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THEORETICAL IDENTIFICATION OF C_{20} FULLERENE AND PREDICTION OF ELECTRONIC PROPERTIES OF ITS SOLID PHASES

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We study gas and solid phases of C_{20} fullerene. By using hybrid density functional theory, we calculate the anion photoelectron spectra of C_{20} isomers and assign one of the experimental spectra to the fullerene structure, so we confirm that the C_{20} fullerene is really synthesized. We next perform local density approximation calculation on polymerized phases of C_{20} fullerene. The most stable system is found to have the orthorhombic structure. Based on calculated electron density of the states, we conclude that the hole-injected sample is a candidate for superconductor.

Keywords: photoelectron spectrum; smallest fullerene; superconductivity

INTRODUCTION

The C_{20} cage cluster, which consists solely of pentagons, is the smallest fullerene and much attention has been paid to it. However, a question remains as to whether this cluster really exists in nature. That is, unlike C_{60} fullerene, the smallest fullerene is not spontaneously formed during carbon condensation or cluster annealing [1]. In addition to the fullerene, the ring and bowl isomers were also studied and it was shown that the relative stability of the three clusters strongly depends on the many-body effect; thus, the most stable isomer has not been theoretically determined [2]. The above question as to the existence of the smallest fullerene was answered by

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Prinzbach *et al.*, who reported that it could be synthesized from the dodecahedrane, $C_{20}H_{20}$, in the gas phase [3]. This cluster, as well as the ring and bowl clusters, was identified by means of anion photoelectron spectroscopy. Although the spectroscopy implied the success of synthesis of the smallest fullerene, clear identification of the observed spectra was not done.

In this paper, we first theoretically analyze observed photoelectron spectra by using a combination method of the hybrid density functional theory (DFT) and time-dependent technique. As a result, we clearly assign one of the measured spectra to the smallest fullerene; therefore, we confirm the experimental claim that the smallest fullerene can be chemically synthesized. Then, we study polymerized phases of the smallest fullerene by using the local density approximation (LDA) within the DFT. Analyzing calculated electron density of states (DOS), we discuss the possibility of the superconductivity of the polymerized phases.

METHOD

To calculate the anion photoelectron spectrum, we use a combination method of the time-dependent technique [4] and the hybrid DFT proposed by Becke [5]. The exchange correlation energy functional of the hybrid DFT is a mixture of those of the Hartree-Fock method, LDA [6], and generalized gradient approximation [7]. We used the standard polarized triple-zeta basis set, conventionally labeled as 6-311G(d) [8], which gives converged results for vibronic coupling of the C_{10} ring cluster [9].

In calculating band structures of polymerized C_{20}, we use the LDA. Soft pseudopotentials are generated following Troullier and Martin [10]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 40 Ry which gives enough convergence of total energy to discuss the relative stability of various carbon phases. We adopt the conjugate-gradient minimization scheme both for the self-consistent electronic-structure calculation and for the geometric optimization. Structural optimization is carried out not only on the internal atomic coordinates of C_{20} but also on each lattice parameter.

RESULTS

We study the anion photoelectron spectrum of the fullerene structure. Two neutral clusters having C_{2h} and C_i symmetries are found to have close energies. Since these two geometries give similar spectra, we here report results of the C_i symmetry only. The case of C_{2h} symmetry was previously studied [9]. The negatively charged cluster is found to have C_i symmetry. To discuss the side bands, we introduce Franck-Condon coupling (Huang-

Rhys) parameter, S_j which is defined in Ref. 4 (This parameter is proportional to the square of the displacement of the j-th mode). As this parameter increases, the side band intensity of the mode becomes large: thus, the Franck-Condon progression is enhanced. One mode (643 cm^{-1}) in the neutral charge state, which has the bond bending character (Fig. 1), has the largest coupling parameter (1.9). This large value is due to the fact that some bond angles of the two charge states are quite different. On the other hand, the bond-stretching modes having high frequencies (1100–1400 cm^{-1}) do not have large values of S_j, since the bond lengths under the two charge states are similar. Due to the large S_j of the 643 cm^{-1} mode, the main peaks in the calculated spectrum have a spacing of about 650 cm^{-1} (Fig. 1). Since there are several modes having substantial displacement, as well as the bending mode, several side peaks, as well as the main peaks, appear. As Figure 1 shows, we obtain good agreement between theory and experiment [3].

We here study polymers synthesized from the smallest fullerene. Unlike C_{60}, C_{20} is very reactive, so the formation of the molecular crystal is

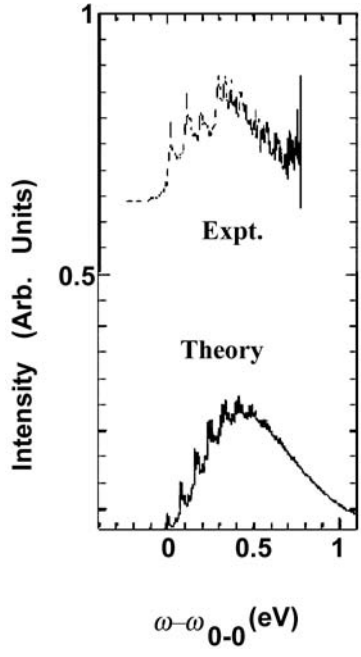

FIGURE 1 Photoelectron spectra of C_{20} anion. ω_{0-0} is the energy difference between the two charge states.

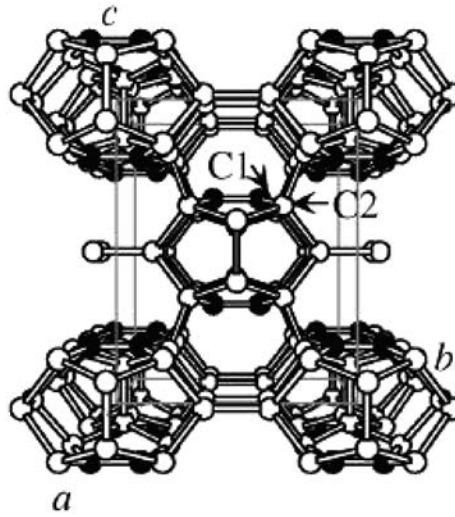

FIGURE 2 Orthorhombic structure of C_{20} polymer. C1 and C2 denote three-folded and four-folded atoms, respectively.

unlikely and instead polymers are expected to be easily formed. Actually, very recently oligomers of C_{20} fullerenes are experimentally observed [11].

We study stability of 1D and 3D systems and find that the most stable system has the orthorhombic structure (Fig. 2). Previously, we found 1D polymers and 3D simple cubic one [12]. These polymers are found to have higher energy than the orthorhombic one [13]. In the orthorhombic structure, the threefold-atoms indicated by black ball in Figure 2 are relaxed inward: As a result, the dangling bonds in the isolated molecules annihilate and the atoms form strong π bonds. Due to this large lattice relaxation, this system has the large indirect band gap of 1.40 eV. We find some DOS peaks below the Fermi energy, whose heights are 1.5–4.5 states/eV/spin/molecule. Therefore, hole injection may cause superconductivity. However, the DOS peaks are lower than that of alkali doped C_{60} [14].

CONCLUSION

By using the hybrid-DFT, we calculated photoelectron spectrum of the smallest fullerene and find that it resembles one of the measured spectra. Therefore, we conclude that the smallest fullerene is really synthesized. Since C_{20} is very reactive, they are easily polymerized and their cohesive

energies are found to be very large. The most stable structure is found to be orthorhombic and is a candidate for a superconductor.

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