Sains Malaysiana 42(5)(2013): 649–654

DFT Calculation of Vibrations in the Clusters of Zinc and Oxygen Atoms

(Pengiraan Getaran bagi Kluster Atom Zink dan Oksigen dengan DFT)

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ABSTRACT

The nanometer size clusters are often present in ZnO. We have calculated the vibrational frequencies of zinc oxide by using the density-functional theory. We synthesized clusters of ZnO starting with ZnO_n and continue with Zn_2O_n, Zn_3O_n and Zn_4O_n with n *= 1, 2, 3 and 4. By minimizing the energy of the Schrödinger equation, we found the bond lengths and the vibrational frequencies of each cluster. These calculated data are compared to the experimentally measured Raman spectra of ZnO_4 to identify the clusters which exist in this material. The density-functional theory in the local density approximation (LDA) is used with double numerical basis set. From this calculation, we find that the bond length for the cluster of ZnO_4 with tetrahedral symmetry (T_d) is 1.923 Å and the vibrational frequencies are 94.4 cm^{-1} and 440.4 cm^{-1} with degeneracy of 3 each. We have made several clusters using zinc and oxygen atoms and have calculated the vibrational frequencies, degeneracies and intensities in each case.*

Keywords: Cluster; density functional theory; Raman spectrum, vibrational frequency; ZnO

ABSTRAK

Kluster bersaiz nanometer selalu wujud dalam ZnO. Kami telah membuat pengiraan frekuensi getaran bagi zink oksida menggunakan teori fungsi ketumpatan. Kluster ZnO dibentuk daripada ZnO_n dan diikuti pula oleh Zn_2O_n, Zn_3O_n dan Zn_4O_n dengan n *= 1, 2, 3 dan 4. Apabila tenaga persamaan Schrödinger diminimumkan, kami dapat mengukur panjang ikatan dan frekuensi getaran bagi setiap kluster. Perbandingan antara data pengiraan ini dengan spektrum Raman hasil daripada keputusan eksperimen dibuat untuk mengesan kluster yang wujud dalam bahan ZnO_4. Teori fungsi ketumpatan dalam penghampiran ketumpatan (LDA) digunakan bersama set asas nombor berganda. Hasil daripada pengiraan ini, kami menemui panjang ikatan bagi kluster ZnO_4 dengan simetri tetrahedron (T_d) adalah 1.923 Å dan frekuensi getaran adalah 94.4 cm^{-1} dan 440.4 cm^{-1} dengan 3 ulangan setiap satu. Kami menghasilkan beberapa kluster menggunakan atom zink dan oksigen dengan frekuensi getaran, ulangan dan keamatan telah dikira untuk setiap kes.*

Kata kunci: Getaran frekuensi; kluster; spektrum Raman; teori fungsi ketumpatan; ZnO

INTRODUCTION

The zinc oxide (ZnO) semiconductor is an interesting material because of the intense laser emission at the gap frequency. This wurtzite type crystal belongs to the space group of C_{6v}^4 ($C6_3mc$). It is useful for the potential applications in optoelectronic devices (Abrashev et al. 1994; Arguello et al. 1969). Using Raman spectroscopy, the frequencies, linewidth and lifetime can be found to give more information about the material. A previous study by Arguello et al. (1969) reported the first order Raman spectrum for a variety of wurtzite structures including ZnO (Abrashev et al. 1994). The frequencies of optical modes have been reported for BeO, ZnO, CdS and ZnS. Abrashev et al. (1994) reported the polarized Raman spectra of Nd_2BaZnO_5 and compared with infra red (IR) absorption. They analyzed the Raman active modes of ZnO_4 tetrahedral that occur in this material after they isolated the frequencies of Nd and Ba. Another material, Nd_2BaCuO_5 has been used in this report by using the same method including IR-absorption. The temperature dependence of the Raman scattering of ZnO has been discussed by Cusco et al. (2007) in the range from 80 to 750K. The discussion in E_2^{high} mode of ZnO found the lifetime at room temperature to be 0.5 ps. Another report also showed the temperature dependence for alloy material, Co doped ZnO using Raman spectroscopy with temperature range from 80 to 800 K (Samanta et al. 2007). Nanostructure of ZnO material with variety of morphology is interesting for the development of devices so it is important to control the growth of morphology. The nanobelts of ZnO nanostructure had been reported by Lucas et al. (2007) by using the combination of Raman spectroscopy and the atomic force microscopy (AFM) from which they found two growth modes of the nanostructure.

In this paper, we report our calculation of vibrational frequencies of several clusters of zinc oxide. The DMol[3] of Accelerys software has been used to calculate the minimum energy of the system by using the density-functional theory (DFT). DFT has been widely used to calculate the vibration of molecules for understanding of the structure. DFT has a reliable result with high accuracy to predict the energy of a molecule. We compared our calculated values to those

experimentally measured from the experimental Raman spectra (Abrashev et al. 1994; Arguello et al. 1969). The bond length of ZnO cluster has also been calculated. In the previous report, we have done calculations on Ge, S and I atoms and found that the calculated vibrational frequencies agree with the Raman frequencies of GeSI glass (Devi et al. 2005). The calculations performed for the clusters of GePS, GeSe, Se and AsO for obtaining vibrational frequencies are extremely successful in terms of comparison with the experimental values (Jemali et. al. 2008, Kassim et. al. 2007; Rosli et al. 2010a, 2010b). The application of the DFT on thymine had been discussed by Zabidi et. al. 2007. This paper also explained the difference between DFT and Hartree-Fock theory. There is a calculation of vibrational frequencies of carbon nitride (Rosli et al. 2010c) which agrees with the experimental data. We found that clusters of atoms were present in the actual material used by the experimentalists to study the Raman spectrum.

CLUSTERS

We use the density-functional theory to obtain the minimum energy of the Schrödinger equation. The local density approximation (LDA) is used to calculate the exchange-correlation term in DFT. The Kohn–Sham equations are solved and vibrational frequencies are deduced (Hohenberg & Kohn 1964; Kohn 1999; Kohn & Sham 1965). The bond length for this cluster is also determined. The cluster which we have calculated are given in Figure 1 and the double-numerical (DN) wave functions were used in all of the computations. The clusters were built starting with one zinc atom with n number of oxygen atoms, where n = 1, 2, 3 and 4. Then in the next step more zinc atoms are used. For example, we built two, three and four atoms of zinc with varying number of oxygen atoms.

The first cluster is diatomic ZnO (Figure 1(a)). This cluster has been calculated and the optimized bond length was found to be 1.867 Å. The vibrational frequency is 490.5 cm^{-1} with intensity of 1.64 (km/mol).

The linear cluster of ZnO_2 (Figure 1(b)) has been built with Zn in the center while both oxygen atoms on the left and the right sides with 180° of angle. The vibrational frequencies (intensities) {degeneracies} are 88.5 (21.8) {2} and 629.6 (0.26) cm^{-1} (km/mol). The bond length for both distances is found to be 1.821 Å. Linear molecule has $3n - 5$ vibrations modes while n is number of molecule. For ZnO diatomic, $n = 2$ so that $3n - 5 = 1$ which is 1 vibration for this cluster. For 3 atoms of ZnO_2 linear, the vibrations mode for this cluster is 4. Our calculation showed 2 vibrations at 88.5 cm^{-1} and 1 vibration at 629.6 cm^{-1}. Another frequency is 494.78 cm^{-1}, however this result has zero intensity due to the symmetry vibration that doesn't change the dipole moment. The vibrations mode for a non linear molecule is $3n - 6$.

The clusters of Zn_nO_n have been built until Zn_4O_4 and the calculated vibrational frequencies of all cluster of Zn_nO_n are shown in the Tables 1 and 2. The bond length of all Zn_nO_n clusters are shown in Table 3 and the stick-ball models of all clusters shown in Figure 1.

TABLE 1. The frequencies, intensities and degeneracies calculated from the first principles for various clusters of zinc oxide

S. No.	Cluster	Frequency (cm^{-1})	Intensity (km/mol)	Degeneracies
1.	ZnO_3 Spoke	93.90	6.71	2
2.		116.69	26.30	-
3.		507.87	0.01	2
4.	ZnO_3 Triangular	93.91	6.71	2
5.		116.70	26.29	-
6.		507.98	0.01	2
7.	ZnO_4 T_d	67.28	0.01	-
8.		94.42	7.08	-
9.		94.44	7.15	-
10.		94.46	7.22	-
11.		440.37	0.16	-
12.		440.40	0.15	-
13.		440.42	0.14	-
14.	ZnO_4 Spoke	99.52	1.71	2
15.		118.17	23.63	-
16.		463.41	0.30	2
17.	ZnO_4 Square	99.32	1.47	2
18.		120.13	23.68	-
19.		463.27	0.36	2
20.	Zn_2O_2 Linear	44.43	19.97	2
21.		547.48	0.39	-

TABLE 2. The frequencies, intensities and degeneracies calculated from the first principles for various clusters of zinc oxide

S. No.	Cluster	Frequency (cm^{-1})	Intensity (km/mol)	Degeneracies
1.	Zn_2O_2 Bytriangular	117.25	18.38	-
2.		371.32	17.91	-
3.		382.35	1.89	-
4.	Zn_2O_4 Dumbbell	13.53	0.04	-
5.		69.43	23.27	-
6.		78.86	30.16	-
7.		473	1.61	-
8.		577.32	0.25	-
9.	Zn_2O_3 Bypyramid	167.98	10.18	-
10.		168.00	10.22	-
11.		302.59	302.59	-
12.		367.25	6.15	-
13.		367.27	6.17	-
14.	Zn_3O Pyramid	73.30	1.17	-
15.		306.33	1.14	-
16.		306.51	1.09	-
17.		373.32	12.54	-
18.	Zn_4O_4 Cube	140.29	0.11	3
19.		318.01	10.82	3
20.		376.32	13.85	3

TABLE 3. The calculated bond length of Zn_nO_n clusters

No	Cluster	Bond Length (Å)		
		Zn - O	Zn - Zn	O - O
1	ZnO_3 Spoke	1.879	-	-
2	ZnO_3 Triangular	1.879	-	3.255
3	ZnO_4 T_d	1.923	-	-
4	ZnO_4 Spoke	1.936	-	-
5	ZnO_4 Square	1.936	-	2.738
6	Zn_2O_2 Linear	1.833	2.360	-
7	Zn_2O_2 Bytriangular	1.960	2.834	-
8	Zn_2O_4 Dumbbell	1.845	2.622	-
9	Zn_2O_3 Bypyramid	2.020	-	2.673
10	Zn_3O Pyramid	2.012	2.825	-
11	Zn_4O_4 Cube	2.032	-	-

RAMAN SPECTRUM

The Raman frequencies of Nd_2BaZnO_5 are measured by Abrashev et al. (1994). From that, the experimentally measured Raman frequency of ZnO_4 measured is 639 cm^{-1} in A_1g symmetry. This value is very close to our calculated values of 629.6 cm^{-1} for ZnO_2 linear cluster. Another experimental value of the Raman frequency is 493 cm^{-1} for internal antistretching vibration. Our calculated vibrational frequencies show nearly same value for ZnO diatomic cluster of 490.5 cm^{-1}. Similarly, the experimental result found the value of Raman frequency of 368 cm^{-1} that is close to our calculated value showed in Table 4.

Another measurement of the Raman spectra of ZnO is done by Arguello et al. (1969). The optical mode of wurtzite-type crystal ZnO gives good understanding with our calculated results. The comparison of experimental frequencies and our calculated vibrational frequencies is shown in Table 5.

ZN_4O_4 RING STRUCTURE

In some of the structures, negative frequencies are found to occur. The negative value of frequency showed the instability of the structure. In the Zn_4O_4 (ring) such an example is found. The frequencies, intensities (degeneracies) calculated for this structure is as follows: -12.91(0.01), 23(0.02), 41.13(0.16), 51.37(0.01), 56.24(4.07), 57.76(0.55), 58.44(1.03), 59.37(3.45), 61.32(0.78), 72.96(36.32), 321.74(0.04), 355.66(22.53), 366.36(21.71), 428.3(0.02), 518.53(0.05), 583.15(2.94), 600.76(0.55), 636.8(0.04) cm^{-1} (km/mol).

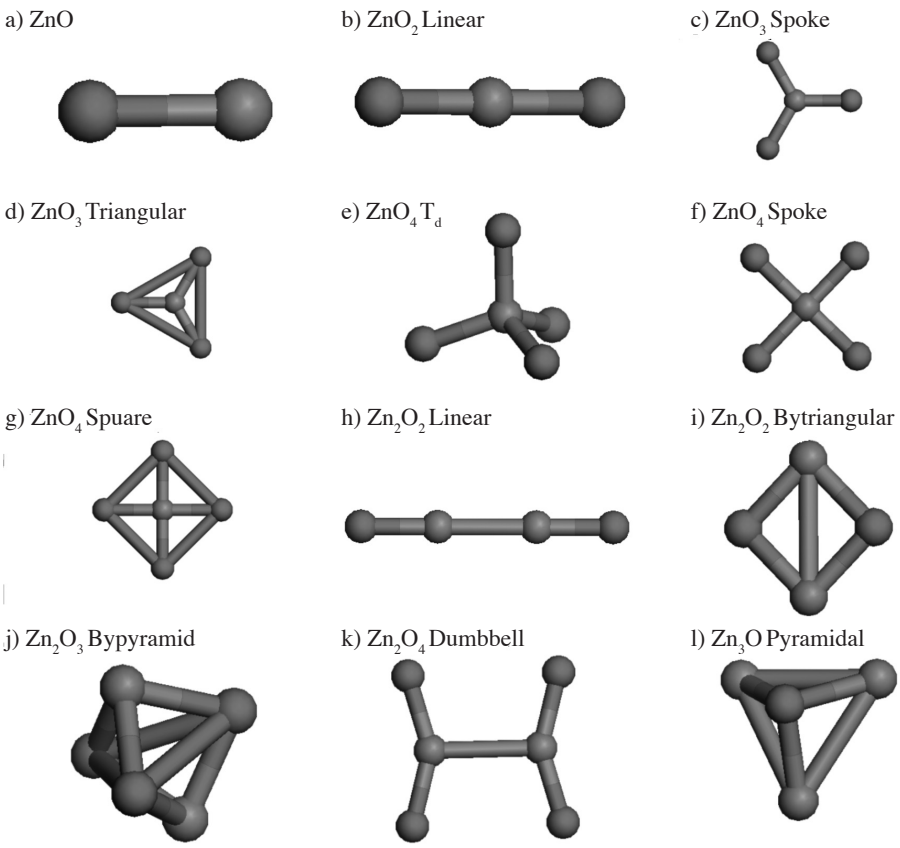

FIGURE 1. The stick-ball models of ZnO clusters minimized to the optimum geometry

TABLE 4. The comparison between calculated and measured vibrational frequencies of ZnO_4 along with their cluster identification

No.	Experimental value Abrashev et al. 1994 (cm^{-1})	Calculated frequency this work (cm^{-1})	Cluster this work
1	639	629.6	ZnO_2 Linear
2	493	490.5	ZnO Diatomic
3	368	367.3	Zn_2O_3 Bypyramid
		373.3	Zn_3O Pyramid

TABLE 5. The comparison between calculated and measured vibrational frequencies of zinc oxide along with their cluster identification

No.	Experimental value Arguello et al. 1969 (cm^{-1})	Calculated frequency this work (cm^{-1})	Cluster this work
1	101	99.3	ZnO_4 Square
		99.5	ZnO_4 Spoke
		93.9	ZnO_3 Spoke
		93.9	ZnO_3 Triangular
		94.4	ZnO_4 T_d
2	444	440.4	ZnO_4 T_d
3	380	382.4	Zn_2O_2 Bytriangular
		376.3	Zn_4O_4 Cube
4	395	--	
5	413	--	
6	579	577.3	Zn_2O_4 Dumbbell
7	585	--	
8	591	--	

The negative value will become observable when light of sufficient energy falls on the structure. Usually $(E_1\text{-}E_2) = h\nu$ will be observed in the data. However, if one value is negative, $E_1\text{-}(\text{-}E_2) = E_1+E_2 = h\nu$. The molecular states E_1 and E_2 will impart the frequency ν to the incident light of frequency ν_{in} so that $\nu\pm\nu_{in}$ will be observed. The vibrational spectrum for the ring structure is shown in Figure 2 and the ring is shown in Figure 3.

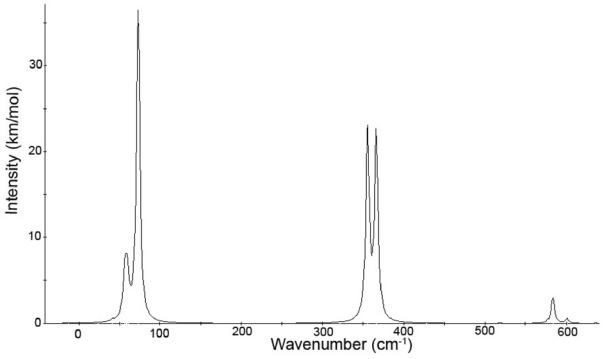

FIGURE 2. The vibrational spectrum of Zn_4O_4 ring structure calculated from the first principles

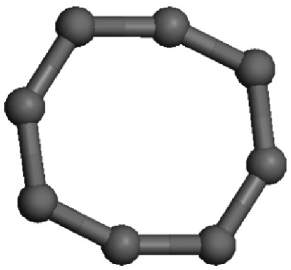

FIGURE 3. The Zn_4O_4 ring structure of bond length 1.872 Å and 1.859 Å. The two bond lengths show the lift of atoms from the plane

CONCLUSIONS

We have performed the *ab initio* calculation of vibrational frequencies for several clusters of ZnO and compared with the experimental data. The calculated values are in accord with the experimental values as shown in Tables 4 and 5. From this calculation we find that the ZnO (diatomic) occurs in the real material and the value for calculated ZnO_2 (linear) agrees with the experimental value. We also found that the bond length for ZnO_4 tetrahedral cluster is 1.923 Å which agrees with the experimental (Abrashev et al. 1994) bond length of 1.94 Å between Zn – O.

ACKNOWLEDGEMENTS

We would like to thank the fundamental research grants scheme (FRGS) of the Ministry of Higher Education and the University of Malaya Research Grants (UMRG) which kindly provided support for the purchase of quadro computers and fellowships. We wish to thank the authorities of Universiti Sains Islam Malaysia for the generous support of the research work.

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Received: 4 October 2011
Accepted: 24 October 2012