

Calculations of the C_2 fragmentation energies of higher fullerenes C_{80} and C_{82}

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Abstract The C_2 fragmentation energies of the most stable isolated-pentagon-rule (IPR) isomers of the C_{80} and C_{82} fullerenes were evaluated with second-order Møller-Plesset (MP2) theory, density-functional theory (DFT) and the semiempirical self-consistent charge density-functional tight-binding (SCC-DFTB) method. Zero-point energy, ionization energy and empirical C_2 corrections were included in the calculation of fragmentation energies for comparison with experimental C_2 fragmentation energies of the fullerene cations. In the case of the most probable Stone-Wales pathway of C_2 fragmentation of C_{80} , the calculated $D_0(C_{80}^+)$ agree well with experimental data, whereas in the case of C_{82} fragmentation, the calculated $D_0(C_{82}^+)$ exceed by up to 1.2 eV the experimental ones, which suggests that other IPR isomers may be present in sufficient amounts in experimental samples. Computer-intensive MP2 calculations and DFT calculations with larger basis sets do not yield much improved C_2 fragmentation energies, compared to those reported earlier with B3LYP/3-21G. On the other hand, semiempirical approaches such as SCC-DFTB, which are orders of magnitude less intensive, yield satisfactory fragmentation energies for higher fullerenes and may become a method of choice for routine calculations of fullerenes and carbon nanotubes.

Figure: C_2 fragmentation energies of C_{80} and C_{82} fullerenes have been calculated with B3LYP/6-31G* model chemistry, with semiempirical self-consistent-charge density-functional tight-binding (SCC-DFTB) method and with the more rigorous MP2 method. The influence of basis set extension and level of theory on the resulting fragmentation energies is discussed.

Keywords *Ab initio* and density-functional theory calculations · Binding energy · Fragmentation energy · Fullerenes · Tight-binding models

Introduction

The kinetic stability of fullerenes, i.e. their stability with respect to fragmentation, has been a topic of considerable interest among both experimentalists and theoreticians during the last decades [1–7]. This is due to the fact that the major isolated-pentagon-rule (IPR) isomers of fullerenes have relatively large C_2 binding energies and, as a result, lose C_2 fragments only at high impact energies. However, the fragmentation process of fullerenes has only been characterized for the most well-known and commercially available fullerenes, and actual values of the dissociation energies $D(C_n)$ of the $C_n \rightarrow C_{n-2} + C_2$ reactions have still not been determined precisely for higher fullerenes (C_n , $n > 70$). Experimentally-deduced C_2 fragmentation energies of the most well-known fullerene, C_{60} , were first reported to be much lower (around 7–8 eV [7–9]) than computed values (11–12 eV [10–12]), but careful consideration of the pre-exponential factor A [13] in the Arrhenius decay law and the effect of radiative cooling in the fragmentation process eventually yielded $D(C_{60}^+)$ values around 10.0 ± 0.2 eV [14, 15], in agreement with calculated

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values, and those obtained from recent metastable-fraction measurements [2].

Although the unimolecular C_2 fragmentation of higher fullerenes has been the subject of fewer experimental and theoretical investigations than that of C_{60} , the interest in their kinetic stability has been recently rekindled [2, 5, 16–20]. Of particular interest is the fragmentation of the C_{80} and C_{82} fullerenes, since the recent experimental data by Peres et al. [5] and Gluch et al. [17] indicate that the value of $D(C_{82}^+)$ should be smaller by ~ 0.9 eV than that of $D(C_{80}^+)$, in contradiction with earlier metastable-fraction measurements of Radi et al. [6] and Barran et al. [21], and with abundance spectra [17] and $D(C_n^+)$ values calculated on the basis of computed heats of fullerene formation [22]. This discrepancy may be associated with the possible contamination of the measured signal by the presence of other fullerenes, containing a different but close number of carbon atoms in their cages, as well as by the presence of other IPR isomers of a given fullerene in the sample.¹

We have recently reported density-functional-theory (DFT) calculations of the possible pathways of unimolecular C_2 fragmentation of the C_{80} [19] and C_{82} [20] fullerenes, and compared calculated fragmentation energies with available experimental data. We previously used the hybrid Becke3 Lee-Yang-Parr (B3LYP) functional [23–25] together with the relatively small split-valence 3–21G basis set [26], since it was shown to yield fairly good results for geometrical and energetic parameters of fullerenes [18, 22, 27]. The choice of this small basis set was based on a compromise between computational efficiency and accuracy of the calculations, and the resulting fragmentation energies agreed well in general with experimental data. In this work, we investigate the influence of larger basis sets with polarization functions more commonly used in conjunction with the B3LYP functional as well as employ a more rigorous *ab initio* level of electronic structure theory. Finally, we also explore the use of semiempirical DFT methods.

Computational procedure

The molecular geometries of the most stable IPR isomers of C_{80} (of D_2 symmetry) and C_{82} (of $C_2(3)$ symmetry)² as well as those of the products of C_2 elimination from their cages, have been optimized with B3LYP [23–25] using the standard 6–31G(d) basis set [26] without symmetry constraints. Single-point energy calculations were also

performed with second-order Møller-Plesset (MP2) theory and the 6–31G(d) basis set for B3LYP optimized geometries. C_2 fragmentation energies $D(C_n)$ were calculated as the difference between the sum of the product energies and the energy of the initial fullerene isomer. Zero-point energy corrections were evaluated on the basis of the B3LYP/3–21G harmonic frequencies. Calculations were also performed with the approximate self-consistent-charge density-functional tight-binding (SCC-DFTB) method, which has been described elsewhere [29, 30]. Calculations were performed for the neutral species since analogous calculations for cations are associated with many problems (especially in the case of wave-function-based methods), namely, finding an appropriate guess wave function, possible difficulties in achieving self-consistent field convergence, and the influence of spin contamination. The fragmentation energies of the cations were then obtained from those of the neutral species, using known experimental ionization energies [31], for comparison with experiment. All B3LYP and MP2 calculations have been carried out employing the Gaussian 03 software [32], whereas SCC-DFTB ones have been performed using the code of M. Elstner and coworkers³ [29, 30].

Results and discussion

As was already shown in previous studies, C_2 fragment excision from the fullerene cage may proceed via either Stone-Wales (SW) transformation [33] followed by C_2 elimination from the adjacent pentagon edge [34], or via C_2 elimination from the pentagon-hexagon bond with formation of a seven-membered-ring C_{n-2} isomer [4]. The fragmentation of the most stable isomers of C_{80} and C_{82} , with D_2 and $C_2(3)$ symmetry, respectively, via both C_2 loss mechanisms, and leading to the most stable fragmentation products (cf. Fig. 1) [19, 20], is first considered in this work.

In order to compare the results of our calculations with those deduced from experimental studies, one needs to include three types of corrections to the calculated electronic $D_e(C_n)$ values: a) the zero-point energy correction (ΔZPE), as the difference between the product and reactant zero-point energies; b) the experimentally-derived [31] ionization energy correction (ΔIE), as the difference between the ionization energies of the C_{n-2} and C_n fullerenes, since all experimental data refer to the cations:

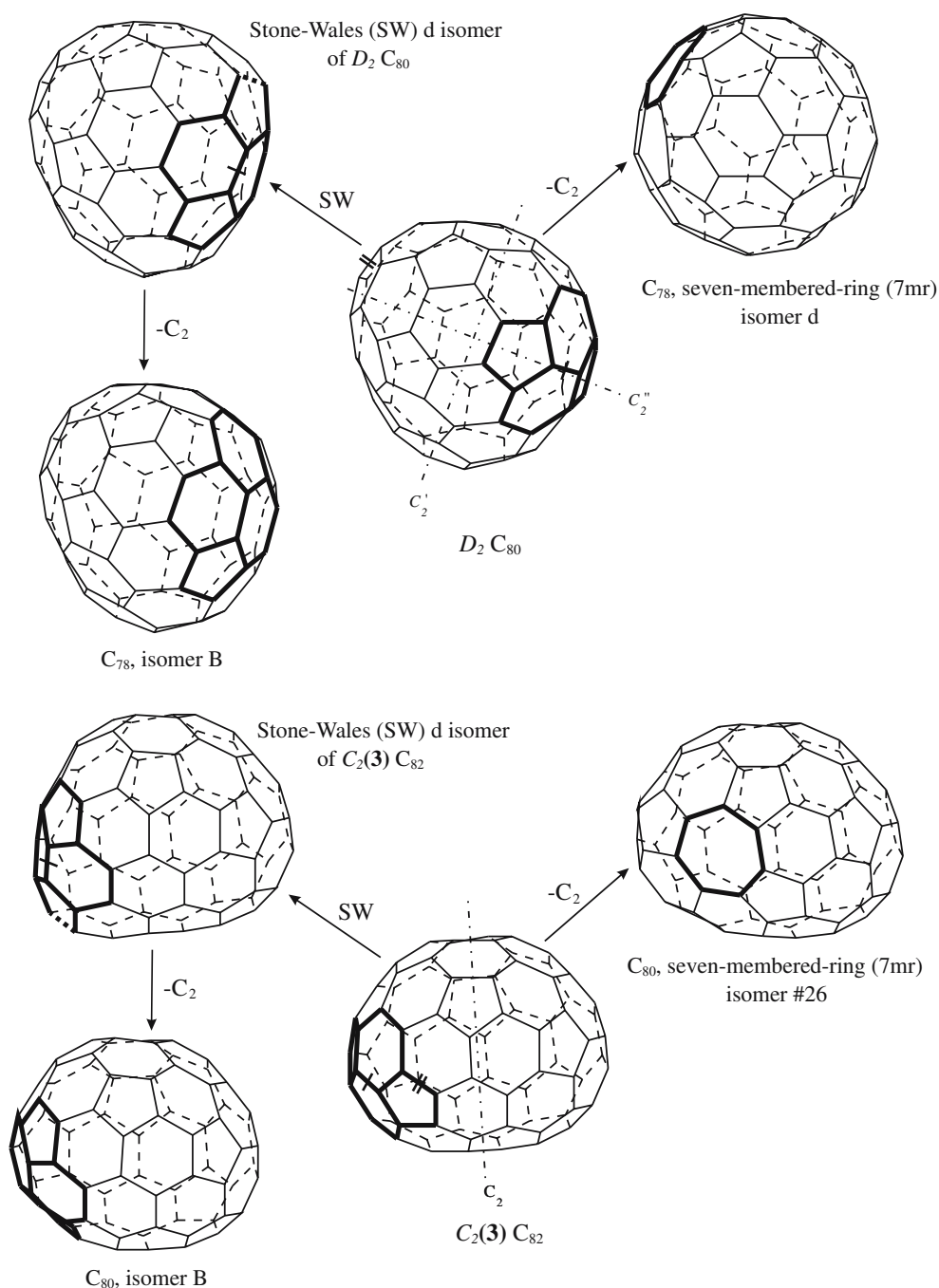
$$D_0(C_n^+) = D_0(C_n) + IE(C_{n-2}) - IE(C_n),$$

¹ Echt O., personal communication

² The IPR isomer notation follows that of Fowler and Manolopoulos [28].

³ Due to the limitations of the code, SCC-DFTB calculations for electronic states other than singlet cannot be performed, and thus, it is not possible to directly calculate the fragmentation energies of the fullerene cations nor to estimate C_2 empirical correction (see below)

Fig. 1 Main C_2 fragmentation pathways of $D_2 C_{80}$ (top) and $C_2(3) C_{82}$ (bottom), and corresponding products following C_2 extraction. The isomer notation follows that from Ref. [19] for C_{80} and Ref. [20] for C_{82} . The SW bond is identified by a short single line perpendicular to the bond, whereas the 5–6 bond from which the C_2 fragment is extracted upon formation of a seven-membered-ring isomer is identified by a double line. Also shown are the C_2 symmetry axes (dot-dashed lines)

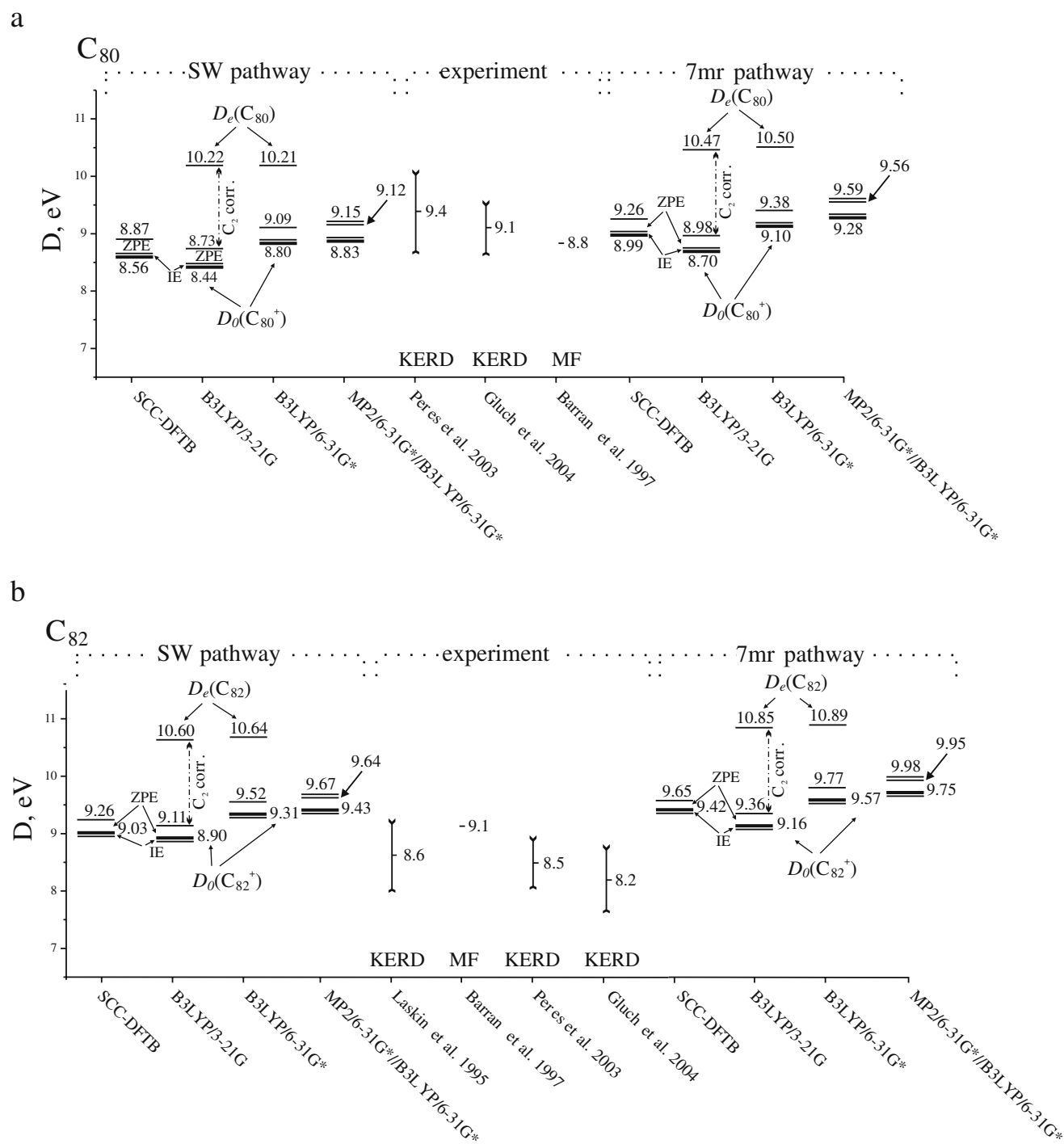


where $D_0(C_n^+)$ and $D_0(C_n)$ are the ZPE-corrected C_2 fragmentation energies of the cationic and neutral fullerene C_n , respectively, and $IE(C_{n-2})$ and $IE(C_n)$ are the ionization energies of the C_{n-2} and C_n fullerenes; and c) an empirical correction to account for the poor description of the C_2 fragment (C_2 corr) at a given level of theory [18].

The results of our calculations are depicted in Fig. 2 together with the available experimental data. Inspection of the data presented in Fig. 2 reveals that the $D_e(C_n)$ values remain almost unchanged upon extension of the basis set from 3–21G to 6–31G* within the DFT framework, most

likely due to the cancellation of errors in the description of the C_n and C_{n-2} species. This is not too surprising, since DFT methods are known to be less sensitive to basis set than *ab initio* methods [35, 36], and is consistent with the results of previous DFT studies by Boese and Scuseria of the C_2 fragmentation of C_{60} [27].

The largest correction to the final $D_0(C_n^+)$ values is the C_2 empirical correction, and the latter is found to decrease significantly with the extension of the basis set from 3–21G to 6–31G* (by 0.37 eV with B3LYP). Furthermore, this correction becomes negligible with MP2/6–31G*, which is



Model chemistry or reported experimental data

Fig. 2 Comparison of the calculated and experimentally measured C_2 fragmentation energies of (a) C_{80} and (b) C_{82} . The experimental data refers either to kinetic-energy-release-distribution (KERD) or metastable-fraction (MF) measurements; the corresponding C_2 fragmentation energies

have been re-normalized to the $D_0(C_{60}^+)$ value of 10.0 eV [14, 15]. Fragmentation energies with and without corrections are denoted as D_0 and D_e , respectively; ΔZPE , ΔIE , and C_2 corr. represent the zero-point energy, ionization energy, and C_2 empirical corrections, respectively

consistent with the overall improvement of the C_2 molecular properties obtained with single-reference methods upon inclusion of electron correlation (up to CCSDT [37]), even though the corresponding wave function has considerable multi-reference character. However, the calculated C-C bond length of the C_2 fragment (1.265 Å) is still 0.022 Å larger than the experimental one (1.243 Å [38]), and MP2/6–31G* overestimates the value of the $^1\Sigma_g^- \rightarrow ^3\Pi_u$ C_2 energy gap (1.45 eV), compared to the experimental value (0.089 eV [39]). For the 6–31G* basis set, the final $D_0(C_n^+)$ values obtained with B3LYP agree within 0.2 eV with those obtained with the MP2 level of theory.

After taking into account all corrections, the final values of $D_0(C_{80}^+)$, calculated for the SW pathway with B3LYP and MP2 and the 6–31G* basis set, lie close to the lower bound inferred from KERD experiments, and are in perfect agreement with the value obtained from the metastable-fraction measurements of Barran et al. [21]. In the case of C_{82} , the calculated SW pathway fragmentation energy is about 1 eV larger than the corresponding KERD values, and is even larger (by 0.2–0.3 eV) than the metastable-fraction value reported by Barran et al. [21]. We believe that this discrepancy could arise from the presence of other C_{82} IPR isomers in experimental samples, leading to the decrease of measured $D_0(C_{82}^+)$ values. This may be caused by the fact that the relative concentrations of the less stable C_{82} IPR isomers become important during the fullerene synthesis at high temperatures [40], and for purely kinetical reasons, they probably do not have enough time to interconvert to the most thermodynamically stable isomer. In this context, one cannot also exclude the possible formation of non-classical fullerene isomers (i.e. those containing one heptagon and 13 pentagons), which have been shown to play an important role in the growth of fullerenes [41]. However, a careful consideration of the comparative stability of one-heptagon isomers versus classical ones is still a challenging task (mainly because of the large number of fullerene structures involved) and goes beyond the scope of the present work.

To gain insight into the range of $D_0(C_{82}^+)$ values for other C_{82} isomers, we have also considered the C_2 fragmentation of two less stable $C_2(5)$ and $C_s(6)$ C_{82} isomers via the SW pathway. In both cases, the fully corrected MP2/6–31G*/B3LYP/6–31G* $D_0(C_{82}^+)$ values were found to be 7.94 eV, which is ~1.5 eV lower than the corresponding $D_0(C_{82}^+)$ value for the $C_2(3)$ isomer. Therefore, the influence of other, less stable, C_{82} isomers on the resulting experimentally-deduced C_2 fragmentation energies cannot be ruled out, and the experimentally determined C_2 fragmentation energies might be those of high-energy isomers of C_{82} . Furthermore, much lower values of C_2 fragmentation energies of other, less stable, C_{82} isomers could result in further C_2 loss from their cages under experimental conditions

until the most stable buckminsterfullerene C_{60} is formed, in agreement with the recently proposed size-down “shrinking hot giant” road of fullerene formation [42].

Interestingly, the SCC-DFTB method, which is known to be very efficient for systems consisting of hundreds of atoms due to some approximations, while yielding geometric and energetic parameters close to those obtained with pure DFT and experimental ones [30, 43], produces $D_e(C_n)$ values very close to the experimental ones. However, inclusion of the corrections for zero-point energy and ionization energy leads to $D_0(C_n^+)$ values which are 0.2–0.3 eV lower, and become even closer to the lower bound of experimental data for the SW fragmentation pathway of C_{80} . This result is in agreement with the recent finding that the SCC-DFTB method describes well the relative stabilities and geometric features of fullerene isomers [44], and therefore, not surprisingly, SCC-DFTB $D_0(C_n^+)$ values do not differ significantly from those calculated with B3LYP/6–31G*. Interestingly enough, the SCC-DFTB $D_0(C_{82}^+)$ values for the fragmentation of $C_2(5)$ and $C_s(6)$ C_{82} isomers (8.12 eV and 7.94 eV, respectively) agree well with MP2/6–31G*/B3LYP/6–31G* results.

To summarize, the previously reported [19, 20] B3LYP/3–21G $D_e(C_n)$ values, corrected only with the C_2 empirical correction, are found to differ from the fully corrected $D_0(C_n^+)$ ones, determined with B3LYP and MP2 and the 6–31G* basis set by only 0.1–0.4 eV. This difference generally does not exceed the experimental errors (cf. Fig. 2), but the computational time required to perform the calculations using B3LYP/6–31G* and MP2/6–31G* increases significantly (at least by a factor of 6 and 73, respectively). On the other hand, the SCC-DFTB method, which is 3 orders of magnitude less computationally intensive than B3LYP/6–31G*, yields fragmentation energies which are within 0.3 eV of those calculated with B3LYP/6–31G*.

Conclusions

We have performed DFT and MP2 calculations of the C_2 fragmentation energies of the most stable IPR isomers of the C_{80} and C_{82} fullerenes, employing the 3–21G and 6–31G* basis sets, in order to estimate the influence of basis set extension and level of theory on the resulting fragmentation energies. Generally, the previously reported values [19, 20] of the C_2 fragmentation energies of the C_{80} and C_{82} fullerenes calculated with B3LYP/3–21G and only including an empirical C_2 correction, agree within 0.4 eV with fully corrected $D_0(C_n^+)$ values, calculated using a larger basis set (6–31G*) and a more rigorous level of theory (MP2), presumably because of cancellation of errors. For the most probable Stone-Wales pathway, the most reliable MP2/6–31G*/B3LYP/6–31G* fragmentation energy of

$D_0(C_{80}^+)$ is close to the lower bound inferred from KERD experiments [5, 17], and is in perfect agreement with the metastable-fraction data of Barran et al. [21]. In the case of C_{82} fragmentation through the SW pathway, the fully corrected $D_0(C_{82}^+)$ value calculated using the same model chemistry exceeds the KERD and metastable-fraction values by ~ 1 eV and 0.3 eV, respectively, suggesting that the presence of other, less stable IPR isomers, in the experimental samples cannot be ruled out. As a matter of fact, the C_2 fragmentation energies of less stable $C_2(5)$ and $C_s(6)$ isomers of C_{82} have been found to be lower by ~ 1.5 eV than the corresponding $D_0(C_{82}^+)$ value for the most stable $C_2(3)$ isomer using the same model chemistry and therefore lie at the lower bound of experimental data. The less computationally demanding SCC-DFTB method yields fragmentation energies of C_{80} and C_{82} within 0.3 eV of B3LYP/6-31G* ones and may be used in the future for routine calculation of fullerene and carbon nanotube properties.

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References

- Campbell EEB, Rohmund F (2000) Rep Prog Phys 63:1061–1109
- Concina B, Gluch K, Matt-Leubner S, Echt O, Scheier P, Märk TD (2005) Chem Phys Lett 407:464–470
- Lifshitz C (2000) Int J Mass Spectrom 198:1–14
- Murry RL, Strout DL, Odom GK, Scuseria GE (1993) Nature 366:665–667
- Peres T, Cao B, Shinohara H, Lifshitz C (2003) Int J Mass Spectrom 228:181–190
- Radi PP, Hsu MT, Brodbelt-Lustig J, Rincon M, Bowers MT (1990) J Chem Phys 92:4817–4822
- Wörgötter R, Dünser B, Scheier P, Märk TD, Foltin M, Klots CE, Laskin J, Lifshitz C (1996) J Chem Phys 104:1225–1231
- Laskin J, Jimenez-Vazquez HA, Shimshi R, Saunders M, de Vries MS, Lifshitz C (1995) Chem Phys Lett 242:249–252
- Laskin J, Lifshitz C (1997) Chem Phys Lett 277:564–570
- Eckhoff WC, Scuseria GE (1993) Chem Phys Lett 216:399–404
- Xu C, Scuseria GE (1994) Phys Rev Lett 72:669–672
- Zhang BL, Xu CH, Wang CZ, Chan CT, Ho KM (1992) Phys Rev B 46:7333–7336
- Hansen K, Campbell EEB (2004) Int J Mass Spectrom 233:215–221
- Tomita S, Andersen JU, Gotttrup C, Hvelplund P, Pedersen UV (2001) Phys Rev Lett 87:073401(1–4)
- Matt S, Echt O, Scheier P, Märk TD (2001) Chem Phys Lett 348:194–202
- Gluch K, Matt-Leubner S, Echt O, Concina B, Scheier P, Märk TD (2004) J Chem Phys 121:2137–2143
- Gluch K, Feil S, Matt-Leubner S, Echt O, Scheier P, Märk TD (2004) J Phys Chem A 108:6990–6995
- Díaz-Tendero S, Alcamí M, Martín F (2003) J Chem Phys 119:5545–5557
- Dolgonos GA, Peslherbe GH (2004) Chem Phys Lett 398:217–223
- Dolgonos GA, Peslherbe GH (2005) Int J Mass Spectrom 241:261–269
- Barran PE, Firth S, Stace AJ, Kroto HW, Hansen K, Campbell EEB (1997) Int J Mass Spectrom 167–168:127–133
- Cioslowski J, Rao N, Moncrieff D (2000) J Am Chem Soc 122:8265–8270
- Becke AD (1993) J Chem Phys 98:5648–5652
- Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785–789
- Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) J Phys Chem 98:11623–11627
- Hehre WJ, Radom L, Schleyer PvR, Pople JA (1986) Ab Initio molecular orbital theory. Wiley, New York
- Boese AD, Scuseria GE (1998) Chem Phys Lett 294:233–236
- Fowler PW, Manolopoulos DE (1995) An Atlas of Fullerenes. Oxford University Press, Oxford
- Porezag D, Frauenheim T, Köhler T, Seifert G, Kaschner R (1995) Phys Rev B 51:12947–12957
- Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, Suhai S, Seifert G (1998) Phys Rev B 58:7260–7268
- Boltalina OV, Ioffe IN, Sidorov LN, Seifert G, Vietze K (2000) J Am Chem Soc 122:9745–9749
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Jr., Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03, Revision B.05, Gaussian Inc., Pittsburgh PA
- Stone AJ, Wales DJ (1986) Chem Phys Lett 128:501–503
- O'Brien SC, Heath JR, Curl RF, Smalley RE (1988) J Chem Phys 88:220–230
- Cramer CJ (2002) Essentials of computational chemistry. Theories and models. Wiley, Chichester
- Koch W, Holthausen MC (2001) A chemist's guide to density functional theory. Wiley-VCH, Weinheim
- Watts JD, Bartlett RJ (1992) J Chem Phys 96:6073–6084
- Huber KP, Herzberg G (1979) Constants of diatomic molecules. Van Nostrand, New York
- Martin M (1992) J Photochem Photobiol A 66:263–289
- Slanina Z, Lee S-L, Kobayashi K, Nagase S (1995) J Mol Struct (Theochem) 339:89–93
- Hernandez E, Ordejon P, Terrones H (2001) Phys Rev B 63:193403(1–4)
- Irle S, Zheng GS, Wang Z, Morokuma K (2006) J Phys Chem B 110:14531–14545
- Elstner M, Frauenheim T, Suhai S (2003) J Mol Struct (Theochem) 632:29–41
- Zheng G, Irle S, Morokuma K (2005) Chem Phys Lett 412:210–216