Vibrational properties of C$_{20}$-based solids

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Abstract. The phonon dispersion relations and IR spectrum of a C$_{20}$-based solid recently identified experimentally [Iqbal et al., Eur. Phys. J. B 31, 509 (2003)] have been computed by density functional perturbation theory. Other competitive structures made by assembling C$_{20}$ clusters have been considered as well. In particular, we have computed the structure and the Raman spectra of two-dimensional polymeric phases of hydrogenated C$_{20}$ clusters which might be formed under different synthesis conditions. Fingerprints of the different phases have been identified in the vibrational spectra which could be used in the experimental search of C$_{20}$-based solids.

PACS. 61.48.+c Fullerenes and fullerene-related materials – 63.20.-e Phonons in crystal lattices – 78.30.-j Infrared and Raman spectra

1 Introduction

The report on the synthesis of the dodecahedral C$_{20}$ cluster in the gas phase from C$_{20}$H$_{20}$ precursors [1] encouraged recent research on the properties of the smallest fullerenes [2–4]. Due to the increase of the electron-phonon coupling with increasing curvature of the graphenic cage, the solid phases of the small fullerenes (C$_{28}$ [5], C$_{28}$ [6], C$_{20}$ [3,4,7]) have been suggested to be good candidates for high-$T_c$ superconductors. In this respect, the C$_{20}$ cluster is the most interesting, being the fullerene with the highest curvature. Experimental evidence on the synthesis of the solid form of the C$_{20}$ cluster has been recently provided as well [2]. The new phase has been identified in a diamond-like amorphous film deposited by ultraviolet laser ablation of polycrystalline diamond onto a nickel substrate and in a benzene atmosphere [2]. Electron diffraction, micro-Raman, and mass spectroscopy measurements combined with ab initio calculations suggested the presence of a crystal with face-centered-cubic symmetry and C$_{20}$ clusters as building blocks [2]. Unlike C$_{60}$, and more similarly to the proposed solid phase of C$_{28}$ [5], the C$_{20}$-based crystal is not bound by van der Waals forces, but is instead stabilized by linking the C$_{20}$ cages (sitting on the fcc lattice) with bridging carbon atoms at the tetrahedral interstitial sites. This leads to an fcc crystal with 22 atoms per unit cell (fcc-C$_{22}$) [2]. Ab initio calculations have shown that fcc-C$_{22}$ can be turned into a metallic system with a large electron-phonon coupling constant ($\lambda = 1.12$) by doping with alkali metals (Li, Na) [3,8]. Another C$_{20}$-based solid has also been predicted on the basis of ab initio calculations [4,9], but its structure turned out to be incompatible with the experimental data of reference [2]. This latter C$_{20}$-based crystal can be seen as originated from the two-dimensional polymerization of C$_{20}$ clusters still on an fcc lattice. The polymerization takes place via [2+2] cycloaddition reaction leading to a 2D polymer similar to the tetragonal phase of polymeric C$_{60}$ [10]. The 2D polymeric planes are further bonded each other via additional intercage covalent bonds leading to a body-centered-orthorombic lattice with a C$_{20}$ cage per unit cell (bco-C$_{20}$ [2,4]). Although inconsistent with the experimental data on the C$_{20}$-based solid of reference [2], this latter structure has a cohesive energy close to that of fcc-C$_{22}$ and it might thus be synthesized under different experimental conditions.

In this paper we investigate further the properties of fcc-C$_{22}$ and bco-C$_{20}$ crystals by reporting the ab initio calculations of phonon dispersion relations and IR spectrum of fcc-C$_{22}$ and of the Raman spectra of hydrogenated forms of bco-C$_{20}$ which could be formed by assembling partially hydrogenated C$_{20}$ precursors. The calculations provide a prediction on the vibrational properties of these new systems which can aid their experimental identification. The calculations are based on density functional theory in the local density approximation. Computational details are given in Section 2; vibrational properties of fcc-C$_{22}$ and hydrogenated bco-C$_{20}$ phases are reported in Sections 3 and 4, respectively. Section 5 is devoted to discussion and conclusions.

2 Computational details

The calculations are performed within density functional theory in the local density approximation as implemented
in the codes PWSCF and PHONONS [11,12]. Norm-conserving pseudopotentials and plane waves expansion of Kohn-Sham orbitals up to a kinetic cutoff of 40 Ry have been used. Phonon dispersion relations, effective charges and dielectric constant \(\varepsilon_{\infty}\) of fcc-C\(_{22}\) have been computed within density functional perturbation theory [11]. Integration over the electronic states in the Brillouin Zone (BZ) is performed on a 2x2x2 Monkhorst-Pack (MP) mesh [13]. The dynamical matrix of fcc-C\(_{22}\) has been computed on a 6x6x6 grid in \(q\)-space. A Fourier interpolation technique provided the dynamical matrix at the other points of the BZ [11]. The IR spectrum of fcc-C\(_{22}\) is obtained from the imaginary part of the dielectric function (the dielectric tensor reducing to a scalar function for a cubic system) given in terms of ab initio phonon polarization vectors \(\eta\) and effective charges \(Z\) as

\[
\varepsilon_2(\omega) = \frac{4\pi^2}{3V} \sum_{\alpha, \beta} \frac{1}{2\omega_j} \left| \sum_{\kappa, \beta} Z_{\alpha, \beta}(\kappa) \eta_{\beta, j}(\kappa) \right|^2 \delta(\omega - \omega_j),
\]

where \(V\) is the unit cell volume, \(\alpha\) and \(\beta\) are Cartesian indices, and \(\kappa\) and \(j\) run over atoms in the unit cell and phonons at the \(\Gamma\)-point, respectively. The \(\delta\)-function in (1) is replaced by a Gaussian function with variance \(\sigma = 5\) cm\(^{-1}\). The geometry of isolated hydrogenated C\(_{20}\) clusters and of hydrogenated bco-C\(_{20}\) crystals have been optimized by Car-Parrinello simulated annealing [14] as implemented in the code CPMD [15]. A time step of 0.12 fs and a fictitious electronic mass of 800 a.u. have been used. Integration of BZ has been restricted to the \(\Gamma\) point in the Car-Parrinello dynamics. Only phonons at the \(\Gamma\) point have been computed for the hydrogenated bco-C\(_{20}\) solids. In this latter case, the dynamical matrix has been obtained from finite differences of the forces for finite atomic displacements. The Raman spectra of the hydrogenated bco-C\(_{20}\) solids have been calculated from ab initio phonons and empirical polarizability coefficients within the bond polarizability model [16] (BPM). Different BPM coefficients have been used for C=C short double bonds (with length < 1.36 Å), other C-C bonds (with length 1.43–1.58 Å) and C-H bonds as given in reference [16].

3 Vibrational properties of fcc-C\(_{22}\)

The crystal structure of fcc-C\(_{22}\) (space group Fm\(_{3}\)) is shown in Figure 1. Eight atoms out of twenty of the cage (atoms \(B\) in Fig. 1) and the interstitial carbon atoms (\(A\)) are \(sp^3\) hybridized. The other twelve atoms of the cage (\(C\)) are \(sp^2\) hybridized forming C=C ethylenic bonds. There are three bond lengths in the crystal: the single \(sp^3\)-like \(B-C\) bond in the pentagonal ring (1.531 Å), the C=C ethylenic-like bond (1.346 Å) long and the single \(sp^3\)-like bond between a cage (equivalent to \(B\)) and an interstitial atom (\(A\)) (1.517 Å). The calculated phonon dispersion relations are reported in Figure 2. The uppermost flat bands correspond to the stretching modes of the ethylenic dimers of the cage. Frequency and symmetry of the \(\Gamma\)-point phonons are given in Table 1.

![Figure 1. The face-centered-cubic structure of the fcc-C\(_{22}\) crystal. The conventional unit cell with four formula units is shown. The crystal belongs to the Fm\(_{3}\) space group. The coordinates of the three independent atoms (A, B, C) in units of the lattice constant \(a = 8.61\) Å are A \(\equiv\) (0.25, 0.25, 0.25), B \(\equiv\) (0.148, −0.148, 0.148), C \(\equiv\) (0.078, −0.217, 0.0). The atoms C and C’ and the other ten of the cage equivalent by symmetry are linked by an ethylenic-like bond 1.346 Å long [2,3].]

![Figure 2. Phonon dispersion relations of fcc-C\(_{22}\) along the high symmetry lines of the Brillouin Zone.](image-url)

The effective charge tensor is finite for all atoms with maximum values in the off-diagonal components of atoms C (Fig. 1). This implies that the effective charge is mainly due to a charge transfer accompanying the bond modulation. The effective charge tensor for atoms A, B