



Disinfection by-products (DBPs) interaction with carbon nanotubes

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Abstract

Properties of carbon nanotubes and its derivatives in various fields are well known. Disinfection by-products (DBPs) have adverse health effect and causes bladder cancer, early-term miscarriage, and birth defects etc. This paper presents the study of geometrical and electrical properties of DBPs, bromonitromethane (BNM). We found five different conformers of the same energy. All have approximately same stability based on energy parameter. We calculated vibrational spectra, with no imaginary frequencies. The adsorption of BNM on carbon nanotubes shows only physisorption. There is no chemical bond formed between the surface of carbon nano-tubes and bromonitromethane.

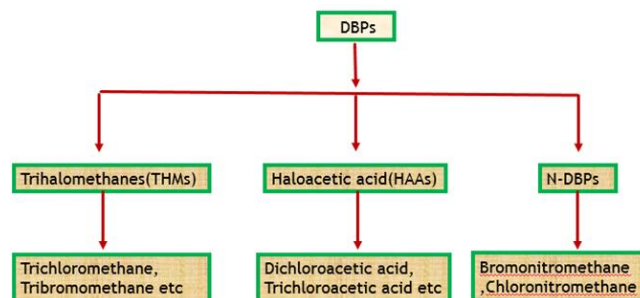
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Introduction

There is no other planet like Earth in our solar system, which has flowing water at its surface. Without water, life as we know it could not exist. Although our planet (Earth) is covered by vast oceans but only a small fraction of the water on Earth is fresh. As the population grows, it becomes more important to understand how to manage and protect our fresh water supply. The multiple burdens of climate change, population growth, urbanization and industrialization have led to decreasing availability of fresh water resources. The world is likely to be confronted with a 40% water deficit if current trends continue. Water covers 71% of the Earth's surface. It is vital for all known forms of life. On Earth approximate 97% of the planet's crust water is found in seas and oceans, 1.7% in groundwater, 1.7% in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, 0.001% in the air as vapor, and precipitation Water is very useful. It generates electricity and waters the grains, fruits and vegetables that people and animals eat. If people misuse chemicals on our crops, lawns, or industry both surface and groundwater supplies may be polluted. A pollutant is a substance introduced that has undesired effects, or adversely affects on the environment. Pollutants may cause long- or short-term damage by changing the growth rate of plant or animal species or human beings. Some pollutants are biodegradable and therefore will not persist in the environment in the long term. Some are non-biodegradable and persist for long term in the environment.

Water is a scarce commodity and a fundamental resource for the human being. The disinfection of drinking water was a major public health improvement during the 20th century that reduced the transmission of deadly waterborne diseases. Disinfection is defined as the process of killing (inactivating) harmful and objectionable bacteria, cysts and other microorganisms (pathogenic) by various agents such as chemicals, heat, ultraviolet light, ultrasonic waves, or radiation.

Several powerful oxidizing agents are used in disinfecting and treating drinking water, and many of these also cause the formation of DBPs. Chemical disinfectants (chlorine, ozone, chlorine dioxide, etc.) are effective in killing harmful microorganisms in drinking water, but they also oxidize organic matter that forms disinfection by-products (DBPs). These are present in most drinking water supplies because of chlorination, ozonation, or treatment with chlorine dioxide. Drinking water disinfection by-products (DBPs) are an unplanned consequence of using chemical disinfectants to kill harmful pathogens in water. Potential health risks of DBPs from drinking water include bladder cancer, early-term miscarriage, and birth defects. Risks from swimming pool DBP exposures include asthma and other respiratory effects. In N-DBPs the characteristic functional group is nitrogen based. Toxicity studies have specified that halonitromethanes, particularly brominated species, are more genotoxic and cytotoxic than most regulated haloacetic acid. The halonitromethanes included bromonitromethane (BNM), dibromonitromethane (DBNM), tribromonitromethane (TBNM), bromochloronitromethane (BCNM), dibromochloronitromethane (DBCNM), bromodichloronitromethane (BDCNM), chloronitromethane (CNM), dichloronitromethane (DCNM), and trichloronitromethane (TCNM).

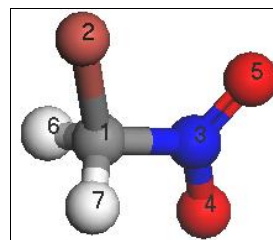


A large number of techniques have been employed for the removal of pollutants from the environment. Some of the methods are effective and some have side effects, so we need to develop a method which can serve as a better substitute for the removal of organic as well as inorganic pollutants. Adsorption of the pollutants is one of the most effective ways for their removal, which does not cause the release of any secondary pollutants. Because of the excellent adsorption properties of carbon nanotubes, it can be useful for the removal of a variety of hazardous organic and inorganic chemicals. Carbon nanotube is an allotrope of carbon. It is a cylindrical type nanostructure. It consists extraordinary thermal conductivity, mechanical strength and electrical properties. Because of these extraordinary properties the CNT are at least 100 times stronger than steel, but only one-sixth as heavy. It is also found as additive to other structural materials. Carbon nanotubes can conduct heat and electricity far better than copper. Mainly nanotubes are of two types one is single-walled carbon nanotubes (SWCNTs) and other is multi-walled carbon nanotubes (MWCNTs). Generally single-walled nanotubes have a diameter of one nanometer. Its structure can be abstracted by wrapping layer of graphene into a cylinder. Graphene is one of the carbonaceous materials like activated carbon. A common sorbent sheet, randomly substituted with heteroatoms, is also an effective sorbent for removal of metal ions, their complexes and other chemical species. Graphene is a densely packed two dimensional sp^2 carbon sheet with one-atom thickness arranged in a hexagonal pattern. In addition, graphene is a zero gap semiconductor. The robust and flexible structure of graphene and carbon nanotubes provides a unique matter for surface chemistry. It is found that the rolling of a single graphene layer into a cylindrical shape produces the SWCNT, similarly the rolling of many concentric SWCNTs into a tubular shape gives the MWCNT. All the forms of graphite are also made of graphene i.e. zero-dimensional fullerene, one-dimensional graphene and three-dimensional graphite. In terms of properties, graphene is unique as it has a soft membrane and at the same time possesses a high Young's modulus, and good thermal and electrical conductivities (Georgakilas *et al.*, 2012). In addition, a single-layer graphene is a zero band gap material and highly transparent, exhibiting optical transmittance of 97.7%. With its high theoretical specific surface area of $2600 \text{ m}^2 \text{ g}^{-1}$, hence carbon nanotubes (CNTs) and graphene provides a rich platform for surface chemistry (Wei *et al.*, 2012). Since CNTs have a great potential to adsorb N-DBPs hence, We started work on the

adsorption study of the various N-DBPs.

Results and Discussion

Halonitromethanes are disinfection byproducts present in chemically-treated drinking water. Toxicity studies have specified that halonitromethanes, particularly brominated species, are more genotoxic and cytotoxic than most regulated haloacetic acid.



Labelled structure of Bromonitromethane

Bromonitromethane is a common DBP under the N-DBP class. To explore the type of interactions established between bromonitromethane and graphene, it is important to find out the most stable conformer of bromonitromethane along with its electronic and structural properties. Hence, I, first carried out our studies on the structural and electronic properties of bromonitromethane to know its chemistry in order to design efficient graphene system for its rapid and effective degradation.

We performed using the DMol³ package available from Accelrys Inc., in the Materials Studio 5.5 package. The exchange-correlation contribution to the total electronic energy was treated in a spin-polarized generalized-gradient corrected (GGA) form of the local density approximation (LDA), with the Perdew-Burke-Ernzerhof (PBE) correlation. The numerical basis sets of double- ζ quality plus polarization functions (DNP) were employed to describe the valence orbitals. Since the use of numerical basis sets minimizes the basis set superposition error (BSSE), they are far more complete than traditional Gaussian functions.

Conformational Analysis of bromonitromethane: The conformational analysis was performed for bromonitromethane by varying the torsion angle $\text{Br}_2\text{-C}_1\text{-N}_3\text{-O}_4$. A total of five conformers were obtained which were equally populated in the gas phase (Fig. 1). Hence, we carried out our studies using conformer I.

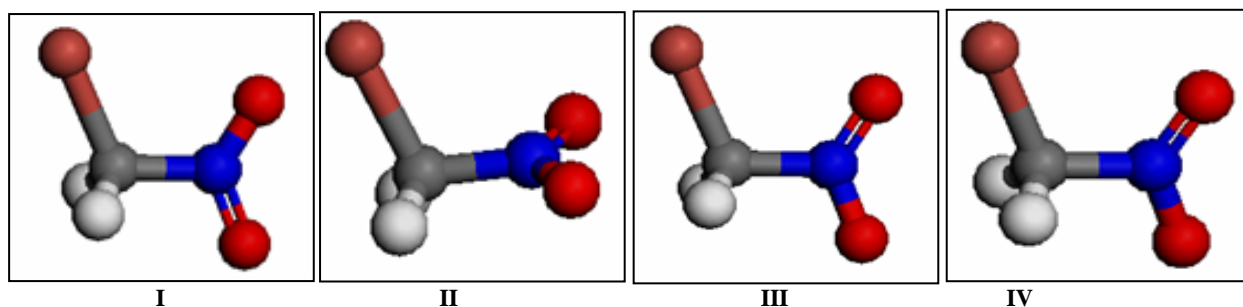


Fig 1: Conformers of bromonitromethane

Structural parameters of bromonitromethane: Till now, no thorough study on the structural and electronic properties of

bromonitromethane has been conducted. Table 1 gives calculated bond parameters.

Table 1: Bond parameters of the optimized bromonitromethane structure calculation.

Bond length(Å)		Bond Order		Bond Angle (°)		ESP charge	
C1-Br2	1.941	C1-Br2	1.0916	Br2-C1-H7	109.317	C1	-0.744
C1-N3	1.526	C1-N3	0.864	H6-C1-N3	106	Br2	0.061
C1-H6	1.092	N3-O4	1.6018	Br2-C1-N3	114.707	N3	0.845
C1-H7	1.091	N3-O5	1.671	Br2-C1-H6	109.301	O4	-0.402
N3-O4	1.236	O4-O5	0.3059	H6-C1-H7	111.4	O5	-0.368
N3-O5	1.224	C1-H6	0.9301	H7-C1-N3	106.083	H6	0.305
		C1-H7	0.9312	C1-N3-O5	120.551	H7	0.303
				C1-N3-O4	112.277		
				O5-N3-O4	127.168		

Orbital Analysis: For isolated bromonitromethane, the HOMO is mainly composed of p-orbitals of bromine, oxygen and nitrogen, which are electron-rich atoms and can donate electron density to the empty metal orbitals of the cluster. LUMO is mainly composed of the anti-bonding orbitals of nitrogen and oxygens of the -NO₂ group along with hydrogens. Both HOMO and LUMO signifies the electron rich bromine and nitro group and electron poor carbon. Negative LUMO energy signifies that the molecule is a good electron acceptor or electrophile.

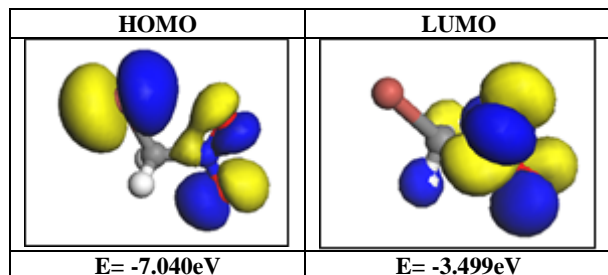


Fig 2: The HOMO E= -7.040eV and the LUMO E= -3.499eV plots of bromonitromethane

Vibrational spectra: The vibrational spectrum of bromonitromethane in gas phase is shown in Fig. 3. No negative frequency was obtained confirming an equilibrium structure on the potential energy surface. Data for the most intense frequency modes is provided in Table 2. The calculated data is in good correspondence with the experimentally obtained FTIR data.

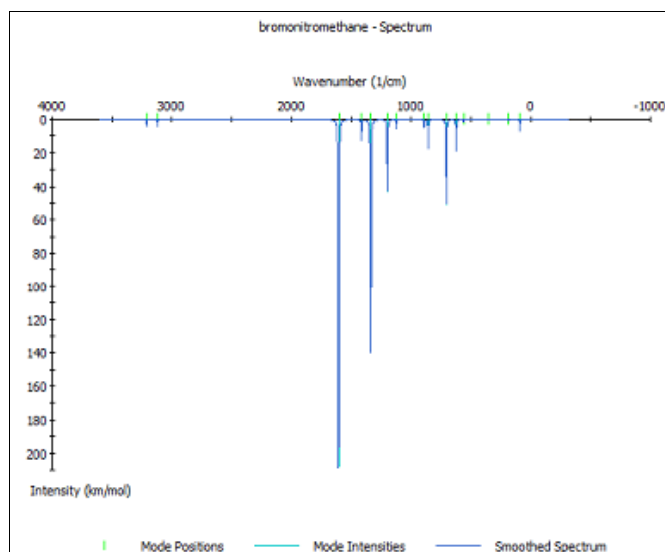
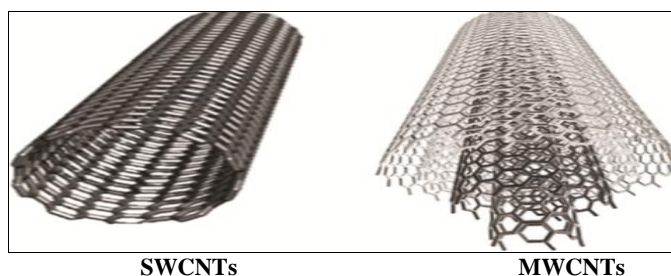


Fig 3: Vibrational spectrum of bromonitromethane

Table 2: Calculated vibrational frequencies of bromonitromethane

Frequency (cm ⁻¹)	Intensity (km/mol)
624.01	19.64
705.17	51.11
856.78	17.41
1197.9	43.55
1337.5	139.45
1415.12	12.37
1606.37	208.75



On putting the bromonitromethane on the surface of carbon nanotubes. We found that the adsorption of BNM on CNT is only a physisorption. There is only vander-wall interaction between carbon nanotube and disinfectant byproduct

(bromonitromethane). There is no chemical bond formation between adsorbent (CNTs) and adsorbate (BNM).

Conclusion

On determining the most stable conformer of bromonitromethane in the gas phase. We found five different conformers of the same. All have approximately same stability based on energy parameter. We calculated vibrational spectra, with no imaginary frequencies, suggesting that the conformer obtained is energetically most stable on the potential energy surface. Frontier molecular orbitals are mainly composed of the p-orbitals of nitrogen, oxygen and bromine atoms. Physisorption is obtained on interaction between disinfectant by-product (bromonitromethane) and carbon nanotubes.

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