Theoretical Identification of the Smallest Fullerene, C_{20}

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By using first-principles calculations, we calculate the vibronic fine structure in photoelectron spectra of $C_{20}{}^{-}$ clusters. Based on our results, we assign one of the recently observed spectra [H. Prinzbach *et al.,* Nature (London) **407**, 60 (2000)] to the fullerene structure and, therefore, confirm the experimental claim that the smallest fullerene is really synthesized.

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Since the fullerene structure of C_{60} was postulated, much attention has been directed to its unique electron properties such as superconductivity and magnetism [1]. Among the fullerenes, C_{20}, which consists solely of pentagons, is the smallest. This fullerene is expected to have larger vibronic coupling than C_{60}; therefore, the solid form of this fullerene is a good candidate for a superconductor [2]. However, this smallest fullerene is not formed spontaneously by carbon condensation or cluster annealing processes [3]. Many theoretical studies have investigated its stability compared with those of isomers (for example, a ring and a bowl) but even the most stable atomic structure is still unknown because the electron correlation effect has a crucial effect on the energetics (for example, see Refs. [4–6]). Therefore, a question remains as to whether this smallest fullerene really exists in nature.

Very recently, it was reported that the C_{20} fullerene could be chemically synthesized, thus the gateway to production of new carbon materials has been opened [7]. The characterization of the fullerene in the above experiment was based on anion photoelectron spectroscopy but assignment of photoelectron spectra is sometimes controversial; indeed, different identifications of carbon clusters were done by two groups who observed spectra that resembled each other [8,9]. The observed spectrum assigned to the $C_{20}{}^{-}$ fullerene is characterized by the peak spacing, 730 cm^{-1}, which is much smaller than that of the ring (2260 cm^{-1}). The origin of this small spacing should be clarified so that the smallest fullerene can be clearly identified, but it was not clearly revealed by experimental study [7]. The spectrum shape is determined by the Franck-Condon principle; thus, accurate information on the geometries and vibrations of the initial and final charge states, as well as electronic structure, is necessary in order to analyze it. Therefore, a reliable calculation should be performed to obtain the information.

In a previous paper, we showed that a first-principles approach combining the hybrid density functional theory (DFT) and the time-dependent technique is useful to clearly identify photoelectron spectra [10]. In this paper, we apply the method to the calculation of $C_{20}{}^{-}$ spectra. The calculation on the fullerene structure well reproduces one of the $C_{20}{}^{-}$ spectra, and, thus, confirms that the smallest fullerene is really synthesized. The peak spacing in the observed spectrum was found to be due to a bond-bending mode.

The vibrational structure of the photoelectron spectra for negative charge clusters is given within the Condon and harmonic approximations as [10]

$$F(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty dt \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_M=0}^{\infty}\left|\int d\mathbf{Q}\,\phi_{\mathbf{0}}^{-}\phi_{\mathbf{n}}^{0}\right|^2 \times \exp\left\{it\left(\sum_{j=1}^{M} n_j\omega_j + \omega_{\mathbf{0}-\mathbf{0}} + i\Gamma - \omega\right)\right\}, \quad (1)$$

where $\phi_{\mathbf{n}}^{-}$ ($\phi_{\mathbf{n}}^{0}$) is the $\mathbf{n}[= (n_{\mathbf{1}}, n_2, \ldots, n_{\mathbf{M}})]$th vibrational wave function of the negative (neutral) charge state and the **0**th (the lowest) vibrational state is assumed for the negative charge state; M is the number of the modes and ω_j is the vibrational frequency of the jth mode in the neutral charge state; Γ and $\omega_{\mathbf{0}-\mathbf{0}}$, respectively, are the phenomenological linewidth and the frequency of the **0-0** transition between the two charge states. Since the observed spectra have the same spacing between the main peaks, the anharmonic effect is expected to be negligible. The value of Γ is an adjustable parameter in this study and is taken to be comparable with the experimental spectra. The integrand in Eq. (1) is exactly given by an analytic expression that takes into account the three effects: the displacement, frequency change, and mode mixing (Duchinsky rotation) of the vibrations between the initial and final charge states [10,11].

In contrast to the generalized harmonic oscillator model (GHOM) that takes into account the above effects, the displaced harmonic oscillator model (DHOM), which considers only the displacement, was conventionally used [12]. According to the DHOM, the Franck-Condon factor is given by a simple expression,

$$\left|\int d\mathbf{Q}\,\phi_{\mathbf{0}}^{-}\phi_{\mathbf{n}}^{0}\right|^2 = \frac{S_1^{n_1}}{n_1!}\frac{S_2^{n_2}}{n_2!}\cdots\frac{S_M^{n_M}}{n_M!} \times \exp(-S_1 - S_2 \cdots - S_M), \quad (2)$$

where S_j is the Franck-Condon coupling parameter defined as $\frac{1}{2}\delta_j^2$, and δ_j is given by $\delta_j = \sqrt{\omega_j \mathbf{D}_j \cdot \mathbf{D}_j/\hbar}$, where $\mathbf{D}_j$ is the projection of the displacement between the geometries of the two charge states into the jth normal mode in the neutral charge state. Therefore, according to the DHOM, the mode with a substantial value of S_j appears in the spectra. Although this DHOM is qualitatively reliable in many cases, we find that there is a substantial difference between the spectrum calculated from the DHOM and that from the GHOM, as shown later.

To evaluate Eq. (1), we calculate the optimized geometries, vibrational modes, and frequencies from first-principles electronic-structure calculations. We adopt the hybrid DFT of Becke's type [13]: The electron many-body (exchange-correlation) energy functional of this theory is the mixture of the functionals of the Hartree-Fock (HF) method and the conventional DFT (the local density approximation [14] and generalized gradient approximation [15,16]). It was established that this hybrid method is in general more accurate than both the HF and the conventional DFT methods [17,18]. In the case of the negative charge state with the doublet-spin level, the spin polarization is considered by using an independent single-particle wave function for the different spin level. We use the standard polarized *triple zeta* (SPTZ) basis set conventionally labeled by 6-311(d) [17]. To evaluate the validity of this basis set, we calculate the Franck-Condon parameter $W = \sum_j S_j$, for monocyclic C_{10}^-. The difference between W calculated from the SPTZ and that from the correlation consistent polarized *quartet zeta* basis set [17], which is considered to be accurate, is small (2%), suggesting that the SPTZ gives the converged W value. Under the optimized geometries, the forces acting on the atoms are less than 0.000 45 Hr/a.u. and the accuracy of atomic positions is estimated to be less than 0.002 Å.

We first determine the geometry of the C_{20} fullerene in the neutral charge state (Table I and Fig. 1). Although it is accepted that the symmetry is lowered from I_h because of the Jahn-Teller effect, previous HF and conventional DFT calculations showed discrepancies in the symmetry of the optimized geometry (D_{5d}, D_{3d}, C_i, and C_2) [6]. On the basis of the hybrid-DFT with the 6-311$G(d)$ basis set, it is concluded that the symmetry of the optimized geometry is C_{2h}. The bond angles are smaller than that of the ideal sp^2 hybridization (120°), so each p_π orbital in the radial direction is hybridized with an s component (Fig. 1); in other words, the hybridization in the σ bonds is characterized not by sp^2 but by $sp^{2+\Delta}$ [19,20]. As the calculated Mulliken charge in Fig. 1 indicates, the electron populations for atoms number 2, 9, 10, 12, 19, and 20 (referring to the numbering scheme of Table I), which have relatively large bond angles, are small. This result is due to the fact that the hybridization of s and p_π orbitals is suppressed as the bond angle increases; thus the hybridized orbital energy increases [19]. The calculated bond lengths range from 1.401 to 1.520 Å. The largest and smallest bond lengths, respectively, are comparable with measured ones of diamond (1.53 Å) and graphite (1.42 Å). The highest frequency mode has the character of bond stretching and the frequency (1432 cm^{-1}) is lower than the optical phonon frequency at the Γ point of graphite (1580 cm^{-1}) and is higher than that of diamond (1331 cm^{-1}).

Next, we examine the geometry of the negatively charged C_{20} fullerene (Table I) and find that the symmetry is C_i, which is lower than that of the neutral C_{20} fullerene. The calculated bond lengths range from 1.399 to 1.520 Å and the difference between each bond length under the two charge states is small ($\leq$0.05 Å). On the other hand, the difference between the bond angles under the two charge states is large. In particular, the bond angle of the 10th atom [and its equivalent atom, 20th one (Fig. 2)] in the negative charge state is found to be much smaller than that of the neutral charge state [Fig. 1(a)]. This large decrease of the bond angle under the negative charge state is due to increase of the electron density of the s-p_π hybridized orbital as indicated by the Mulliken charge [Fig. 1(b)]. We find that the highest occupied molecular orbital (HOMO) of the negative charge state has a large amplitude at the 10th atomic site (Fig. 2); thus it causes the increase of the electron density at that site.

In the following, we study the photoelectron spectrum of the anion. The values of S_j are tabulated in Table II. One mode (643 cm^{-1}) in the neutral charge state, which has the bond-bending character (Fig. 2), has the largest parameter (2.7). This mode has large amplitudes at the 10th and 20th

TABLE I. Atomic coordinates in Å of C_{20} and C_{20}^-. The coordinate of ($N + 10$)th atom is given by the inversion of that of the Nth atom. In C_{20} having the C_{2h} symmetry, the mirror symmetry plane is the y-z one and the rotational axis of C_2 is x.

		C_{20}			C_{20}^-	
Atom number	x	y	z	x	y	z
1	−0.760	1.936	−0.040	−0.752	1.922	−0.001
2	−1.172	1.153	1.103	−1.163	1.132	1.177
3	−1.957	0.000	0.701	−1.971	0.005	0.800
4	−1.957	0.000	−0.701	−1.901	0.024	−0.635
5	−1.193	1.221	−1.167	−1.211	1.232	−1.128
6	0.760	1.936	−0.040	0.747	1.959	−0.040
7	0.000	0.701	1.811	0.025	0.664	1.837
8	−1.193	−1.221	1.167	−1.125	−1.196	1.190
9	−1.172	−1.153	−1.103	−1.166	−1.125	−1.089
10	0.000	0.742	−1.832	−0.028	0.798	−1.940

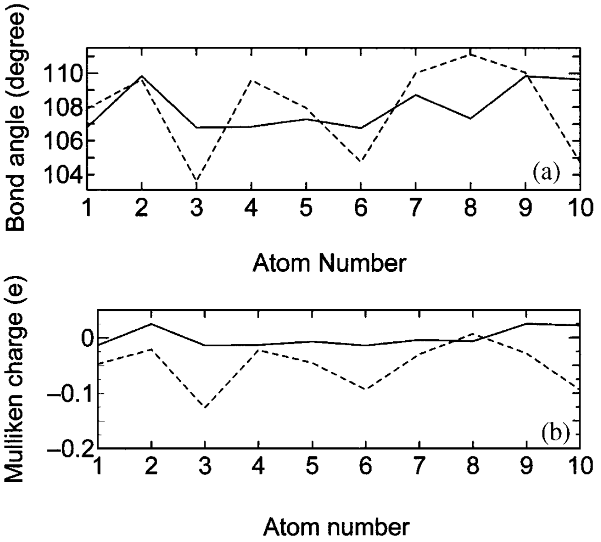

FIG. 1. Bond angles (a) and Mulliken populations (b) in the optimized geometries of neutral (solid line) and negatively charged (dotted line) C_{20} fullerenes. The values of bond angles are averaged over the three dihedral angles at each site. The Mulliken population represents the sum of the nuclear and electron charges in each atomic region. The atom numbers on the horizontal axes are consistent with those of Fig. 2.

atoms, where the bond angle variation between the two charge states is very large. This large variation explains why this mode has the large Franck-Condon coupling parameters S_j. 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. We then calculate the spectrum by assuming $\Gamma = 50\ \text{cm}^{-1}$, which well reproduces the experimental spectrum. Because of 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. 3). Since there are several modes having substantial displacement, as well as the bending mode, several side peaks, as well as the main peaks, appear. The spectra determined from the GHOM and from DHOM are substantially different, indicating that the DHOM is less accurate (Fig. 3). As shown in Table II, under the two charge states, the distributions of the coupling parameters (S_j and S'_j) against frequency are quite different, incidating that the Duchinsky effect is important.

The experimental spectrum shows the Franck-Condon progression with a spacing of $730 \pm 70\ \text{cm}^{-1}$ (Fig. 3). Comparing the measured spectrum with the calculated one, we conclude that this spacing is due to the bond-bending mode, whose calculated frequency is 643 cm^{-1}, but there remains a very small difference in frequency between theory and experiment. The experimental spectrum shows that the peaks due to this mode are split and this splitting is well reproduced by our calculation.

Since the calculated first peak (indicated by 0 in Fig. 3), which is caused by the 0-0 transition between the two charge states, has a small intensity, we speculate that the experimentally detected first peak (indicated by 1) corresponds to the second peak (also indicated by 1) in the theoretical spectrum. This measured first peak corresponds to the binding energy of 2.25 eV; therefore the 0-0 transition energy is estimated to be 2.16 eV, which is obtained by subtracting the vibrational energy (730 cm^{-1}) from 2.25 eV. Theoretically, the 0-0 transition energy is evaluated as $E_{0\text{-}0} = \hbar[\delta\omega + \frac{1}{2}\sum_{j=1}^{M}(\omega_j - \omega'_j)]$, where $\hbar\delta\omega$ is the difference between the electronic energies under the two charge states, and ω'_j is the vibrational frequency of the negative charge state. From our hybrid DFT calculation, we obtain the value, $E_{0\text{-}0} = 2.21$ eV, which is close to the experimental value (2.16 eV).

The spectrum corresponding to the ring cluster has been experimentally well identified [7], so we compare it with the spectrum of the fullerene. The results of the present hybrid DFT calculation using the SPTZ basis set is similar to those of the past calculation using the correlation consistent polarized *double zeta* basis set [10], but we find that there is some quantitative difference between the two calculations. The geometries of the neutral and negatively charged ring isomers have alternations of bond length and bond angle (the lengths of the neighboring bonds are different from each other and the bond angles of the

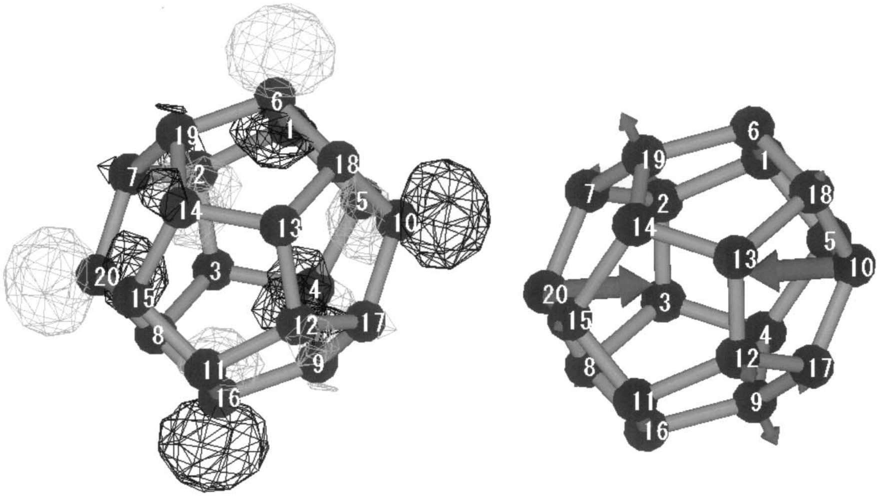

FIG. 2. The HOMO of the negatively charged C_{20} fullerene (left-hand side) and the vibrational mode with a frequency of 643 cm^{-1} in the neutral charge state (right-hand side). On the left-hand side, the dark and light wires indicate the amplitude values, 0.05 $\text{a.u.}^{-3/2}$ and -0.05 $\text{a.u.}^{-3/2}$, respectively.

TABLE II. Vibrational frequencies and Franck-Condon coupling of the C_{20} fullerene; ω_j (ω'_j) and δ_j (δ'_j), respectively, are the frequency and displacement of the jth mode in the neutral (negative) charge state. The frequencies ω_j, ω'_j, in cm^{-1}, are presented along with the character of the vibrational modes.

ω_j	$S_j(=\frac{1}{2}\delta_j^2)$	ω'_j	$S'_j(=\frac{1}{2}\delta_j'^2)$
146 (b_g)	0.2	178	0.2
352 (b_g)	0.8	189	0.1
534 (a_g)	0.8	296	0.5
639 (b_g)	0.1	416	0.1
643 (a_g)	2.7	419	1.3
772 (a_g)	0.8	503	0.2
1122 (a_g)	0.1	592	1.0
1276 (a_g)	0.2	665	0.7
1405 (a_g)	0.2	820	0.2
		973	0.1
		1309	0.1

neighboring atoms are also different), and, therefore, the symmetries are C_{10h}. The vibrational mode whose frequency is 2121 cm^{-1} has a substantial value of S_j (0.43). The calculated spectrum thus shows that the Franck-Condon progression has a spacing of 2121 cm^{-1} (Fig. 3), which is close to the measured one (2260 ± 100 cm^{-1}). Similar peak spacings were detected in previous experimental studies [8,9]. The theoretical value of $E_{0\text{-}0}$ is 2.86 eV, which is only slightly higher than the measured one (2.44 eV) [7]. Our calculation shows that $E_{0\text{-}0}$ of the ring is higher than that of the fullerene (2.21 eV), and it is consistent with experimental results.

In conclusion, we calculated photoelectron spectra of C_{20}^- by using the hybrid DFT. Since our calculations and experiments agree well, we can clearly assign the spectra to atomic structures. In particular, the observed peak spacings and $E_{0\text{-}0}$ were reproduced by theory. We could thus assign one of the observed spectra to the fullerene. Previous theories have not been sufficiently validated since they gave contradicting results on the energetics of C_{20} isomers and on the symmetry of the fullerene structure, and theoretical and experimental results on the fullerene were not compared. This study theoretically explains the experimental data on the fullerene, and confirms the validity of the hybrid DFT for photoelectron spectra.

Since the existence of the smallest fullerene, C_{20}, was confirmed by this study, understanding of physical properties of carbon solids synthesized from this fullerene is very important. We theoretically found that there are several crystal forms produced by condensation of the smallest fullerene, and some are hopeful candidates for superconductors [21].

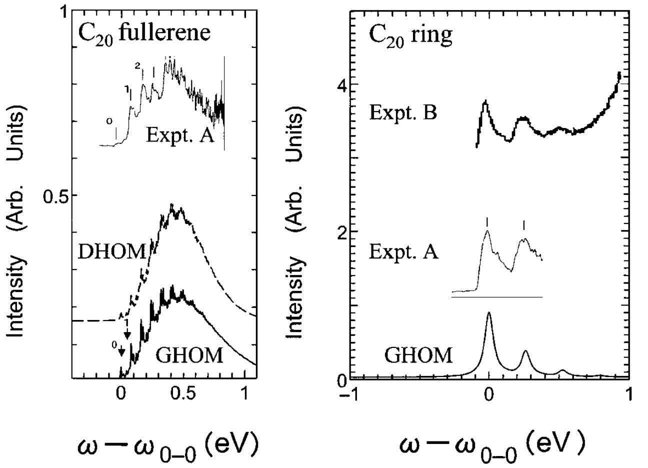

FIG. 3. Photoelectron spectra of the fullerene (left-hand side) and a monocyclic ring (right-hand side). Theoretical calculations are based on the GHOM (solid line) and DHOM (dashed line). Γ is assumed to be 50 (300) cm^{-1} on the left-hand (right-hand) side. Experimental data, A and B, are deduced from Refs. [7] and [8], respectively.

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