LYP gives lower energy than that obtained by MPW1PW91 as an exchange-correlation. The difference is about 0.06609 a.u. using the basis set 6-311++G(3df). The ground state energy of ozone molecule is -225.46144 a.u. in the DFT(B3LYP) level of approximation with 6-311++G(3df) basis set. This value of the energy of an ozone molecule is lower than full Configuration Interaction energy obtained by Banichevich [27], and MEG4 and EX-MEG4 energy values obtained by Ohtsuka et al. [26]. Further, the calculations in different basis sets show that the energy values obtained are basis set convergent. From the ground state energy of an ozone molecule and oxygen atom we have estimated the binding energy of ozone molecule by subtracting the three times energy of an oxygen atom from the energy of ozone. It is estimated to be 5.79 eV in the DFT(MPW1PW91) level of approximation and it agrees to the previously reported value 6.17 eV [35] by around 6%.

Ozone dimer: The equilibrium configuration of ozone dimer has been presented in Fig.2. The distance between two oxygen atoms from a central atom of the same ozone molecule is 1.42 Å. This means that when ozone dimer forms the bond distance increases in comparison to the bond distance of the monomer. The angles 2O-1O-3O and 5O-4O-6O are equal and it is 103.97º. The distance between two central atoms of ozone dimer is 2.65 Å and the distance between two nearest oxygen atoms of different ozone molecules is 1.42 Å. The geometry is slightly different than that reported by Murai et al. [30]. The binding energy defined by equation (2) is estimated to be 0.0403 eV in the DFT(B3LYP)/6-311G(3df) level of approximation which agrees within 1% of the previously reported value of Murai et al. [30] using MOPAC.
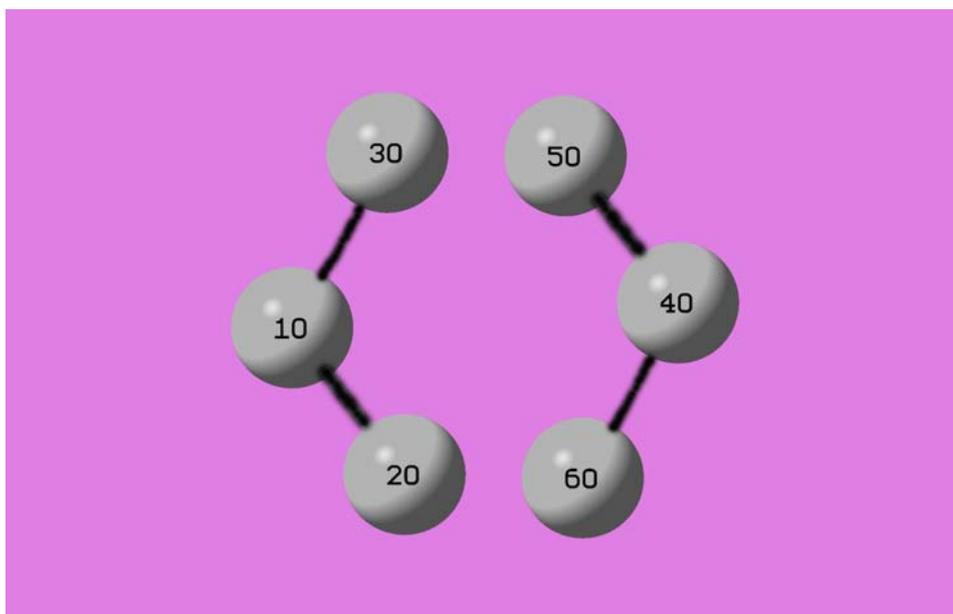

Figure 2

Ozone trimer: Figure 3 shows the equilibrium structure of an ozone trimer (cluster of three ozone molecules) obtained in the DFT(B3LYP)/6-31G level of approximation. Isomer of ozone trimer is also a linear chain however a linear chain has energy higher than the nonlinear structure presented in the figure. The bond distance from a central atom to any other atom is the same in all the three molecules which is 1.26 Å. The angle between three oxygen atoms in a molecule is also the same in all three molecules of the cluster and has value 117.80º. The distances between central atoms (1O-4O), (1O-7O) and (4O-7O) are 3.71 Å, 3.56 Å and 3.68 Å respectively. The binding energy of the ozone trimer is estimated to be 0.1097 eV in the DFT(MPW1PW91)/6-311G* level of approximation and this value of the binding energy agrees to that obtained by Murai et al. [30] within 1%. Murai et al. have used the MOPAC program to study the stability of the ozone cluster.
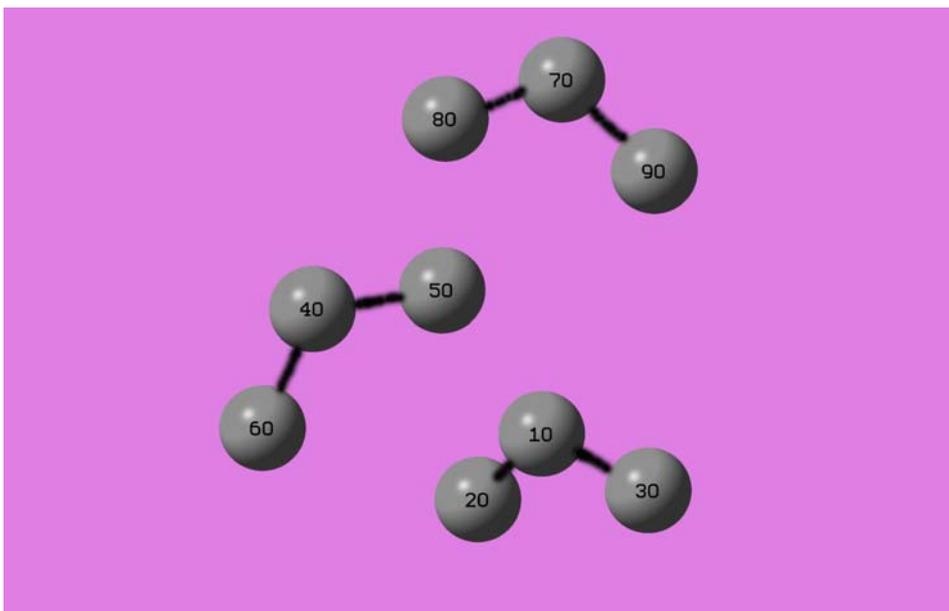
Figure 3

Ozone tetramer: Figure 4 shows the equilibrium structure of an ozone tetramer (cluster of four ozone molecules) obtained in the DFT(B3LYP)/6-31G level of approximation. Many input configurations were tried to get the ground state configuration of ozone tetramer. We also tested for different isomers of ozone tetramer. It is found that a linear chain of four ozone molecules also becomes stable. However a linear chain has energy higher than the nonlinear structure presented in figure 4. The distance between two oxygen atoms of the same ozone molecules in the ozone tetramer is obtained as follows: d(1O-2O) = 1.62 Å, d(2O-3O)=1.46 Å, d(4O-5O)=1.99 Å, d(5O-6O)= 1.26 Å, d(7O-8O)= 1.29 Å, d(8O-9O) =1.87 Å, and d(10O-11O) =1.63 Å and d(11O-12O)=1.46 Å. Similarly, the angles at the atoms, 2O, 5O, and 8O are 96.59º whereas the angle at 11O is 117.8º. This means that the configuration of an isolated ozone monomer is different than that of the monomer in a cluster of four ozone molecules. The intermolecular distances are obtained as follows: d(2O-11O)= 2.86 Å, d(5O-11O)= 3.71 Å, d(2O-8O)= 3.29 Å and d(5O-8O) = 2.68 Å. The dihedral angle made by the central atoms of four molecules i.e. the dihedral angle (2O-8O-5O-11O), is -46.46º. The binding energy of tetramer of ozone clusters is estimated to be 0.519 eV and 0.222 eV in the DFT(B3LYP) and DFT(MPW1PW91) levels of approximation with 6-31G* basis set. This binding energy confirms that the ozone cluster of four molecules exists, which was not confirmed by Murai et. al using MOPAC.
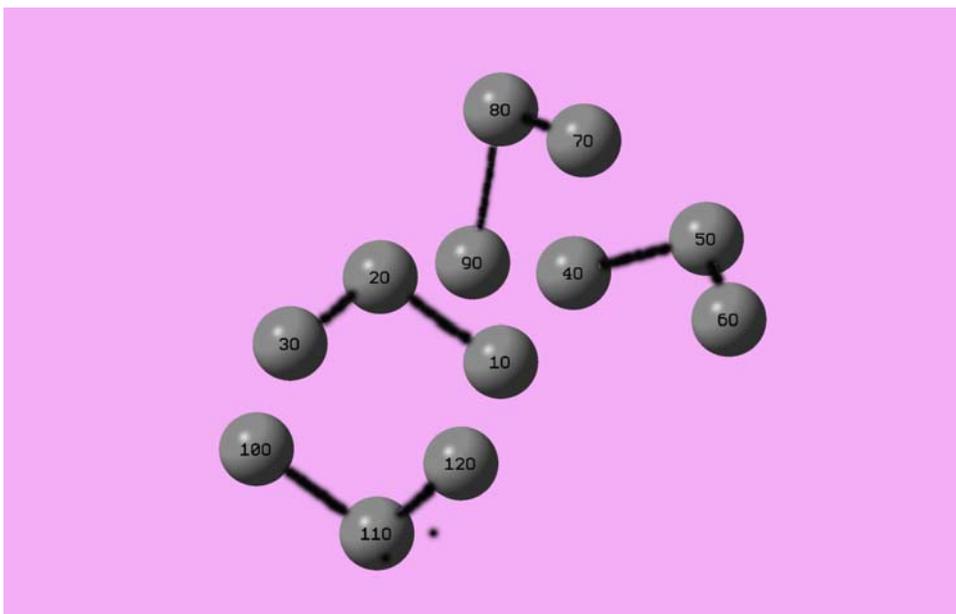
Figure 4

Ozone pentamer: Figure 5 shows the equilibrium structure of ozone pentamer (cluster of five ozone molecules) obtained in the DFT(B3LYP)/6-31G level of approximation. Many input configurations were tried to get the ground state configuration of ozone pentamer. Isomer of ozone pentamer is also studied. It is found that a linear chain of five ozone molecules also becomes stable. However, a linear chain has energy higher than the nonlinear structure presented in figure 5. The distance between two oxygen atoms of the same ozone molecules in the ozone pentamer is obtained as follows; d(1O-2O) = 1.26 Å, d(1O-3O)=1.26 Å, d(4O-5O)=1.27 Å, d(4O-6O)= 1.26 Å, d(7O-8O)= 1.26 Å, d(7O-9O) =1.26 Å, d(10O-11O) =1.24 Å, d(10O-12O)=1.85 Å. D(13O-15O)= 1.25 Å, d(13O-14O)= 1.84 Å. Similarly, the angles at the atoms, 1O, 4O, 7O, 10O and 13O are 117.73º, 117.69º, 117.80º, 104.13º and 104.08º, respectively. The geometry of individual ozone molecule in the ozone pentamer is found to be slightly different from an isolated ozone monomer in terms of bond length and bond angle. The intermolecular distances are obtained as follows; d(1O-4O)= 3.74 Å, d(1O-7O)= 3.56 Å, d(4O-7O)= 3.68 Å, d(10O-13O)=2.89 Å and d(10O-4O) = 4.71 Å. The dihedral angles defined by the position of the 4O-10O-13O-1O is 6.92º whereas defined by 10O-13O-1O-7O is -19.26º. The binding energy of pentamer of ozone clusters is estimated to be 0.606 eV and 1.038 eV in the DFT(B3LYP) and DFT(MPW1PW91) levels of approximation with 6-31G* basis set.
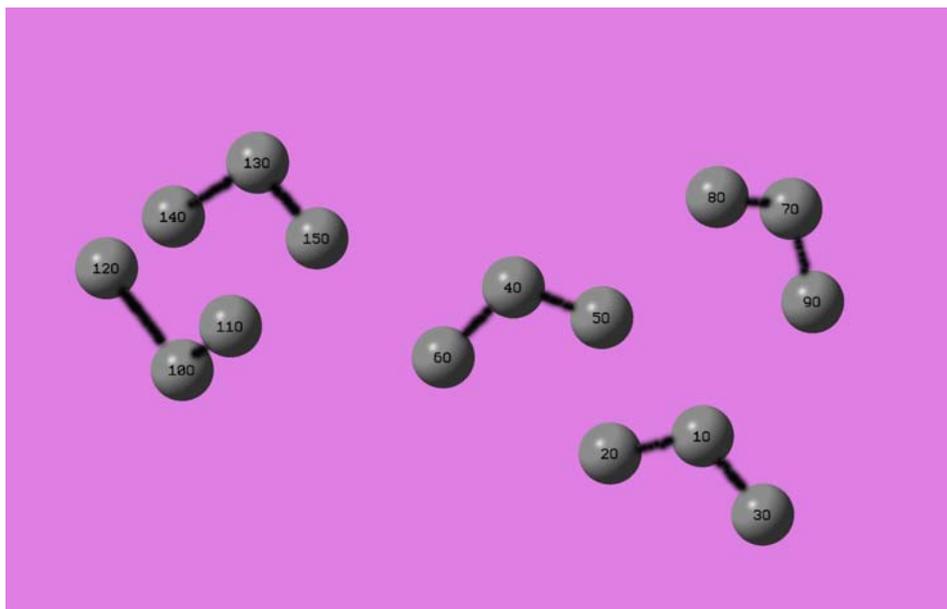
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Figure 5

Ozone hexamer: Figure 6 shows the equilibrium structure of ozone hexamer (cluster of six ozone molecules) obtained in the DFT(B3LYP)/6-31G level of approximation. Many input configurations were tried to get the ground state configuration of ozone hexamer. Isomer of ozone hexamer is also obtained. It is found that a linear chain of six ozone molecules also becomes stable. However, a linear chain has energy higher than the nonlinear structure presented in figure 6. The distance between two oxygen atoms of the same ozone molecule in the ozone hexamer is obtained as follows: d(1O-2O) = 1.47 Å, d(2O-3O)=1.46 Å, d(4O-5O)=1.82 Å, d(5O-6O)= 1.30 Å, d(7O-8O)= 1.72 Å, d(7O-9O) =1.38 Å, d(10O-11O) =1.46 Å, d(11O-12O)=1.47 Å. D(13O-15O)= 1.38 Å, d(13O-14O)= 1.53 Å, d(16O-17O)=1.32 Å and d(16O-18O)=1.32 Å. Similarly, the angles at the atoms, 2O, 5O, 8O, 11O, 13O and 16O are 106.62º, 105.35º, 108.04º, 106.71º, 108.68º and 117.67º, respectively. The geometry of individual ozone molecule in the ozone hexamer is found to be slightly different from an isolated ozone monomer in terms of bond length and bond angle. The intermolecular distances are obtained as follows: d(2O-11O)= 2.31 Å, d(8O-5O)= 3.53 Å, d(5O-13O)= 3.52 Å, d(11O-13O)=4.45 Å, d(2O-16O) = 3.36 Å, d(8O-13O)=3.26 Å and d(5O-16O)=4.17 Å. The dihedral angles defined by the position of the 5O-13O-8O-16O is -59.83º, 5O-16O-2O-11O is 55.68º and 8O-5O-16O-2O is 55.9º 2. The binding energy of pentamer of ozone clusters is estimated to be 2.794 eV and 2.727 eV in the DFT(B3LYP) and DFT(MPW1PW91) levels of approximation with 6-31G basis set.
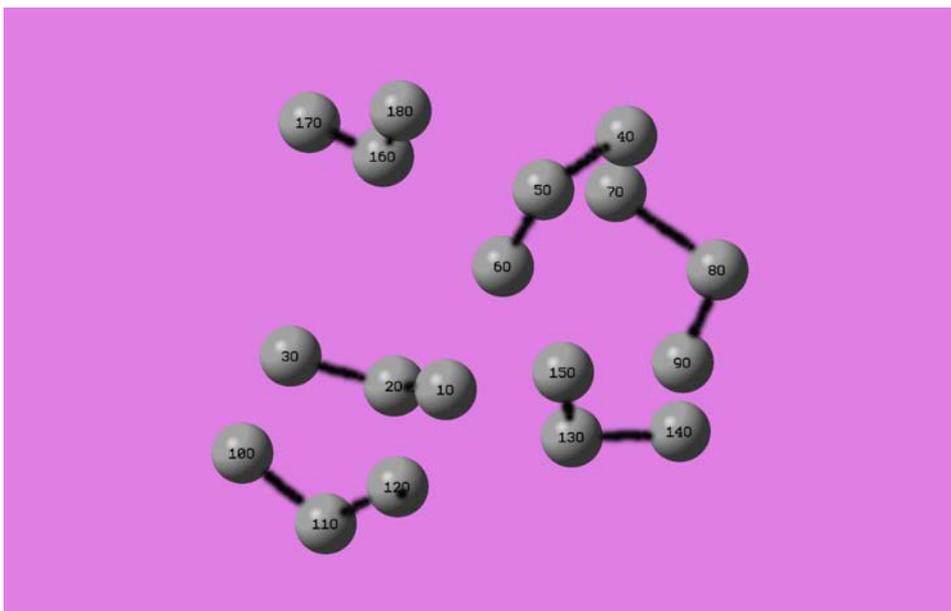
Figure 6

IV. Conclusions and concluding remarks

DFT calculations with B3LYP and MPW1PW91 exchange-correlation functionals have been performed with various basis sets of increasing size and flexibility to study the stability of ozone clusters up to the size of six. The DFT calculations show that the ozone clusters ((O3)n), of sizes n=1-6 are stable. The results are tested for their consistency by the convergence of their ground state energy values with respect to the use of basis sets with increasing size and/or complexity. Our investigations show that ozone clusters of sizes more than three can exist, which was not confirmed by the earlier work of Murai et al. [30]. In the future, one could verify these theoretical findings using experiments and further extend the work to include clusters of sizes more than six molecules of ozone.

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