Vibrational Frequency Calculations of $Ag_xge_{x-1}se_{2x+1}$ glass using DFT

L.G.Garba

Department of Physics, Northwest UniversityKano-Nigeria

Abstract:*The vibrational frequencies of Ag_2, Ag_3, Ag_4, Ag_5, Ag_6, $AgGe$, Ag_2Ge, Ag_3Ge, Ag_4Ge, $AgGe_2$, Ag_2Ge_2, Ag_3Ge_2, Ag_4Ge_2, $AgGe_3$, Ag_2Ge_3, Ag_3Ge_3, Ag_4Ge_3, $AgGe_4$, Ag_2Ge_4, Ag_3Ge_4, $Ag4Ge4$, $AgSe$, Ag_2Se, Ag_3Se, Ag_4Se, $AgSe_2$, Ag_2Se_2, Ag_3Se_2, Ag_4Se_2, $AgSe_3$, Ag_3Se_3, $AgSe_4$, Ag_2Se_4 and Ag_4Se_4 are theoretically computed from the first principles by using density functional theory. The clusters are built in plane, pyramidal or ring shape configurations. We calculate the vibrational frequencies for all of the 47 clusters. The bond lengths and bond angles of all of the molecules are calculated. The vibrational frequencies of all of the clusters are calculated by using a variety of wave functions. We use the single zeta wave functions as well as the double zeta wave functions with and without the polarization. The experimental Raman spectra show almost a continuum of small frequencies. In particular below 100 cm^{-1}, the Raman response is due to particle size in the sample, where light scattering is a result of scattering from the edges of the particles. The spectra of glassy $GeSe_2$ are considerably modified by addition of silver. Most of the Raman spectra are weak and occur near 200 cm^{-1}. We made clusters of pure silver and calculated the vibrational frequencies in all cases. Ag_2 oscillates weakly at 185 cm^{-1}. Due the metallic character, the intensity of Ag_2 is very small. The Ag_3 oscillates at 117 cm^{-1}. The pyramidal Ag_4 has a vibrational frequency of 107 cm^{-1} whereas the square shaped molecule Ag_4 oscillates at 140 cm^{-1}. The ring of Ag_5 oscillates at 141 cm^{-1}. The pyramidal Ag_5 has oscillations near 178 cm^{-1} and Ag_6 ring oscillates near 132 cm^{-1}. The calculated frequencies of the clusters $AgSe_2$, planar-Ag_3Se, Ag_2Ge_2, Ag_2Ge and planar Ag_3Ge are in the neighborhood of those found experimentally. We have determined the bond lengths and angles for the minimum energy configuration in all cases. Our calculated frequencies are usually very near the measured values.*

Keywords:*AgGeSe glass, DFT, Raman, vibrations.*

I. Introduction

The effect of Silver (Ag) doping on the properties of glasses is of considerable interest [1-4]. In particular, in some cases, there are two sub lattices in such a way that one sub lattice remains a solid whereas the other starts melting. In Silver iodide, AgI, at some high temperature, the Iodineatoms remain stationary whereas Silver atoms start moving. This property is known as "superionic conductivity" because the thermal conductivity becomes very large. It will be of interest to find the effect of doping by superionic atoms such as silver. The glasses are also characterized by their long relaxation times[5] due to self-organization and soft modes in which case the frequency of a phonon goes to zero[6]. There is a phase transition in the rigidity[7] as a function of concentration of one of the atoms. Recently, we have developed the expertise [8-11] to optimize the bond distances and angles for the minimum energy of the Schrödinger equation. We are able to calculate the frequencies of vibrations of clusters of atoms to a very high accuracy. Since these calculated values can be compared with those measured by the Raman spectra for a real glass, we find that our predicted values are very good. In this way, we can identify the clusters actually present in the glass.

In this paper, we report the results of our first principles calculations of the formation of clusters of atoms in a glass, $Ag_xGe_{x-1}Se_{2x+1}$. We have calculated the vibrational frequencies of about 40 clusters of atoms and report here those which are closest to the experimental values obtained from the Raman spectra of AgGeSe glass. We also find the vibrational frequencies in the pure Ag metal. The Ag_2 molecule oscillates but the number of these molecules is very small. The Ag_3 is also weak but pyramidal Ag_4 is reasonably strong. We thus report the formation of molecular clusters in a metal. We report a detailed study of vibrations in $AgSe_2$, Ag_3Se, Ag_2Ge_2, Ag_2Ge, Ag_3Ge and Ag_3Ge_3. We find that the vibrational frequencies of these clusters are in the proximity of the experimental values.

II. Silver Clusters

We use the density functional theory to make clusters of atoms and optimize the geometry for the minimum energy of the Schrödinger equation. Since Ag is a metal, the molecule formation is very weak. The Ag_2 molecule is found to stabilize at the bond distance of 262.4 pm (Pico meter) and its oscillation frequency is 185 cm^{-1} in single zeta wave function (SZ) but the intensity is almost zero, so that it will not be observable as a peak in the vibrational spectrum. The same values are obtained when double zeta wave function (DZ) is used. In

the case of double zeta wave function with polarization (DZP), the bond length is reduced to 260.5 pm and the oscillation frequency is reduced to 176.8 cm^{-1} but the intensity continued to be zero. The results obtained with triple zeta wave function with polarization (TZP) are similar to those of DZP. The triple zeta with double polarization (TZ2P) gave 256.4 pm for the bond distance and 181.8 cm^{-1} for the oscillation frequency but the intensity is still zero. Similarly, 4 zeta with four polarizations (QZ4P), results are about the same as that of TZP. This type of wave functions has been applied to methane molecule by Sherrill et al [12] and also to water dimmer[13].

In Ag_3 the bond distance of the optimized triangle is 277.1 pm and the vibrational frequency is 117.2 cm^{-1} in the single zeta wave function. These values remain unchanged when double zeta wave function is used. When the double zeta wave function with polarizations is used, the bond length of the triangle is slightly reduced to 276 pm and the frequency also reduces to 111.1 cm^{-1}. When triple zeta wave function is used the bond length is still 276 pm but the frequency is reduced to 110.8 cm^{-1}. Compared with Ag_2, which has almost zero intensity, the Ag_3 is having a strong peak. Hence, Ag_2 is not formed and Ag_3 is the smallest cluster, which vibrates in silver metal.

The clusters of atom Ag_4 are very interesting because one of them is of pyramidal structure but the square shape planar ring structure is also stable. In the case of pyramidal structure bond length is 287.8 pm and the angle is strictly 60 degrees as expected. The vibrational frequency is 107 cm^{-1} when single zeta wave function is used. The double zeta wave function (DZ) gave the same values as those obtained from single zeta (SZ). However, when double zeta wave function with polarization (DZP) is used, the frequency reduced to 100.4 cm^{-1}. The triple zeta with polarization (TZP) gave the same values as DZP. The frequencies as well as the bond lengths in the TZ2P are found to be 273.9 pm and 161.9 cm^{-1}. The QZ4P gave 276 pm and 161.9 cm^{-1} for the pyramidal bond length and the vibrational frequency, respectively. The square shaped Ag_4 clusters has a vibrational frequency of 140.7 cm^{-1} and the length of the square is 273.9 pm when single zeta wave function is used. The double zeta wave function gave almost the same values as the single zeta. The cluster Ag_5 forms a ring as well as a pyramid. In the five sided ring, the bond length is 272.3 pm and the vibrational frequency is 140.9 cm^{-1}. The double zeta wave function gave the same value as the single zeta. In the case of double zeta with polarization, the bond length is 271.6 pm whereas the frequency is 131.4 cm^{-1}. The TZP values are 271.7 pm for the five sided bond length and the vibrational frequency is 131.26 cm^{-1}. The TZ2P gave 264.1 pm for the bond length and 147.5 cm^{-1} for the frequency. The QZ4P values are 264.2 pm and 147.3 cm^{-1}, respectively. The clusters Ag_5 in the pyramidal form gave two strong bonds. First a square of four atoms is formed with bond distance 286.6 pm. Then on top one more atom is placed which is at a distance of 276.6 pm from each of the four atoms. The vibrational frequencies are 69.2 cm^{-1} (2 values), 87.2 cm^{-1} (one strong value), 146.1 cm^{-1} (2 weak values) and 178.9 cm^{-1} (one strong value). The DZ values are same as those of SZ. The DZP values are 286.7 pm for the square bond length and 274.8 pm for the on top atom. The frequencies, intensities and degeneracies are given in table 1.

TABLE 1: **The vibrational frequencies of the Ag_5 pyramid by using DZP wavefunctions and degeneracies.**

S/N.	Frequency(cm^{-1})	Intensity	Degeneracy
1.	64.6	0.488	2
2.	81.8	2.273	1
3.	139.7	0.146	2
4.	169.8	1.683	1

The Ag_6 ring in single zeta wave function has a bond length of 270.8 pm and a strong vibration at 131.9 cm^{-1} with degeneracy 2 and weak lines at 114.1, 165.7, 167.6 and 172.1 cm^{-1}. In the case of DZP, the bond length changed to 270.1 pm which is only a minor change compared with the unpolarised single zeta function. However, in the case of DZP, the vibrational frequencies (intensities) are changed to 103.6 (0.03), 122.5 (2.8), 124.2 (2.77), 154.1 (0.004), 155.8 (0.004), 160.4 (0.007) cm^{-1}(arb. units). It is clear that there is a strong ring oscillation as about 123 cm^{-1}.

III. The Agse Clusters

The $AgSe_2$ has Se-Ag bond length 260.3 pm and Se-Se bond length 237.2 pm when single zeta function is used. The frequencies (intensities) are 146.8 (0.16), 2113 (6.31), 238.5 (1.18) cm^{-1} (arb. units). The double zeta wave functions give Se-Ag distance 265.4 pm and Se-Se distance 251.8 pm and frequencies (intensities) 129.4 (1.74), 176.8 (8.05), 266.9 (0.73) cm^{-1}(arb. units). The DZP gave Se-Ag distance 262.2 pm, Se-Se distance 240.5 pm and frequencies (intensities) of 139.7 (1.23), 177.5 (7.9), 292.3 (0.24) cm^{-1}(arb. units). The vibrational spectrum of $AgSe_2$ calculated from the first principles shown in Fig. 1.
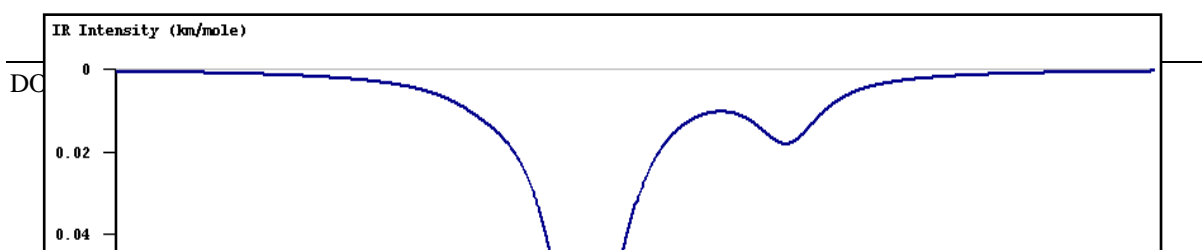
FIGURE 1: The vibrational spectrum of $AgSe_2$ calculated from first principles showing two strong vibrations.

The Ag_3Se has a single Se in the centre of a triangle, which is built from three Ag atoms. The bond length is 256.0 (Pico meter) when single zeta (SZ) is used. In the DZP, the bond length changed to 252.2 pm. The vibrational frequencies (intensities) are given in table 2.

TABLE 2: The vibrational frequencies and intensities of Ag_3Se in single zeta (SZ) as well as double zeta with polarization (DZP) wave function for Ag_3Se.

| S/No.	Frequency cm^{-1} (SZ)	Intensity	Degeneracy	Frequency cm^{-1} (DZP)	Intensity (DZP)
1.	28.63	1.85	2	31.2	1.95
2,	51.59	10.14	1	56.5	8.71
3.	223.71	0.66	2	217.7	0.16

We show a picture of the charge density in Fig.2.
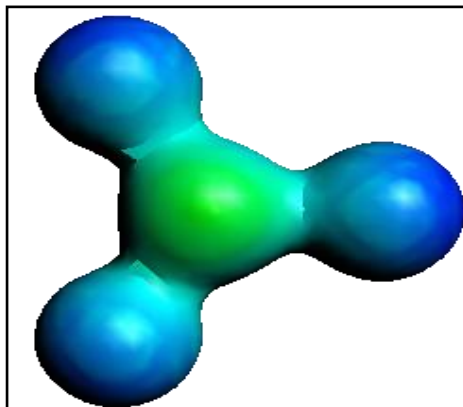
FIGURE 2: A picture of the charge density of Ag_3Se by using SZ wave functions.

IV.   The Agge Clusters

(a) The Ag_2Ge_2 has the Ag-Ge distance of 251.5 pm, Ge-Ag-Ge angle of 88 degrees and Ag-Ge-Ag angle of 92 degrees when single zeta wave function is used. The frequencies (intensities) are 184.4 cm^{-1} (4.75) and 201.9 cm^{-1} (7.48) when double zeta wave function is used, the bond length comes out to be 264.0 pm, Ge-Ag-Ge angle 62.5 degrees and Ag-Ge-Ag angle comes out to be 121.3 degrees. The frequencies (intensities) are 107.2 cm^{-1} (0.135), 201.6 cm^{-1} (8.2). The double zeta with polarization gave Ag-Ge bond length of 261.8 pm, Ge-Ag-Ge angle of 61.1 degree and Ag-Ge-Ag angle of 118.9 degrees. The frequencies (intensities) in the double zeta with polarization are 100.37 (0.25) and 196.3 (6.71).

(b) The Ag_2Ge has Ag-Ge distance of 258.5 pm and Ag-Ge-Ag angle 71.7 degrees. The vibrational frequencies with SZ are 67.1 (0.005), 168.3 (0.272) and 215.02 (0.227). The DZ values are Ag-Ge distance 258.3 pm and bond angle 71.6 degrees. The frequencies (intensities) are, 67.1 (0.004), 169.05 (0.277) and 215.7 (0.227). The values calculated for DZP wave function are, Ag-Ge bond distance 253.4 pm and bond angle Ag-Ge-Ag is 74.5 degrees. The vibrational frequencies and intensities are 58.2 (0.006), 175.15 (0.255) and 215.2 (0.244). The TZP functions gave Ag-Ge bond distance 254.1 pm and bond angle Ag-Ge-Ag of 74.1

degrees. The vibrational frequencies for the TZP are 59.5 (0.004), 172.45 (0.243), 213.1 (0.253), cm^{-1} (km/mol). A charge density plot of Ag$_2$Ge is shown in Fig.3.
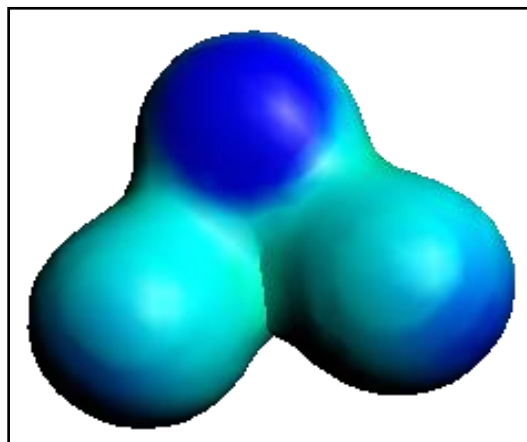
FIGURE 3: A picture of charge density of Ag$_2$Ge calculated from single zeta wave functions.

(c) The Ag$_3$Ge with Ag$_3$ on the corners of a triangle and Ge in the centre gives Ge-Ag bond length of 255.2 pm and Ag-Ge-Ag angle of 120 degrees as it should be for the centre of an equilateral triangle. The vibrational frequencies (intensities) are 22.6 (1.26) two values, 117.4 (12.9) one value and 227.9 (0.034) two values when DZ is used. For DZP, Ge-Ag bond distance is 251.7 pm and Ag-Ge-Ag angle is 120 degrees as it should be for a triangle. The frequencies (intensities) are 38.8 (0.026) two values, 124.2 (0.000001) one value and 226.2 (2.43) two values, cm^{-1} (km/mole).

(d) The system Ag$_3$Ge$_3$ is hexagonal with alternate Ag and Ge atoms with Ge-Ag distance 246.4 pm. The SZ vibrational spectrum is shown in Fig.4.
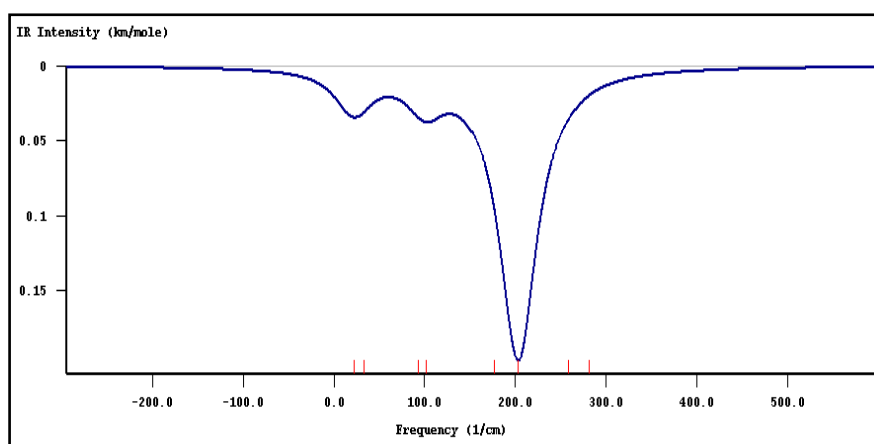
FIGURE 4: The vibrational spectrum of Ag$_3$Ge$_3$ hexagon calculated by using the first principles with SZ wave functions**.**

The calculated frequencies (intensities) are 22.4 (1.125) two values, 101.2 (1.87) one value, 202.62 (7.65) two values, 258.8 (0.07) two values when SZ wave functions are used. When DZ wave function is used the bond length Ge-Ag comes out to be 254.0 pm and the frequencies (intensities) [degeneracies] are, 64.1 (0.037), 168.5 (5.22), 224.8 (2.51) cm^{-1} (km/mole). The DZP bond length is 250 pm and the frequencies (intensities) [degeneracies] are 61.2 (0.005) [1], 168.6 (4.331) [2], 222.02 (3.045) [2], cm^{-1} (km/mole). The charge density of Ag$_3$Ge$_3$ is shown in Fig.5.
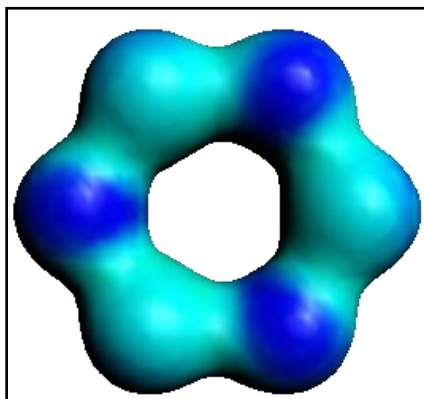
FIGURE 5: The charge density plot of Ag_3Ge_3 by using SZ wave functions.

V.   Comparison Of Calculated Values With Experimental Raman Spectra

We show in Fig. 6 the experimental Raman spectra of glassy $GeSe_2$ and glassy $Ag_4Ge_3Se_9$. The experimental work has been done by Dejus et al[14].
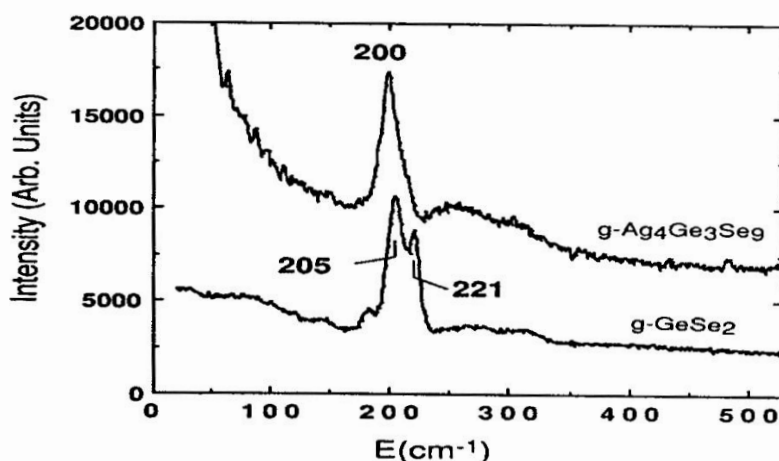

FIGURE 6: The experimental Raman spectra of glassy $GeSe_2$ and $Ag_4Ge_3Se_9$.

The g-$GeSe_2$ has a strong Raman line at 205 cm^{-1} and another at 221 cm^{-1}. There are some weak lines, which are not identified. When silver is added the 221 cm^{-1} goes inside the 200 cm^{-1} line and hence becomes difficult to resolve, but there is a broad line at 200 cm^{-1}. There is a continuum below 100 cm^{-1} and small oscillations are hidden within the noise. In our calculations, it is clear that there is absorption near 215 cm^{-1} in Ag_2Ge (SZ), which is near the experimental value of 221 cm^{-1}. The continuum below 100 cm^{-1} is due to particle size but Ag_2Ge has a mode at 67 cm^{-1}.

VI.   Conclusions

Extensive calculations of clusters of atoms constituting Ag and Ge atoms were performed. The calculated values of the vibrational frequencies show that Ag_2Ge is formed in the glass. The calculations also show that in Ag metal, Ag_3 is the smallest cluster formed which is of the size of 0.277 nm.

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