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Raman and infrared-active modes in MgO nanotubes

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ABSTRACT

Finite magnesium oxide nanotubes are investigated. Stacks of squares and hexagons of MgO clusters are constructed and studied by the density-functional theory (DFT). Optimized structures are slightly distorted stacks of polygons. Frequencies of radial breathing modes and radial twisting modes show strong size effect. Raman and infrared activity of the modes present a dependence on parity of layer. The activity can be deduced in the low-dimensional system, based on the symmetry and selection rules. A suggestion for experimental characterization between squares and hexagons cross-sections of nanotubes by Raman and infrared is proposed.

1. Introduction

MgO is an important material in applications. It is known as an inert material with a high melting point, as a typical wideband-gap insulator. And its substrate has been widely used for high-Tc superconductor (HTSC) thin-film coating applications worldwide. When it is used as a substrate for nanoparticle catalysts, the main physical properties need to be better understood for the transition from solid state to molecule scale. This has prompted numerous studies of MgO clusters. Saunders [1,2] published mass-spectra and collision-induced-fragmentation data for sputtered MgO cluster ions and found enhanced stabilities for $(MgO)^{+}_{n}$ clusters with $n = 6, 9, 12$ and 15. Stacks of polygonal MgO rings have been found by the Hartree–Fock calculations for small clusters [3–5]. These results were interpreted in terms of clusters built possibly from hexagonal $(MgO)_3$ sub-units. In recent years, structural and electronic properties of MgO nanotubes have been analyzed [6,7]. A strong shape dependence of electronic properties in small MgO clusters has been found by Moukouri and Noguera using a tight binding calculation [8,9]. Geometries and bond lengths, binding energies, the degree of ionicity in the bonds and the electronic gaps are analyzed as a function of diameter and length of MgO nanotube clusters in our previous work [10,11]. Here, we focus our interests on activity of the modes in MgO nanotubes, which are stacks of squares and hexagons. The rest of the paper is organized as follows. Section 2 gives an outline of geometrical structure and computational method. In Section 3 the results and discussion are presented. Conclusions are summarized in Section 4.

2. Geometrical structure and computational method

When the number of units is more than 30, MgO clusters are consistent with cubic nanocrystal structures [5,12]. So it is an apt choice that we optimize the structure and calculate the frequency of $(MgO)_{mn}$ $(m \times n \leqslant 27)$ nanotubes, where m means m-membered rings (m-MR), n is the number of layer, and m and n are integers. The cross-sections of 2MR and 3MR nanotubes are squares and hexagons, respectively. As presented in Fig. 1, the optimized structures are slightly distorted stacks of polygons. Small and large spheres are used to represent O and Mg atoms, respectively. Clusters geometries were optimized using the density-functional theory (DFT)-based Becke's hybrid three-parameter exchange functional [13] combined with the Lee–Yang–Parr correlation functional [14] (B3LYP) method with the 6-31G(d) basis set. It is well established that key factors in the computation of reliable electronic properties are the basis set choice and the theoretical model that is used. Such as, calculations of electric (hyper)polarizability of gallium arsenide clusters with different basis set and theoretical model, same trends of results are observed, the

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difference is relatively stable [15,16]. The vibrational frequencies for MgO nanotube clusters that were studied using the B3LYP/6-31G(d) level matched closely with IR-REMPI vibrational spectra, and were also similar to MgO bulk material [11]. So it is an economic choice to yield reliable results for MgO nanoclusters. Gaussian 03 software package was used throughout [17].

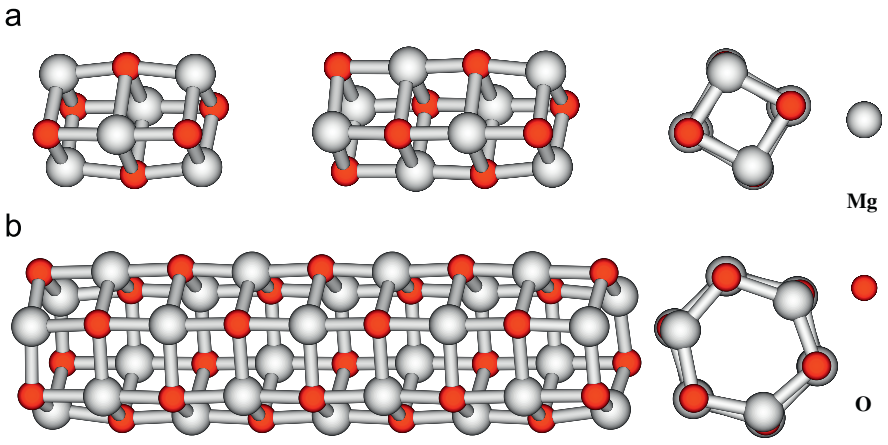

Fig. 1. The optimized geometries of MgO nanotubes (a) 2MR nanotubes: 2M3L, 2M4L and (b) 3MR nanotube: 3M9L. Side views and top views are shown.

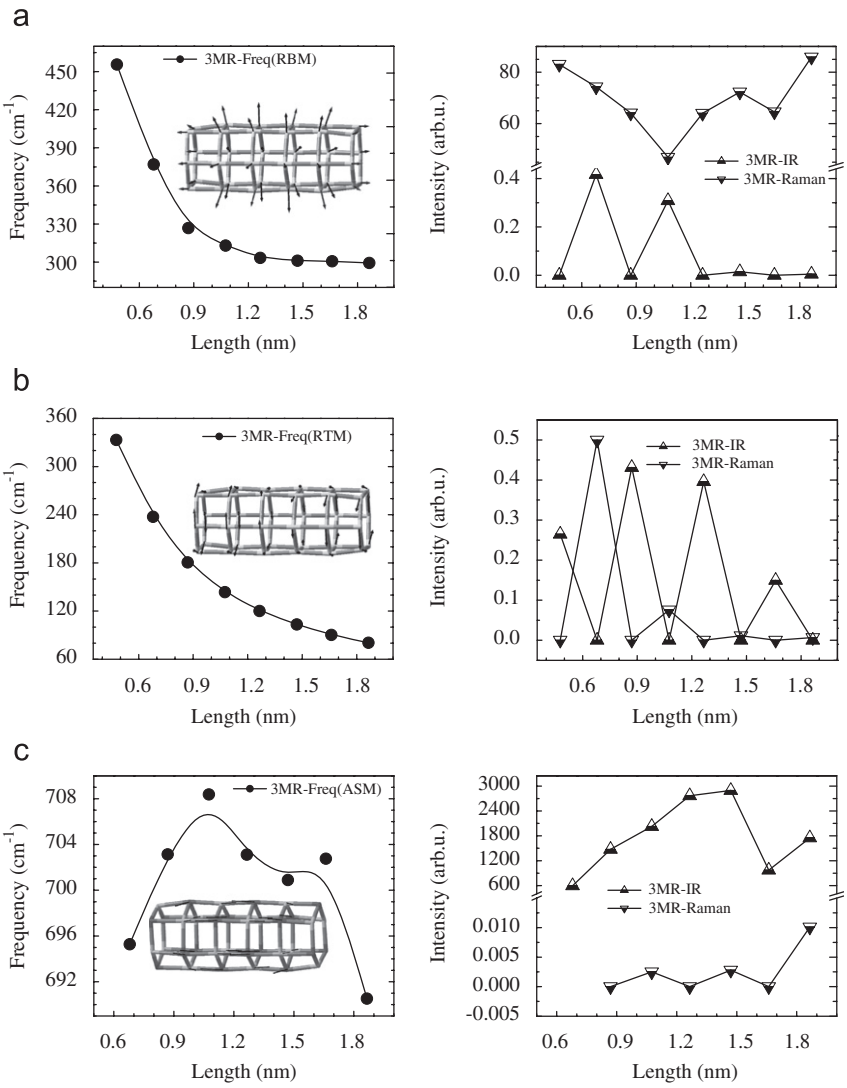

Fig. 2. Frequency and intensity of vibrations in MgO 3MR nanotubes as a function of length: (a) frequency of breathing mode (left side), Raman and IR activities of the mode (right side), (b) frequency of radial twisting mode (left side), Raman and IR activities of the mode (right side) and (c) frequency of axial stretching mode (left side), Raman and IR activities of the mode (right side).