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Infrared Absorption and Raman Spectra of BNNT - Fluorouracil: A Density Functional Theory Study

Bahjat B. Kadhim[1], Haider O. Muhsen[2]

Department of Physics, College of Science, Al-Mustansiriyah University, Baghdad, Iraq

Abstract: ***Vibration properties of representative (6,0) zigzag single-walled boron nitride nanotubes (SWBNNT) and the single-walled nanotube with anti-cancer drug(5-florouracil) are studied by density functional theory (DFT) calculationsat the B3LYP/6-31G level . The diameter and length of the pristine (6, 0) BNNT are about 6.90 and 6.50 Å, respectively. Redial breathing modes (RBM) of (B–N) bond vibration is (504.88) cm^{-1} for BNNT, for complex (BNNT/5-furacil) the breathing mode is(511.87)$cm^{-1}$and The strongest peak of the IR spectra is(1493.42cm^{-1}) which represents the stretching mode of B-N bonds and the second peak at (1435.78 cm^{-1}) represents the bending mode of B-N bonds. The Raman spectrumof 5-florouracil with BNNTa maximum peak at (3544.69 cm^{-1}) that represents the stretching mode of hydrogen atoms attached to nitrogen atoms for BNNT and the second peak at (2694.49 cm^{-1}) which represents the stretching mode of hydrogen atoms attached to boron in BNNT. The wave number at regions (1571.33-1723.85) cm^{-1}very important, the drug can be active in this region.The structure with no imaginary frequency can be more stablethat means the SWBNNT can act as a suitable drug carrier.The (HRMM) longitudinal optical (LO) vibration frequency at (12.14cm^{-1}). Reduced mass is reached (11.75amu) which is nearly to the reduced mass between two atoms B and N while the (HFCM) for the complex vibrations (21.02mDyne/Å) symmetric stretching mode vibration frequency at (1826.58cm^{-1}) between (C=O) atoms and bending (scissoring) mode between (N-H)atoms in drug molecular.Gaussian 09 program used to perform all computations.***

Keywords: Density functional theory(DFT); SWBNNT; Infrared spectra; Raman spectra; Reduce mass

1. Introduction

The application of nanotechnology in disease treatment, monitoring, diagnosis and in the mastery of biological systems in the single molecule or molecular group area is denote to as nano drug. The major aim of nano drug is the design of the substance capable of forking up and target pharmaceutical, therapeutic and diagnostic factors. Iijma discovered the kind of drug delivery system carbon nanotube in 1990 [1].After the discovery of carbon nanotubes (CNTs) in experimental studies , Blase et al, in 1994,theoretically predicted the possibility of obtaining boron nitride nanotubes (BNNTs) and initiated an investigation on their distinctive properties [2]. The binary compounds of groups III and V are always semiconductors and suggested as proper alternative materials for the CNTs. Among these materials, the tubular structure properties of the group III-nitrides, e. g., boron nitride (BN), aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) are more studied [3,4] . Boron nitride nanotubes (BNNTs) is a nanostructure with similar morphology and different properties from carbon nanotubes (CNTs) [5].An BN nanotube is composed of alternating atoms of boron and nitrogen but BN is mostly found in the same phases, which produces atomic structures similar to those of CNT. Its various chiralities, such as zigzag, chiral and armchair .On the other hand, different from CNTs which are highly toxic to the human body and, depending on their chirality, can be semiconductors and conductors BNNTs of different chirality show good biocompatibility and are always semiconducting with a wide band gap [2].strength, chemical inertness, , polarizability, piezoelectricity inherent for BN, in couple with a cylindrical geometry, small diameter, and quantum confinement inherent for NTs, all promise unique properties and perspective applications in terahertz electronics and nanotechnology. [2,6] Cancer is the name given to a family of diseases that vary in rate of growth, state of cellular differentiation, diagnostic detectability, invasiveness, metastatic potential and response to treatment and prognosis. It's occur when cells become abnormal and keep dividing, forming new cells without any control or order. Normally, cells divide to form new cells only when the body needs them. When cells divide uncontrollably, a mass of excess tissue formed called a tumor. Tumors can be non-cancerous (benign) or cancerous (malignant)[7]. Many medications are being using as individual or in combination; one of the most commonly used medicines is 5-fluorouracil, [8] In 1959 5-fluorouracil (5-FU)was synthesized by Duschinsky and co. workers ,while Heildelberger and co. workersdemonstrated its anti-tumor activity. Since then the fluorinated pyrimidine has been use as a chemotherapeutic agent in the treatment of a large number of malignant tumors [7]. The 5-FU is a heterocyclic aromatic organic compound with a structure similar to that of the pyrimidine molecules of DNA and RNA differencing itself by the fact that the fluorine atom supersede the hydrogen atom at the C-5 position in the uracil unit [9].Infrared (IR) and Raman spectroscopies have been standard methods of analytical pharmacy and chemistry for a long time. IR and Raman spectra, which are complementary to each other, provide images of vibrations of the atoms of a compound. Therefore,both techniques also referred to as vibrational spectroscopy.In other words, IR spectroscopy based on the absorption of electromagnetic radiation by a molecular system, whereas Raman spectroscopy relies upon inelastic scattering of electromagnetic radiation by a molecular system [10]. Spectroscopy is more useful in the quality analysis of the medicinal preparation by Infrared Spectroscopic studies carried out for the standardization of drug and an attempt was made to correlate with the traditional system of medicine for the curative property by Infrared Spectroscopic.Raman spectroscopy is a useful technique for application in biomedical diagnostics [11].

2. Theoretical Procedures

The optimized structure and vibrational spectra were calculatedusing Gauss View and Gaussian 09 program package [12] on a PC (Lenovo® G50 that has processor Intel® core (TM) i7-5560u CPU 2.4 GHZ 2.4 GHZ with 8-GB RAM).Gaussian 09 generally referred to as an Ab-initio electronic structure program, while 09 referred to year 2009. Gaussian, a commercial quantum chemical software package from Gaussian incorporation is considered by many to be the industry standard in the area of molecular modeling and computational chemistry.Gaussian is capable of running all of the major methods in molecular modeling, including molecular mechanics; Ab-initio; semiempirical, and density functional theory (DFT) [13]. The representative models of (6, 0) zigzag single-walled BNNTs in which the ends of nanotubes were saturated by hydrogen atoms to avoid dangling bonds effectby keeping three covalent bondsfor each B and N atoms of nanotubes [14] as shown in figure (1.b). The diameter and length of the pristine (6, 0) BNNT are about 6.90 and 6.50 Å, respectively. The number of atoms in SWBNNTs are 48 atoms (18 boron atoms, 18 nitrogen atoms, and 12 hydrogen atoms). Nanotubes formed using a nanotube modeler package [15]. The selected drug (5-fluorouracil) was made using Gauss View. All nanostructures, pristine BN model and complex (the single-walled nanotube with fluorouracil) are individually optimized by using density functional theory (DFT) at B3LYP (beck three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional) [16] level of theory using the Gaussian 09 set of programs. The standard 6–31G (d) basis set used for all models. Calculations were made first to optimize the structure andobtain the vibrational frequencies, IR intensities, and then they were continuedto obtain the RA scattering strength of each band and, thus, the "calculated RA spectrum". From vibrational study can defined the stability of the BN nanostructure. The structure with no imaginary frequency said to be more stable [17].

Typical units used to report IR data are reciprocal centimeters (cm^{-1}), and the most common IR spectrophotometers cover the mid-IR region, (4000 to 400) cm^{-1}.For a nonlinear polyatomic molecule with N atoms, there are 3N – 6 degrees of internal vibrations. Linear molecules will have 3N – 5 degrees of internal vibrations.For an N-atomic molecule this amounts to 3N coordinates, of these3N coordinates, 3 are reserved for translations and 3 are reserved for rotations, which leaves 3N – 6 coordinates for internal vibrations[18], These internal degrees of freedom correspond to the number of independent normal modes of vibration. A normal mode called infrared-active, if this mode alters the electric dipole moment of the molecule. Otherwise, a vibrational mode said to be Raman-active, if this mode changes the molecular electric polarizability. Thus, as a rule of thumb, strong IR bands related to polar functional groups, whereas non-polar functional groups give rise to strong Raman bands [10].The quantities, reduced mass and force constant of each atom inthe structures are calculatedand it can be used for the understanding of vibrational modes. The frequency of vibration related to thereduced mass and force constant by the relation[19]:

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad (1)$$

v: The frequency of the vibration.
k: Force constant.

The reduced mass μ of two particles of masses $m_a$and $m_b$is given by:

$$\mu = \frac{m_a m_b}{m_a + m_b} \quad (2)$$

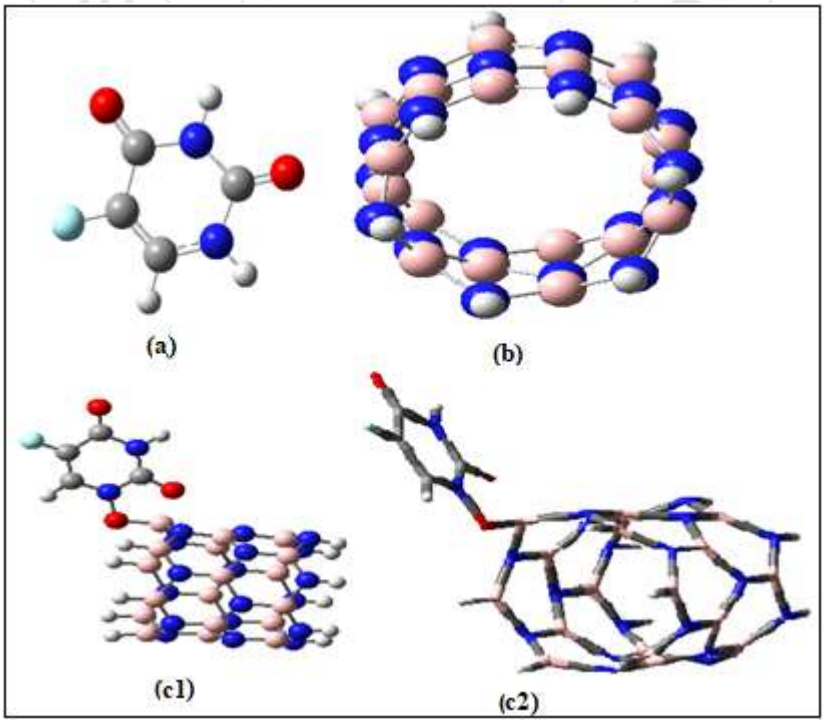


Figure 1: The structures of optimized molecular by B3LYP/6-31G (d) method. (a) 5- FU, (b) Nanotube (6, 0), and the complex (c1 as ball and bond, c2 as tubes).

3. Results and Discussion

Density Functional Theory (DFT) can be used to theory investigation. Thecomputer using for drug design and analyze interaction between drug and receptors (nanotube) and give optimal fit .IR spectroscopy has been extensively use in both qualitative and quantitative pharmaceutical analyses. Raman spectroscopy is now becoming widely utilized in the pharmaceutical sciences, too. Vibrational spectroscopy can be used to the drugs identification [10]. Figure 1.a, b and c, shows the optimized 5-fU, nanotube (6,0), and nanotube(6,0)- fluorouracil(complex) by DFT method at B3LYP/6-31G(d) level.

The optimized structure of the pristine BNNT has the B-N bond length 1.45 Å while the B-N-B and N-B-N angles are 117.9˚ and 119.9˚, respectively. The presented results in this work are in agreement with report provided by Ali Sultani et al [20], and the bond length at about 1.2 Å and 1.02 Å for (B-H) and (N-H) bonds respectively. For complex the averaged value for B-N bond lengths are 1.46 A˚ that is slightly longer than those in the pristine model.

The IR spectra of BNNTis provided in Figure (2)using B3LYP/6-31G (d) method. The number of vibrationalfrequency modes for BNNT is characterized by (*3N- 6*) normalmodes;where ***N*** is the number of atoms in the molecule.The quantity Epsilon ***ε*** is a measure of the absorbing power of the sample at a particular wave number, ***ν***, and it has called the molar absorption coefficient or the molar absorptivity. In the regions (2672-2703cm^{-1}) and the regions (3541-3546cm^{-1})represents stretching vibrations with different modes for (B-H)and (N-H)bond this can be analyzed as follows : The (B – H) and (N – H) symmetric stretching vibrations of BNNT in the region (2703.97) and (3546.02) cm^{-1} respectively, is very useful when spectroscopy is used for analytical purposes. While (2672.04) and (3541.56) cm^{-1} asymmetric stretching vibrations for (B-H) and (N-H) bond respectively,the radial breathing mode (RBM) of (B–N) bond vibration is (504.88 cm^{-1}). The symmetric stretching is happening when the same atomsvibrate in the same phase, and the asymmetric stretching is happening when the bonds vibrate in different phases. A maximum peak at (1491 cm^{-1}) which represents the stretching mode of B-N bonds and the small peak at (1429 cm^{-1}) represents the bending(rocking) mode of B-N bonds.in regions (792.77cm^{-1}) and (850.17cm^{-1}) represents bending mode of N-H and B-H bond. After binding the nanotube with 5- fluorouracil(complex), the number of vibrational frequency modes for complex are characterized by 171 (3N-6) normal vibrational modes as show in figure (2.b)that's canbe analyzed as follows:

The (N – H) bending vibrations of BNNT in the regions (828.55) and (1389) cm^{-1}, (B-H) bending vibrations of BNNT in the regions (858.90 and 1053.93) cm^{-1},thebending vibrations of drug moiety in the regions (872.68, 3278.84) and (3589.22) cm^{-1} for (C-H) and (N-H) also the (C=O) bond at (1826.58) cm^{-1} bending vibration for the drug. The stretching vibrations in the regions (2660.53-2681.98) cm^{-1}asymmetric stretching and (2694.49) cm^{-1} symmetric stretching for (B-H) bond, the (N-H) asymmetric and symmetric stretching (3543) and (3544.69) cm^{-1}respectively.Symmetric radial bending breathing modes (RBM) of (B–N) bond vibration is (511.87) cm^{-1}.From figure (2.b), it can be notice that themaximum peak at (1493.42cm^{-1}) which represents the stretching mode of B-N bonds and the small peak at (1435.78) cm^{-1} represents the bending mode of B-N bonds.The wave number at region (1571.33-1723.85) cm^{-1}very important, the drug can be active in this region. The Raman spectrum of BNNT are provide in Figure (3.a). One can identify two main peaks at high frequencies, first at (2703.97) cm^{-1} for (B – H) bond and second at (3546) cm^{-1} for (N – H) bond symmetric stretching modes. Figure (3.b)shows the Raman spectrum of complex. The calculated vibrational spectra of drug with BNNT have been divided into two main regions, the first region;

A wave number region (<2000 cm^{-1}) the first peak at (1826.58) cm^{-1} which represents the bending (twisting) mode of (c=o) in the drug,(1571.33) cm^{-1} which represents the active drug moiety and the third peak at (1329 cm^{-1}) which represents the vibration for a drug with nanotube. The second region (> 2500 cm^{-1})with a maximum peak at (3544.69) cm^{-1} that of hydrogen atoms attached to nitrogen atoms and the second peak at (2694.49 cm^{-1}) of hydrogen atoms attached to boron in BNNT which represents the symmetric stretching mode. While the small peak at (3278.48 cm^{-1}) between the two peaks that represents bending mode of hydrogen atoms attached to carbon atom in drug moiety.From the figures and results, one can be show that the active region in IR is within less activity in Raman and this is due to different in selection rule as the different in intensity between IR and Raman for the same frequency and symmetry.

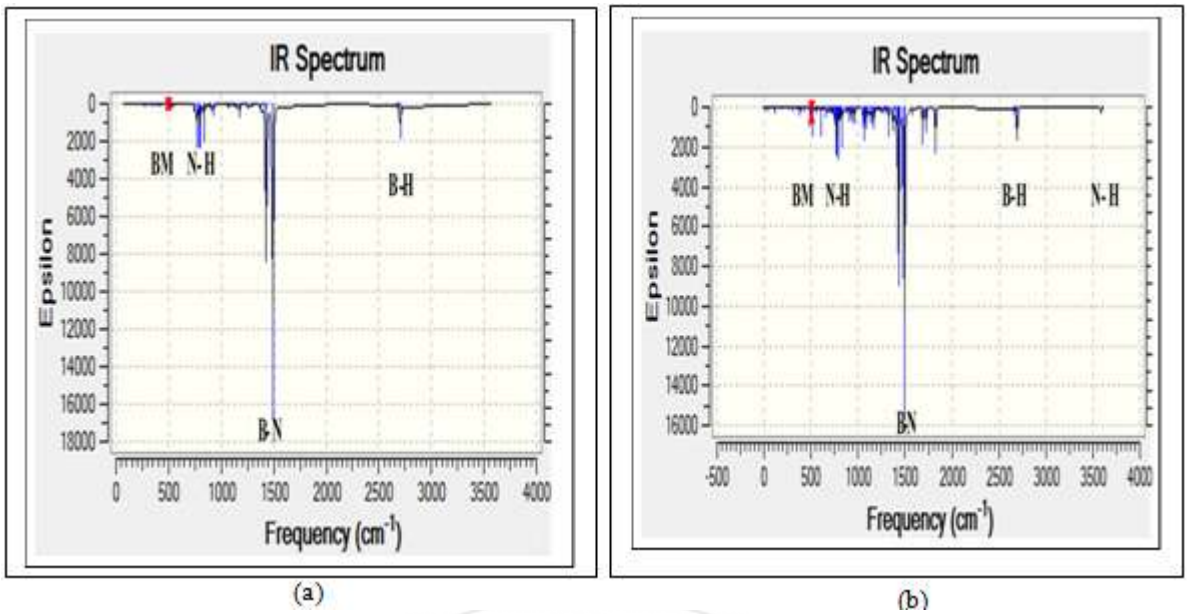


Figure 2: Calculated IR spectra of molecules, (a) SWBNNT, (b) SWBNNT with 5-Fu.Using B3LYP/6-31G (d) method.

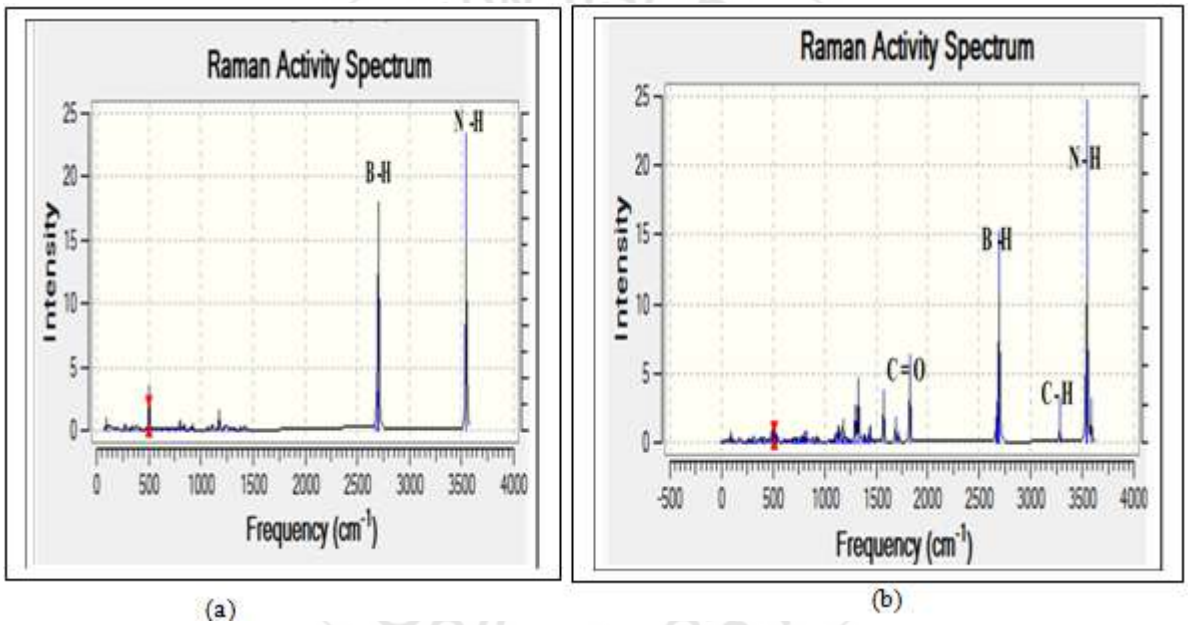


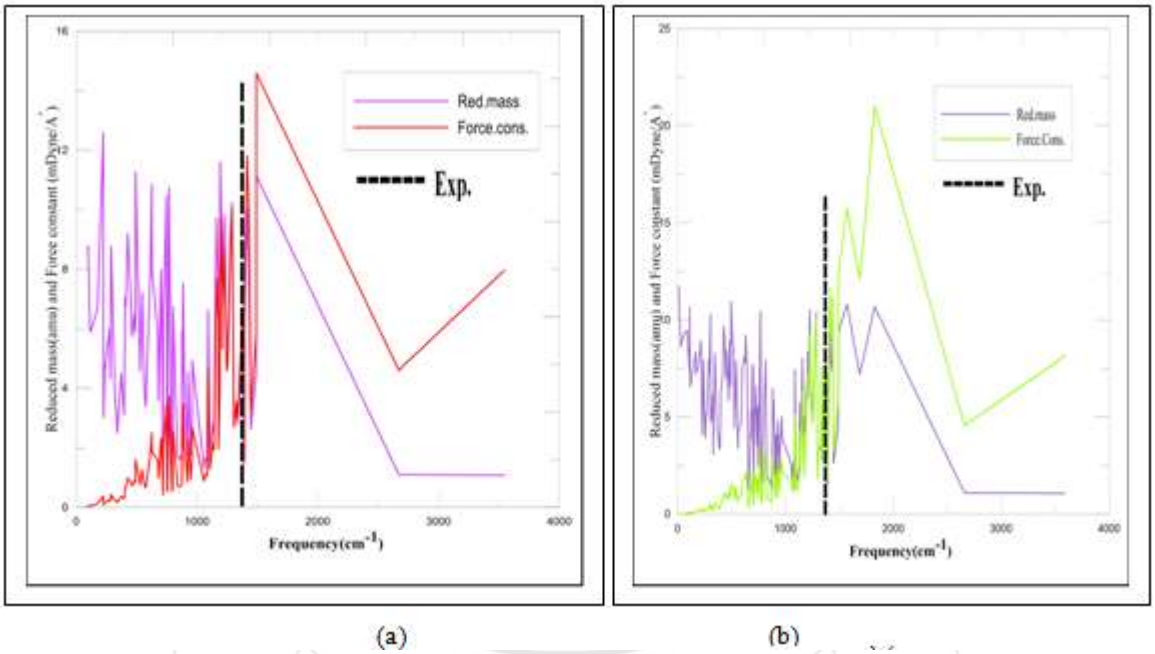
Figure 3: Calculated Raman spectra of molecules, (a) SWBNNT, (b) SWBNNT with 5-Fu.using B3LYP/6-31G (d) method

Figure (4.) show the reduced mass and force constant for SWBNNT and SWBNNT/drug (Complex).The dashed line represents the bulk experimental BN longitudinal optical (LO) vibration frequency at 1305cm^{-1}(39.12THz) [21].The highest reduce mass mode (HRMM) for SWBNNT longitudinal optical (LO) vibration frequency at (224.68cm^{-1}). The reduced masses reached (12.58amu) which is nearly to the reduced mass between two atoms B and N. The highest force constant mode (HFCM) for the SWBNNT vibrations (14.58mDyne/Å) symmetric stretching mode vibration frequency at (1491.12cm^{-1}) between (B-N) atoms.All the vibrations after (2672.04cm^{-1}) are all hydrogen atoms with B and N atoms since they all have the approximate reduced mass equal to (1amu) as shown in figure(4) (a). The (HRMM) longitudinal optical (LO) vibration frequency at (12.14cm^{-1}).Reduced mass is reached (11.75amu) which is nearly to the reduced mass between two atoms B and N whilethe (HFCM) for the complex vibrations (21.02mDyne/Å) symmetric stretching mode vibration frequency at (1826.58cm^{-1}) between (C=O) atoms and scissoring (Bending) mode between (N-H)atoms in drug molecular as show in figure (4)(b). From the figure(4) (b) it can be noticed the effect of the drug on the reduced mass and force constant while the reduced mass decreases the force constant increased clearlybecause the frequency of vibration is proportional to the square root of force constant.The vibrations after(2660.53cm^{-1})are all hydrogen atoms with the other atoms in complex since they all have the approximate reduced mass equal to (1amu) and force constants keep increasing. The relations related to frequency of vibration, reduced mass and force constantexplained by equations (1) and (2).

4. Conclusions

In conclusion, we have studiedthe optimization and the vibration properties (IR , Raman spectra, Reduce mass and Force constant) of the(6, 0) SWBNNT and SWBNNT with

5-furacil anti-cancer drug molecule based on density functional calculations. Infrared spectral is one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectra is that virtually any sample in virtually any state may be studied.Raman spectral is a powerful tool for determining information in biological specimens. The wave number at region (1571.33-1723.85) cm^{-1}very important, the drug can be active in a region.The nanotubes structure with no imaginary frequency can be more stablethat means the SWBNNT can act as a suitable drug carrier.Calculation of IR and Raman spectra showed a good picture of how the SWBNnanotube conjugate not affecting the main structure of the drug (5-florouracil).



(a) (b)

Figure 4: Reduced Masses and Force Constant as a function of frequency for: (a) SWBNNT and (b) Complex.The dashed line represents the bulk BN LO vibration frequency [21].

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