Terahertz vibrational properties of water nanoclusters relevant to biology

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Abstract Water nanoclusters are shown from first-principles calculations to possess unique terahertz-frequency vibrational modes in the 1–6 THz range, corresponding to O–O–O “bending,” “squashing,” and “twisting” “surface” distortions of the clusters. The cluster molecular-orbital LUMOs are huge Rydberg-like “S,” “P,” “D,” and “F” orbitals that accept an extra electron via optical excitation, ionization, or electron donation from interacting biomolecules. Dynamic Jahn–Teller coupling of these “hydrated-electron” orbitals to the THz vibrations promotes such water clusters as vibronically active “structured water” essential to biomolecular function such as protein folding. In biological microtubules, confined water-cluster THz vibrations may induce their “quantum coherence” communicated by Jahn–Teller phonons via coupling of the THz electromagnetic field to the water clusters’ large electric dipole moments.

Keywords Water clusters • Terahertz • Vibrational • Vibronic

1 Introduction

Scientific interest in water nanoclusters has been motivated by their possible roles in biology [1, 2], atmospheric science [3, 4], and astrophysics [5], as well as by their relevance to the structure and properties of liquid water [6]. In a recent letter by this author and collaborators [7], it has been suggested that because of their large electric dipole moments, protonated water clusters such as $(\text{H}_2\text{O})_{21}\text{H}^+$ shown in Fig. 1 may contribute significantly to the observed strong THz emission from water vapour under optical stimulation. Experiment and theory agree that not only can such water clusters be produced but they also occur optimally

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Fig. 1 Ground-state density-functional molecular-orbital states and vibrational modes of the $(\text{H}_2\text{O})_{21}\text{H}^+$ protonated water “buckyball.” **a** Cluster molecular-orbital energy levels. The HOMO-LUMO energy gap is approximately 3 eV. **b** Wavefunctions of the lowest unoccupied cluster molecular orbitals. **c** Vibrational spectrum. **d** The 1.5-THz vibrational mode. The *vectors* show the directions and relative amplitudes of the O–O–O “bending” oscillations of the cluster “surface” oxygen atoms (in red) coupled to the hydronium (H_3O^+) oxygen ion vibration

in certain numbers (so-called magic numbers) and configurations of water molecules [3, 8–10]. Prominent among the magic-number water clusters that have been identified are ones having the “buckyball-like” pentagonal dodecahedral structure [9, 10] shown in Fig. 2a. These clusters have a closed, ideally icosahedral symmetry formed by 20 hydrogen-bonded water molecules, with their oxygen atoms at the vertices of 12 concatenated pentagons and with 10 free exterior hydrogen atoms, as illustrated for $(\text{H}_2\text{O})_{21}\text{H}^+$ and $(\text{H}_2\text{O})_{20}$ clusters in Figs. 1d and 3a, respectively.

2 Water nanocluster electronic structure and THz vibrations

Figure 1 shows the computed density-functional ground-state molecular-orbital energies and vibrational modes of the $(\text{H}_2\text{O})_{21}\text{H}^+$ or $(\text{H}_2\text{O})_{20}\text{H}_3\text{O}^+$ cluster. Of particular importance are the “squashing” and “twisting” vibrational modes of the otherwise ideal pentagonal dodecahedral cluster shown in Fig. 2a. Density-functional calculations for the electrically neutral pentagonal dodecahedral water cluster, $(\text{H}_2\text{O})_{20}$, and arrays thereof, shown in Fig. 3 have also been performed, yielding the vibrational modes displayed in Fig. 4. These results are very similar to those for $(\text{H}_2\text{O})_{21}\text{H}^+$ in Fig. 1. Common to the water clusters studied

Fig. 2 **a** “Squashing” and “twisting” vibrational modes of a pentagonal dodecahedron. Hg and Hu designate the key irreducible representations of the icosahedral point group corresponding to these modes. **b** Schematic representation of the double potential energy wells for Jahn–Teller distorted water buckyballs and the resulting reduction of the energy barrier for chemical reaction of these water clusters along the reaction path defined by the normal mode coordinates Q_s

are: (1) lowest unoccupied (LUMO) energy levels like those shown in Fig. 1a, which correspond to the “S”-, “P”-, “D”- and “F”-like cluster “surface” orbital wavefunctions shown in Fig. 1b; and (2) bands of vibrational modes between 1 and 6 THz, shown in Figs. 1 and 4, due to O–O–O “squashing” (or “bending”) and “twisting” motions of the type illustrated in Fig. 2a between adjacent hydrogen bonds. The vectors in Figs. 1 and 4 represent the directions and relative amplitudes for the lowest THz modes corresponding to the O–O–O “bending” (or “squashing”) motions of the water-cluster “surface” oxygen ions. Surface O–O–O bending vibrations of water clusters in this energy range have indeed been observed experimentally [11]. Near-ultraviolet excitation of an electron from the HOMO to the LUMO (Fig. 1a) can put the electron into the bound “S”-like cluster molecular orbital mapped in Fig. 1b.

Fig. 3 **a** Pentagonal dodecahedral $(\text{H}_2\text{O})_{20}$ “water buckyball”; **b** an array of three dodecahedral water clusters; **c** an array of five dodecahedral water clusters

c

b

a

Fig. 4 **a** Vibrational spectrum of a pentagonal dodecahedral (H_2O)₂₀ “water buckyball”; **b** lowest-frequency THz vibrational mode of the cluster; **c** vibrational spectrum of an array of three dodecahedral water clusters; **d** lowest-frequency THz vibrational mode; **e** vibrational spectrum of an array of five dodecahedral water clusters; **f** lowest-frequency THz vibrational mode. The vectors show the directions and relative amplitudes for the O–O–O “bending” motions responsible for the “squashing” mode of the cluster “surface” oxygen atoms

Occupation of the LUMO produces a metastable bound state of such a water cluster, even when an extra electron is added, the so-called hydrated electron. In contrast, a water monomer or dimer has virtually no electron affinity. Infrared absorption can further excite the cluster LUMO “S”-like electron into a higher LUMO such as the “P”-like cluster orbital in Fig. 1b. Infrared excitations within the LUMO manifold can then decay vibrationally according to the Franck–Condon principle. The lowest-frequency vibrations of water clusters induced by optical pumping should be the 1–6 THz “surface” modes of Figs. 1c, d and 4.

3 Water nanocluster chemical activity

While liquid water is not usually thought of as an “active” substance, hydrated-electron water nanoclusters are another matter, due to the effectively large reactive cross sections of the cluster “surface” molecular orbitals mapped in Fig. 1b. Experimental studies of

the thermal energy chemical reactions of size-selected hydrated-electron clusters $(\text{H}_2\text{O})_n^{-1}$ attribute their strong reactivity to the spatial delocalization of the excess electron at the cluster surface [12]. Thus, charged water nanoclusters can function as electron reservoirs for chemical reactions involving electron transfer to or from the reacting species. In the oxidation of carbon compounds, hydrated-electron delocalized orbitals originating on the water-cluster surface oxygen atoms can readily overlap with the reactive carbon (e.g., $p\pi$) orbitals, promoting oxidation. The proximity of the highest occupied dodecahedral water-cluster excess-electron “S” orbital to the lowest unoccupied, nearly degenerate cluster “ P_x, P_y, P_z ” orbitals (Fig. 1a, b) suggests the strong possibility of coupling between the hydrated electron and the THz-frequency cluster “squashing” modes shown in Figs. 1, 2a, and 4 via the pseudo or dynamic Jahn–Teller (JT) effect [13]. Such cluster “squashing” modes associated with icosahedral symmetry are known to be JT-active in the case of electron-doped buckminsterfullerene [14]. JT coupling in the water clusters leads to a prescribed symmetry breaking of the pentagonal dodecahedron along the THz-frequency vibrational squashing mode coordinates Q_s , lowering the cluster potential energy from A to the equivalent minima A' shown in Fig. 2b. Because of the large JT-induced vibrational displacements (large Q_s) of water-cluster surface oxygen atoms, the energy barrier for expulsion of water oxygen or OH radicals and their oxidative addition to reactive carbon atoms is lowered from E_{barrier} to E'_{barrier} , as shown in Fig. 2b. A more detailed discussion of the JT effect as an activation mechanism in chemical reactions and catalysis is found in [13]. The practical use of water clusters stabilized in nanoemulsions to break down and more completely burn particulate matter precursor molecules, as well as serving as a combustion oxygenate in fossil fuels, has been demonstrated [15, 16]. Finally, water-cluster THz modes may facilitate electron and proton transfer in photosynthesis [17].

4 Electrical dipole moments of water nanoclusters

The calculated ground-state dipole moment of the $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster is approximately 10 Debyes, as compared with the 1.86 D moment of water monomer. THz vibrations induced by optical pumping produce large oscillating electric dipole moments exceeding 10 D. Since the power radiated from an oscillating dipole is proportional to the square of the dipole moment, an optically excited water cluster ion like $(\text{H}_2\text{O})_n\text{H}^+$ is a potentially strong source of THz radiation [7]. Ambient water vapour containing 10^{17} cm^{-3} water monomers typically contains only 10^4 to 10^6 $(\text{H}_2\text{O})_n\text{H}^+$ clusters cm^{-3} , whereas neutral water dimer and cluster concentrations are as high as 10^{10} to 10^{12} cm^{-3} [3, 4]. Nevertheless, isolated $(\text{H}_2\text{O})_n\text{H}^+$ clusters can in theory be pumped collectively by photons into resonant vibrational (phonon) modes of lowest frequencies 1–6 THz, analogous to a Bose–Einstein condensation, acquiring giant electric dipoles of the order of 10^5 to 10^7 D cm^{-3} [18]. This greatly enhances the possible contribution of water clusters to radiation absorption and emission and has been argued to explain the strong far-infrared and submillimeter absorption of radiation in Earth’s atmosphere [3, 4].

5 Protein folding and drug action

Pentagonal water clusters have been experimentally identified as being key to the hydration and stabilization of biomolecules [1, 2]. Such examples indicate the tendency of water

Fig. 5 **a** Water cluster bonding to a valyl amino acid residue in insulin. A principal bonding molecular-orbital wavefunction is shown. **b** Coupling of the water cluster lowest-frequency THz vibrational mode to the valyl and neighboring amino acid residue “bending” modes that promote protein folding

pentagons to form closed geometrical structures at biomolecular interfaces including amino acids (Fig. 5) and nucleotides (DNA, RNA) [19]. The “restructuring” or clustering of water molecules may even determine biological cell architecture [20]. Approximately 70% of the human body is water by weight. Much of that water is believed to be restructured or nanostructured [2], which affects biomolecular processes including protein stability, enzyme activity, and proton transfer. Some diseases (e.g., Alzheimer’s, Parkinson’s, type II diabetes, and cataracts) are associated with the “misfolding” of proteins. Water—“restructured” as nanoclusters of the above-described type—plays a key role in the proper folding of proteins. The misfolding of proteins, making them dysfunctional and disease-causing, is likely associated with the failure of water molecules to congregate in clusters that properly interact with the protein. The development of drugs to treat such diseases should therefore be focused on the restoration of water clustering at the protein interfaces. Water cluster “surface” THz vibrational modes like the ones shown above are especially important because they couple or “resonate” with THz-frequency “bending” vibrations of the amino-acid residues in proteins. An example is shown in Fig. 5 for the protein, insulin, where a pentagonal water cluster bonds to a valyl amino acid residue. A principal bonding molecular-orbital wavefunction is shown. The water cluster lowest-frequency THz vibrational mode, induced by the dynamic Jahn–Teller effect [13] from the orbital degeneracy, couples to the valyl and neighboring amino acid residue “bending” modes that promote protein folding. This property may also be relevant to the action of drugs, as exemplified in Fig. 6, where a water cluster bonds to the active center of an anthracene anticancer drug [21]. A principal bonding molecular-orbital wavefunction is shown. The water cluster lowest-frequency THz vibrational mode couples to the anthracene bending mode believed to promote drug attack and intercalation on the DNA of cancer cells.

Fig. 6 **a** Water cluster bonding to the active center of an anthracene anticancer drug. A principal bonding molecular-orbital wavefunction is shown. **b** Coupling of the water cluster lowest-frequency THz vibrational mode to the anthracene bending mode that is believed to promote drug attack and intercalation on the DNA of cancer cells

6 Quantum coherence in biology

There are environments in biology where water molecules may be confined in linear or “filamentary” arrays, like the one shown in Fig. 7a, instead of in globular arrays like those shown in Fig. 3b, c. One example is the microtubule, a principal component of the cytoskeleton—hollow polymeric cylinders approximately 25 nm in diameter composed of the protein tubulin. Microtubules are dynamic structures that help to determine biological cell shape and facilitate intracellular transport. As a first step toward modeling, the water confined to a microtubule, a linear array of pentagonal dodecahedral water clusters, has been confined to a cell with periodic boundary conditions on the ends of the cell and an electron added to the array to simulate electron donation from a surrounding microtubule. Density-functional calculations of the lowest energy structure were performed and produce the stable configuration and vibrational spectrum shown in Fig. 7. Two primary bands of THz vibrational modes are found, in common with the results obtained for globular arrays of water clusters shown in Fig. 4. The lowest-frequency THz vibrational modes, such as the one displayed in Fig. 7c, communicated by Jahn–Teller phonons [13] via coupling of the THz electromagnetic field to the water clusters’ extraordinarily large electric dipole moments [7], may lead to the “quantum coherence” or “Bose–Einstein-like” condensation of interacting water clusters confined to microtubules [22]. While the human body is 70% water by weight, the normal human brain is approximately 90% water. It is possible that this

Fig. 7 **a** Linear array of water clusters under periodic boundary conditions. **b** THz vibrational spectrum of the array with added electron to simulate electron donation from a surrounding microtubule. **c** Low-frequency THz vibrational mode of the array

Fig. 8 First-principles density-functional calculations for water confined in carbon nanotubes produce stable water nanoclusters ("structured water")

quantum-coherent dynamical Jahn–Teller system of water clusters and the quantized THz electromagnetic field confined within the hollow inner cores of brain microtubules may be relevant to conscious thought processes, consistent with controversial ideas promoted by Hameroff and Penrose [23]. Recent inelastic neutron scattering measurements [24] on carbon-nanotube-confined water have given evidence that the ground-state wavefunction of the confined nanowater corresponds to a strongly anharmonic local double-well potential of the type shown schematically in Fig. 2, consistent with the presence of water nanoclusters undergoing symmetry-breaking dynamic-Jahn–Teller-induced THz vibrations of the types shown in the above figures. First-principles density-functional calculations for water confined in carbon nanotubes have been performed, producing stable linear water-nanocluster (“structured-water”) configurations like those shown in Fig. 8. Two primary bands of THz vibrational modes similar to those shown in Fig. 7 have been found. The unique 1–6 THz water-cluster vibrational modes underlie nanofluidic flow and greatly influence the electronic and other physical properties of the nanotubes.

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