

First-principles studies on pure and doped C₃₂ clusters

Q Sun, Q Wang, J Z Yu, K Ohno and Y Kawazoe

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Received 12 August 2000, in final form 6 November 2000

Abstract

On the basis of first-principles calculations, pure and doped C₃₂ clusters are studied. Among the nine structural isomers, the fullerene structure with D₃ symmetry is found to be the most stable. Due to the small size of the C₃₂ cage, Li and Na atoms can be stably encapsulated, while K and Be atoms are not. On encapsulation, the bond length of the H₂ molecule is reduced while the vibration frequency is increased. Substitutional doping is more favourable than endohedral doping for Si atoms. Because of the sp²-bonding features of C atoms, the Si atom is also threefold coordinated in substitutional doping; however, the existence of one dangling bond in the Si atom makes this doped heterofullerene reactive at the Si site, and H termination can produce substantial energy gain.

1. Introduction

It is well known that carbon atoms have very flexible bonding features: sp³ hybrid orbitals form strong σ -bonding, while sp² and sp¹ hybridizations form σ - and π -bondings. Therefore, carbon systems can exhibit very rich structures: graphite, diamond, fullerene, carbon nanotubes, amorphous carbon, porous carbon, graphite intercalation compounds (GIC), and so on. These carbon-based materials display various unique properties, from insulating to superconducting. Since the discovery [1] and large-scale synthesis [2] of C₆₀, numerous studies have been devoted to fullerene systems in the last two decades. In recent years, with the advent of flexible and precise experimental techniques, well controlled small carbon clusters became experimentally accessible, and attract much attention: small clusters C_n ($n < 20$) with ring structures [3–6], C₂₀ [7, 8], C₂₈ [9, 10], C₃₂ [11], and C₃₆ [12–15]. Detailed studies on these small carbon clusters are very important not only as regards understanding the formation mechanism of fullerene [16, 17], but also in many practical fields such as astrophysics, stellar chemistry, and combustion processes [18–21]. Among the small carbon clusters, C₃₂ is particularly interesting, since it is very stable with a large gap of 1.3 eV, as found recently [11]. Moreover, the C₃₂ cluster is closely related to C₆₀ by a duality relationship, where the atoms in one structure correspond to ring centres of the other. In spite of the fact that fullerene itself and its derivatives have become a fashionable topic in both experimental and theoretical studies, compared with the other fullerene clusters, study on C₃₂ is still incomplete, e.g., it is well known that many fullerene cages can trap atoms or molecules—but how about the C₃₂ cluster?

To the best of our knowledge, no study on this question has yet been reported, which has motivated us to perform first-principles calculations.

2. Computational method

Ab initio methods based on density functional theory (DFT) are well established tools for studying structural properties of materials. Among them, the plane-wave basis and pseudopotential method combined with DFT has provided a simple framework, in which the Hellmann–Feynman forces are used to perform geometry optimization. In the present calculations, we have used a powerful *ab initio* ultrasoft pseudopotential scheme with a plane-wave basis (the *Vienna Ab Initio Simulation Program* (VASP)) [22, 23]. The method is based on the finite-temperature local density functional theory developed by Mermin [24], where the variational quantity is the electronic free energy. Finite temperature leads to the broadening of the one-electron levels and is helpful for improving the convergence of Brillouin-zone integrations. The electron–ion interaction is described by a fully non-local optimized ultrasoft pseudopotential [25, 26]. The minimization of the free energy over the degrees of freedom of electron densities and atomic positions is performed using the conjugate-gradient iterative minimization technique [27]. The edge length chosen for the cubic supercell is 18 Å. In such a big supercell, just the Γ point is sufficient to represent the Brillouin zone. The generalized-gradient approximation (GGA) is adopted for the exchange–correlation potential [28]. The structure optimization is not restricted to certain symmetries, and the optimization is terminated when all the forces acting on the atoms are less than 0.01 eV Å⁻¹.

3. Results and discussion

As a test, the calculation was performed for the C₂ molecule; the equilibrium bond length obtained is 1.25 Å, in agreement with other calculations [29].

3.1. Structures of C₃₂

Since there are many structural isomers for 32-atom carbon clusters, it is impossible to consider all of them. We choose two kinds of structure: one is the so-called fullerene structure [30], where the cage contains only pentagonal and hexagonal rings and the atoms are threefold coordinated; the other one is a non-fullerene structure. Figure 1 shows the initial structures for the nine isomers considered; the first six isomers have fullerene structures, and, according to Euler's rule, there are 48 edges and 18 faces composed of twelve pentagons and six hexagons; the last three isomers are non-fullerene structures. Isomer 7 consists of twelve hexagons and six squares; the six squares are arranged as three pairs perpendicular to three orthogonal axes. Isomer 8 is formed by six squares and eight centred hexagons; this is the most stable structure for the spherical B₃₂ cluster [31]. Isomer 9 is composed of a central belt of two parallel ten-atom rings capped on each side by a pentagonal pyramid; the two halves of the cluster are staggered with respect to each other. Table 1 lists the total binding energies and gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). We find that isomer 6 in the fullerene structure is the most stable with the largest HOMO–LUMO gap (1.29 eV), which is quite close to the experimental value (1.30 eV) [11], and the average binding energy per atom is 8.39 eV, smaller than the corresponding value of 8.72 eV for C₆₀ [32]. In terms of the spiral representation [30], the structure for isomer 6 is in the sequence [5556565655656555], where there are two groups of three pentagons abutted, at variance with the isolated-pentagon rule proposed by Schmalz *et al* [33]. In the first seven

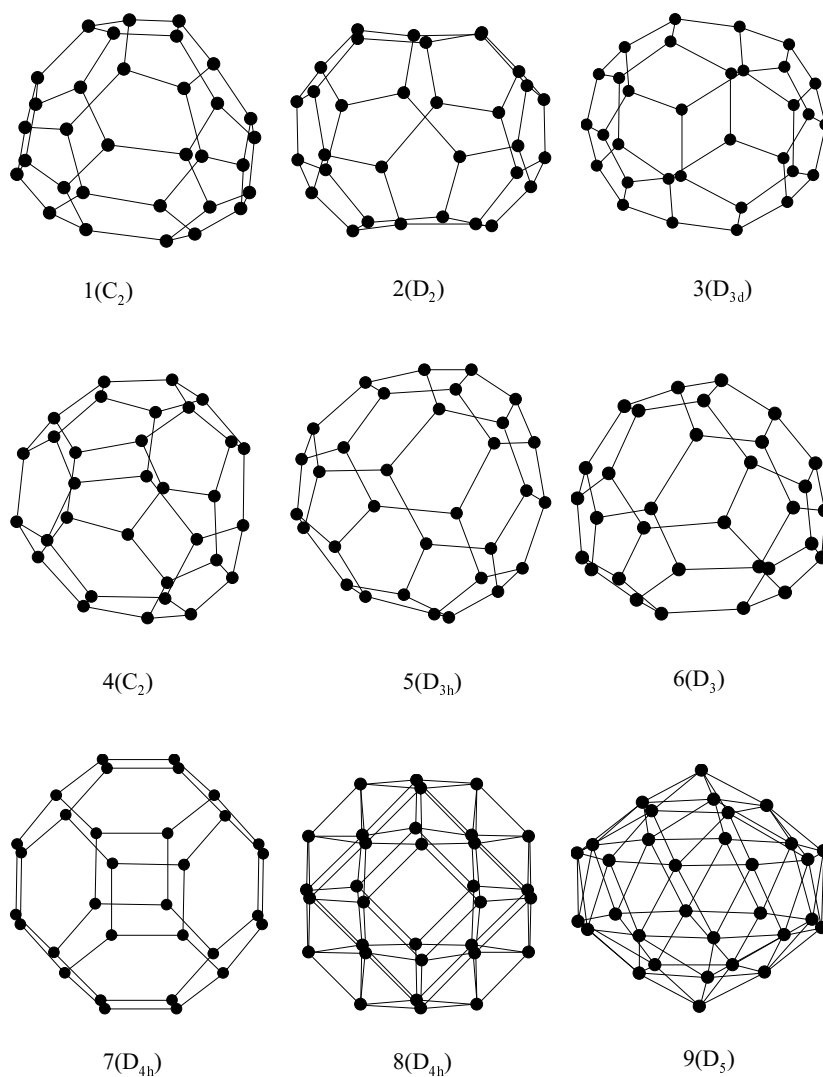


Figure 1. Nine structural isomers calculated for the C_{32} cluster.

isomers, every C atom has three coordinations conforming to the usual valence requirements of sp^2 bonding, so the total binding energies are much lower than those of the last two isomers. In particular, isomer 6 is more stable than isomer 8, indicating that carbon atoms are quite different from boron atoms as regards bonding features. On the basis of the most stable D_3 structure of the C_{32} cluster, the doping properties are discussed below.

3.2. Atom@ C_{32}

The idea [1] that fullerene might be able to encapsulate atoms and molecules has been verified by the successful synthesis of a range of endohedral fullerenes, in which metallic or non-metallic species are trapped inside the carbon cage [34], displaying very interesting physical and chemical properties such as pseudoatom behaviour, magnetism, and superconductivity.

Table 1. Total binding energies E (eV) and the HOMO–LUMO gaps Δ (eV) for nine isomers.

Isomer	E	Δ
1	–266.244	0.426
2	–265.542	0.272
3	–265.673	0.572
4	–267.413	0.894
5	–265.077	1.280
6	–268.497	1.291
7	–262.280	0.680
8	–188.453	0.700
9	–188.452	0.100

Extensive studies have been devoted to endohedral fullerene C_n with $n = 28, 36, 60, 70, 74, 82,$ and 84 [35–39]. How about the situation in C_{32} clusters? For the most stable D_3 structure, table 2 lists the results for doping with Li, Na, K, and Be, where δE is the energy gain upon doping, the energy reference is taken to be zero for the pure C_{32} cluster, and r is the average length of the bond between C atoms. We see that due to the small size of the cage only Li and Na atoms are stably encapsulated. It has been found recently that Na is the largest alkali atom to be intercalated into C_{36} crystal without causing severe structural distortion [40]. In the C_{32} cluster, the doped atoms are located nearly at the centre of the cage. The changes in the mean C–C bond length indicate that the cage is slightly enlarged by encapsulation.

Table 2. Energy gains δE (eV) and mean C–C bond lengths r (Å) for doped clusters.

Cluster	δE	r
C_{32}	0.0	1.4555
$Li@C_{32}$	–2.3012	1.4596
$Na@C_{32}$	–1.1660	1.4627
$K@C_{32}$	+0.5933	1.4689
$Be@C_{32}$	+0.2982	1.4599

3.3. $H_2@C_{32}$

As a simple case of molecule encapsulation, we study $H_2@C_{32}$. In the C_{32} cluster, as stated above, there are two groups of three pentagons abutting, where the two special common vertices are labelled as P1 and P2, shown in figure 2. For the most stable D_3 structure, we consider two configurations: the H_2 structure is orientated perpendicular and parallel to the axis connecting P1 and P2, labelled as configurations I and II; their total binding energies are –274.232 eV and –274.248 eV, respectively. Configuration II is more stable. For the equilibrium bond length of the free H_2 molecule, we get the value of 0.765 Å, in agreement with the experimental result of 0.75 Å [41]. However, after encapsulation, the bond length is reduced to 0.74 Å, similar to what has been found for $H_2@C_{60}$ [37]. The formation energy is defined as the difference between the total binding energies: $\Delta E = E(H_2@C_{32}) - E(C_{32}) - E(H_2)$; for $H_2@C_{60}$, $\Delta E = 0.05$ eV [37]; but due to the smaller size of the C_{32} cage, more energy is needed, and for $H_2@C_{32}$, $\Delta E = 1.00$ eV.

In order to calculate the vibration frequency of H_2 in a C_{32} cage, the host atoms were kept fixed at their equilibrium positions; the light mass of the hydrogen atom justifies this approach. Anharmonic effects are important in H_2 : for the free molecule, the harmonic frequency is

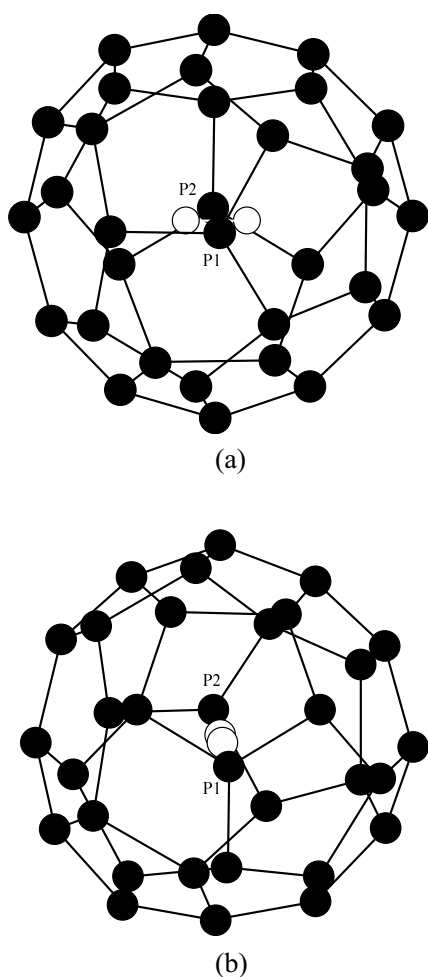


Figure 2. Two configurations for the H₂@C₃₂ cluster: perpendicular (a) and parallel (b) to the axis connecting P1 and P2. The empty circles stand for the H atoms.

4400 cm⁻¹ [41], while the anharmonic effects lower this value by 239 cm⁻¹ to 4161 cm⁻¹ [42]. In calculating the vibration frequency of H₂, we consider the anharmonic effect up to the fourth order of H–H-bond displacement. Around the equilibrium bond length r_0 , the potential energy can be expressed as [43]

$$E(r) = E(r_0) + \frac{M\omega_h^2}{2}(r - r_0)^2 + \alpha(r - r_0)^3 + \beta(r - r_0)^4. \quad (1)$$

From the harmonic frequency ω_h , the vibration frequency ω can be obtained as follows:

$$\omega = \omega_h + \frac{3h}{(2\pi)^2 c M} \left[-\frac{5}{2} \left(\frac{\alpha}{M\omega_h^2} \right)^2 + \frac{\beta}{M\omega_h^2} \right] \quad (2)$$

where c and M denote the speed of light and the reduced mass. By fitting $E(r)$ for several points, we obtain $\omega_h = 4411$ cm⁻¹ and 4676 cm⁻¹, $\omega = 4201$ cm⁻¹ and 4452 cm⁻¹ for free and encapsulated H₂, respectively. Compared with the free H₂ molecule, upon encapsulation in C₃₂, the bond length is reduced, while the vibrational frequency is increased, similar to the situation for H₂@C₆₀ [37].

3.4. The nature of the bonding in SiC₃₁

Substitutionally doped heterofullerenes with silicon atoms are also of great interest. Although Si belongs to the same group as C, its chemical behaviour is quite different. The chemistry of C is characterized by very flexible bonding features; it is able to form single, double, and triple bonds with itself and with other atoms. However, the larger number of core electrons in Si makes it much more difficult for two Si atoms to form double and triple bonds. Consequently, Si prefers to form multidirectional single bonds (sp³). This feature is quite obvious for pure Si clusters, which are known to adopt compact three-dimensional structures. For this reason, the stability and bonding features of substitutionally doped heterofullerenes are quite active subjects. Recently, substitutionally doped heterofullerene C_{2n-q}Si_q clusters were successfully synthesized using laser vaporization for 2n = 32–100 with q < 4 [44] and 2n = 32–80 with q < 3 [45].

For the simplest case, based on the most stable structure of D₃ for the C₃₂ cluster, we study the SiC₃₁ cluster with two configurations: in the first one, the Si atom occupies the common vertex of three pentagons abutting; and in the second one, the Si atom is at the common vertex of the pentagon and hexagon; these are labelled as configurations A and B. After full optimization, the Si atom still is coordinated with three carbon atoms. The main reason is that in a fullerene cluster, C atoms prefer to have sp² bonding, and if a Si atom is bonded with four C atoms, sp²-bonding features will be destroyed for some C atoms, which is energetically unfavourable. The total binding energies for the two configurations are –263.699 eV and –263.735 eV, respectively. Configuration B is more stable.

Although the Si atom in the C-atom cage is threefold coordinated, essentially the Si atom prefers sp³ bonding. Therefore, there is still one dangling bond at the Si site, which can be terminated by hydrogen. Upon H termination, the total binding energy increases by 4.496 and 4.228 eV for configurations A and B, respectively, confirming that even in the sp² environment of the carbon cage, the Si atom still potentially prefers sp³ bonding. In fact, in nanostructured SiC films grown by soft landing of Si–C clusters, x-ray photoelectron spectroscopy (XPS) reveals evidence for a mixing of sp² and sp³ hybridizations in carbon-rich local phases [46]. Therefore, doped heterofullerenes with silicon atoms are expected to be very reactive at Si sites, which offers a path towards the polymerization of fullerene.

Table 3 lists the total binding energies, bond lengths, and energy gains for H termination. In SiC₃₁, the Si–C bond length is about 1.83 Å, larger than in the SiC molecule (1.72 Å) [47]. Upon H termination, the Si–C bond length is enlarged further, but the mean C–C bond length is not changed. The Si–H bond length is about 1.48 Å. Figure 3 shows a schematic representation of the structures of SiC₃₁ (a) and HSiC₃₁ (b) clusters.

Table 3. Total binding energies *E* (eV), energies δ gained upon H termination of the dangling bond in Si, and mean bond lengths *r*(C–C), *r*(Si–C), and *r*(Si–H) (Å).

Cluster	Configuration	<i>E</i>	δ	<i>r</i> (C–C)	<i>r</i> (Si–C)	<i>r</i> (Si–H)
SiC ₃₁	A	–263.699		1.456	1.831	
SiC ₃₁	B	–263.735		1.457	1.833	
HSiC ₃₁	A	–268.195	–4.496	1.456	1.861	1.479
HSiC ₃₁	B	–267.963	–4.228	1.457	1.852	1.478

Another question is that of whether the Si atom prefers endohedral or substitutional doping. To compare Si@C₃₂ and SiC₃₁, we calculated the average binding energy per atom ϵ , which can give information on the stability of clusters with different sizes, as used for boron–nitrogen–mixture clusters [48]. We found that Si@C₃₂ and SiC₃₁ have the same HOMO–LUMO gap

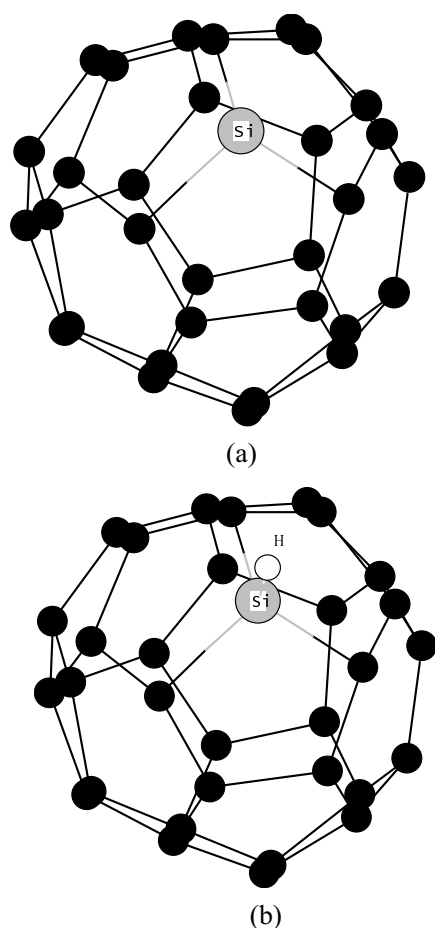


Figure 3. A schematic representation of the structures of SiC_{31} (a) and $HSiC_{31}$ (b) clusters.

of 0.7 eV, but have different values of ϵ , which are -8.149 and -8.242 eV, respectively, suggesting that substitutional doping is more favourable for Si. In fact, what the experiment found is a substitutional doping of SiC_{31} , and not an endohedral doping of $Si@C_{32}$ [44, 45].

4. Conclusions

In conclusion, pure, endohedrally doped, and substitutionally doped C_{32} clusters have been studied using density functional calculations with the GGA. The structure and properties are totally governed by the sp^2 -bonding features of C atoms, which makes the fullerene structure more stable, while the Si atom is still threefold connected with C atoms. Because of the small size of the C_{32} cage, it is not easy to trap atoms or molecules inside.

Acknowledgments

QS would like to express his sincere thanks to Professor P W Fowler for his help. The authors would like to express their sincere thanks to the Materials Information Science Group of the Institute for Materials Research, Tohoku University, for their continuous support of the HITAC S-3800/380 supercomputing facility.

References

- [1] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162
- [2] Krätschmer W, Lamb L D, Fostiropoulos K and Huffman D R 1990 *Nature* **347** 354
- [3] Dugourt P, Hudgins R R, Tenenbaum J M and Jarrold M F 1998 *Phys. Rev. Lett.* **80** 4197
- [4] Greer J C 1999 *Chem. Phys. Lett.* **306** 197
- [5] Handschuh H, Ganteför G, Kessler B, Bechthold P S and Eberhardt W 1995 *Phys. Rev. Lett.* **74** 1095
- [6] Saito M and Okamoto Y 1999 *Phys. Rev. B* **60** 8939
- [7] Hata K, Ariff M, Tohji K and Saito Y 1999 *Chem. Phys. Lett.* **308** 343
- [8] Galli G, Gygi F and Golaz J 1998 *Phys. Rev. B* **57** 1860
- [9] Portman S, Galbraith J, Schaefer H F, Scuseria G E and Lüthi H P 1999 *Chem. Phys. Lett.* **301** 98
- [10] Kim J, Wilkins J W and Canning A 1998 *J. Chem. Phys.* **108** 2631
- [11] Kietzmann H, Rochow R, Ganteför G, Eberhardt W, Vietze K, Seifert G and Fowler P W 1998 *Phys. Rev. Lett.* **81** 5378
- [12] Piscoti C, Yarger T and Zettl A 1998 *Nature* **393** 771
- [13] Jagadeesh M N and Chandrasekhar J 1999 *Chem. Phys. Lett.* **305** 298
- [14] Fowler P W, Heine T, Rogers K M, Sandall J P B, Seifert G and Zerbetto F 1999 *Chem. Phys. Lett.* **300** 369
- [15] Rosato V, Celino M, Benedek G and Gaito S 1999 *Phys. Rev. B* **60** 16 928
- [16] Helden G V, Gotts N G and Bowers M T 1993 *Nature* **363** 60
- [17] Lin Y T, Mishra R K and Lee S L 1999 *Chem. Phys. Lett.* **302** 108
- [18] Bettens R P A and Herbst E 1997 *Astrophys. J.* **478** 585
- [19] Bernath P F, Hinkle K H and Keady J J 1989 *Science* **244** 562
- [20] Gerhardt P, Löffler S and Homann K H 1987 *Chem. Phys. Lett.* **137** 306
- [21] Fulara J, Lessen D, Freivogel P and Maier J P 1993 *Nature* **366** 439
- [22] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
Kresse G and Hafner J 1994 *Phys. Rev. B* **49** 14 251
- [23] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **55** 11 169
- [24] Mermin N D 1965 *Phys. Rev. A* **137** 1141
- [25] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [26] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [27] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045
- [28] Perdew J P 1991 *Electronic Structure of Solids* ed P Ziesche and H Eschrig (Berlin: Akademie)
- [29] Porezag D, Frauenheim Th, Köhler Th, Seifert G and Kaschner R 1995 *Phys. Rev. B* **51** 12 947
- [30] Fowler P W and Manolopoulos D E 1995 *An Atlas of Fullerenes* (Oxford: Clarendon)
- [31] Boustani I, Rubio A and Alonso J A 1999 *Chem. Phys. Lett.* **311** 21
- [32] Bastuğ T, Kürpick P, Meyer J, Sepp W D, Frick B and Rosén A 1997 *Phys. Rev. B* **55** 5015
- [33] Schmalz T G, Seitz W A, Klein D J and Hite G E 1988 *J. Am. Chem. Soc.* **110** 1113
- [34] Stevenson S 1999 *Nature* **401** 55
- [35] Bethune D S, Johnson R D, Salem J R, de Vries M S and Yannoni C S 1993 *Nature* **366** 123
- [36] Guo T, Smalley R E and Scuseria G E 1993 *J. Chem. Phys.* **99** 352
- [37] Cioslowski J 1991 *J. Am. Chem. Soc.* **113** 4139
- [38] Ohtsuki T, Ohno K, Shiga K, Kawazoe Y, Maruyama Y and Masumoto K 2000 *J. Chem. Phys.* **12** 2843
- [39] Grossman J C, Côté M, Louie S G and Cohen M L 1998 *Chem. Phys. Lett.* **284** 644
- [40] Grossman J C, Louie S G and Cohen M L 1999 *Phys. Rev. B* **60** R6941
- [41] Huber K P and Herzberg G 1979 *Constants of Diatomic Molecules (Molecular Spectra and Molecular Structure IV)* (New York: Van Nostrand Reinhold)
- [42] Stoicheff B P 1957 *Can. J. Phys.* **35** 730
- [43] Landau L D and Lifshitz E M 1977 *Quantum Mechanics* 3rd edn (Oxford: Pergamon)
- [44] Pellarin M, Ray C, Lenmë J L, Vialle J L, Broyer M, Blase X, Mélinon P, Kéghélian P and Perez A 1998 *Phys. Rev. Lett.* **80** 5365
- [45] Ray C, Pellarin M, Lenmë J L, Vialle J L, Broyer M, Blase X, Kéghélian P, Mélinon P and Perez A 1999 *J. Chem. Phys.* **110** 6927
- [46] Mélinon P, Kéghélian P, Perez A, Ray C, Lenmë J L, Pellarin M, Broyer M, Boudelle M and Champagnon B 1998 *Phys. Rev. B* **58** 16 481
- [47] Bernath P F, Rogers S A, O'Brien L C, Brazier C R and McLean A D 1988 *Phys. Rev. Lett.* **60** 197
- [48] Seifert G, Fowler P W, Mitchell D, Porezag D and Frauenheim Th 1997 *Chem. Phys. Lett.* **268** 352