

# Theoretical investigations on Zundel cation present inside boron-nitride nanotubes: Effect of confinement and hydrogen bonding



Manoj K. Tripathy<sup>a</sup>, Naresh K. Jena<sup>b</sup>, Alok K. Samanta<sup>b</sup>, Swapan K. Ghosh<sup>b</sup>, K.R.S. Chandrakumar<sup>b,\*</sup>

<sup>a</sup> Research Reactor Services Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

<sup>b</sup> Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, India

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## ABSTRACT

The properties of protonated water systems in nano-confinement differ significantly from its bulk counterparts mainly due to the geometric constraint and nature of water-medium interactions. Herein, we have investigated the structure, vibrational spectra and proton transfer energetics of Zundel cation (ZC) under the confinement of boron-nitride nanotubes (BNNTs) by varying the degree of confinement in a systematic manner. Our results based on dispersion-corrected density functional theory (DFT) based methods reveal that the structure of ZC is significantly modified under the confinement and the nature of interaction largely depends on the diameter of BNNT. The ZC effectively forms hydrogen bonds through  $H_{\text{water}} \cdots N_{\text{BNNT}}$  with BNNT. Among the BNNTs considered in the present study, the maximum interaction energy of ZC and minimum energy barrier for proton transfer are observed for the case of BNNT(5,5). This implies that this particular nanotube can facilitate the proton to easily hop between water molecules of a confined protonated water system.

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## 1. Introduction

Water molecules confined in pores of nanoscale dimension portray entirely different behavior compared to the bulk water [1]. In these nanopores, the geometric constraint offered by the confinement medium along with the diverse nature of water-medium interactions can have significant effect on various physical and chemical phenomena such as diffusion, proton transfer (PT) etc. In particular, few studies on water confined in various nanoporous structure have established that the dimension of the nano-channel plays a major role in deciding the static and dynamic properties of the confined water molecules [2,3]. Among the various nanoporous materials, primarily the carbon nanotubes (CNTs) have been investigated [4–6] because CNTs are one of the most promising candidates for technologically important applications [7] in different areas, such as desalination [8], isotope separation [9], energy storage devices and flow sensors [10]. Water molecules undergo molecular ordering to form 1D linear chain configuration or 2D ladder like structures in narrow nanotubes (diameter less than  $\sim 10$  Å) depending on the diameter of the nanotube [4,11]. In wider nanotubes, stacked-ring structures are formed with a linear chain of water molecules present at the center of the nanotube [11–13]. In general, a reduction in the number of hydrogen bonds of confined

water molecule is observed [4,13,14] and the restricted coordination of water molecule inhibits the solvation of proton and cause the proton transfer (PT) mechanism inside CNTs to be different from bulk water. In case of such confined nanotubes, PT is in general, facilitated by a favorable pre-alignment of water molecules whereas in bulk liquid, water solvent reorganization is required prior to PT [6]. It has been reported that the proton mobility can be remarkably enhanced by a factor 40 in CNT as compared to the bulk water [15]. Cao and co-workers have shown that the PT in water confined CNTs takes place through Zundel–Zundel mechanism [16] instead of Eigen–Zundel–Eigen mechanism that is being followed in a normal Grotthuss mechanism in bulk water [17,18]. The Eigen cation ( $O_4H_5^+$ ) is a hydronium ion ( $H_3O^+$ ) symmetrically co-ordinated by three water molecules whereas, the Zundel cation ( $O_2H_5^+$ ) is the symmetric protonated water dimer.

Although effect of confinement on the protonated water systems has been studied in detail under carbon nanotubes, such investigations have been scarcely carried out for the case of boron-nitride nanotubes (BNNTs). BNNTs are structural analogues of CNTs with alternative carbon atoms of CNT substituted by boron and nitrogen atoms, possess wider band gap, greater thermal stability and more resistant to chemical oxidation in comparison to the carbon structure counterpart [19–21]. There are also reports which show the selective ion transport characteristics of BNNTs [22–24]. These exciting properties with their unique morphology have motivated researchers to explore the possibility of using

\* Corresponding author.

E-mail address: [krs@barc.gov.in](mailto:krs@barc.gov.in) (K.R.S. Chandrakumar).

BNNTs in nano medicine [25], water purification [22,26] and as gas sensors [27]. However, there are only a few reports in literature dealing with water confined in BNNT [28,29] and these studies have demonstrated the superior water permeation properties of BNNTs as compared to CNTs. More interestingly, it has been observed that the inclusion of partial charges (obtained through a density functional theory (DFT) calculation) in the molecular dynamics (MD) simulations can significantly enhance the wetting behavior and reduce the diffusion coefficient of confined water molecules in BNNT(5,5) [29]. It has also been reported that the surface polarity of the nano-channel modulates the water-channel interaction and plays a key role in altering the properties of the confined water molecules [30]. Therefore, further study at *ab initio* level on the structure and energetics of protonated water systems is required for the molecular level understanding of BNNT based nanofluidic systems. Accordingly, in the present work, we have performed DFT based calculations to investigate the structure, vibrational spectra and proton transfer energetics (energy barrier) in Zundel cation (ZC), i.e. protonated water-dimer, under the confinement of single walled BNNTs by varying the degree of confinement in a systematic manner. In what follows, we have demonstrated that the structure of the ZC is significantly modified under the confinement of BNNT and the interaction largely depends on the diameter of the BNNT. It has also been shown that the remarkable effect of marginal change in degree of confinement on the energy barrier for the PT process and explain why the BNNT(5,5) can possibly favor the fast transport of proton under confinement.

## 2. Computational details

ZC is the most prevalent ion in the linear chain of protonated water cluster [31] and also observed in the structure of large protonated water clusters ( $H^+(H_2O)_n$ ) [31–33]. This ion has been extensively used as a model system to study the proton transfer process in water in several theoretical studies [34–36]. Based on these studies, we have selected this prototypical ion to investigate the structure and the energetics of PT process under the confinement of BNNTs. The equilibrium structure for the ZC is initially obtained in gas phase. Then the complexes comprising of ZC and BNNTs have been optimized to get the minimum energy structure of the BNNT–ZC complexes. The structure of the BNNT framework is in general observed to be least affected during the course of optimization. The potential energy surface (PES) for the PT processes in ZC, both in the case of gas phase and under the confinement of CNTs is constructed by scanning the proton at the center of the O–O axis of the two water molecules. The terminal atoms of the BNNTs are saturated with dangling hydrogen atoms to minimize the end effects. The variation in confinement length (or the degree of confinement) has been achieved by selecting BNNTs of different diameters and herein, we have considered the armchair BNNTs ranging from BNNT(4,4) to BNNT(8,8) with the corresponding diameter of 5.7–11.2 Å.

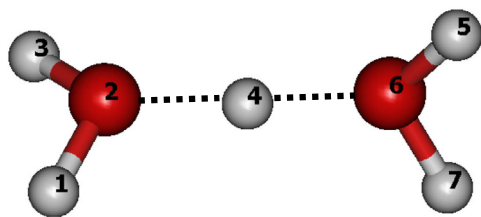


Fig. 1. The optimized structure of the isolated ZC. The atoms shown in red color are the oxygen atoms. The remaining atoms are the hydrogen atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

All the calculations have been performed by employing density functional theory with B3LYP exchange–correlation hybrid functional as implemented in TURBOMOLE program [37]. The reliability of DFT calculations in describing the ZC and other hydrogen-bonded systems has been already tested with respect to other schemes such as MP2 and CCSD, through several studies [38,39]. The correlation-consistent triple-zeta basis set augmented with diffuse basis functions (augCC-pVTZ) is used for ZC, whereas for the nanotube framework, simple contracted Gaussian basis sets (SVP or split valence with polarization) are used. Since in these types of systems, dispersion interaction plays an important role, dispersion correction has been incorporated in all the calculations [40]. The infra-red vibrational modes of the confined ZC have been calculated by freezing the coordinates of the BNNT framework and following the NumForce module of the TURBOMOLE program. A scaling factor of 0.9687 has been used for the calculated vibrational frequencies [41].

## 3. Results and discussion

### 3.1. Structure and energetics of proton transfer in isolated ZC in gas phase

Before discussing the effect of confinement due to BNNT on ZC, we first discuss the structure and energetics of proton transfer in isolated ZC. The important geometrical parameters of the optimized structure (Fig. 1) obtained in the present study along with other theoretical results are summarized in Table 1. It can be inferred from Table 1 that the results obtained with hybrid density functional, B3LYP with dispersion correction in combination with a good basis set are in excellent agreement with high level methods like MP2 or CCSD [38,39,42]. The computed interaction energy of  $H_3O^+$  with  $H_2O$  is  $-36.3$  kcal/mol which is close to the reported MP2 result of  $-34.2$  kcal/mol [39] and indicates the presence of a strong hydrogen bonding between the proton with two water molecules in ZC.

Table 1

Important structural parameters of the isolated ZC. The numbers in the first row corresponds to the atoms as shown in Fig. 1. Bond distances ( $R$ ) are in angstrom and bond angles ( $\theta$ ) are in degree.

Source	$\theta_{(1-2-3)}$	$R_{(1-2)}$	$\theta_{(2-4-6)}$	$R_{(2-4)}$	$R_{(2-6)}$	$\Delta E$ (kcal/mol)
Present study	109.9	0.97	174.3	1.20	2.40	$-36.3$
CCSD/DZP <sup>a</sup>	108.90	0.973	174.10			$-36.3$
MP2(FC)/QZT <sup>b</sup>	109.06	0.968	173.70	1.197		

<sup>a</sup> Ref. [38].

<sup>b</sup> Ref. [42].

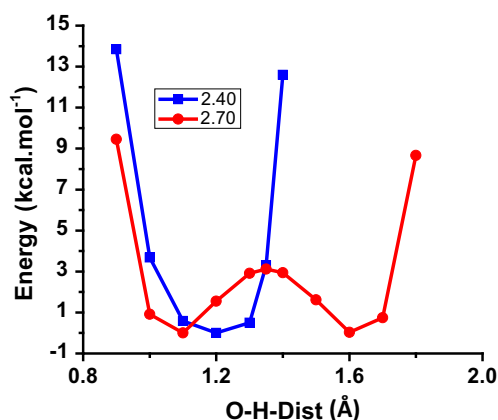


Fig. 2. PES of ZC at different value of inter-oxygen distance of isolated ZC.

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