Difficulties and Virtues in Assessing the Potential Energy Surfaces of Carbon Clusters via DMBE Theory: Stationary Points of C_κ (κ=2-10) at the Focal Point

C. M. R. Rocha[†], Jing Li[‡] and A. J. C. Varandas[†‡] *

[†]*Department of Chemistry and Coimbra Chemistry Center,*
University of Coimbra
3004-535 Coimbra, Portugal.

[‡]*School of Physics and Physical Engineering,*
Qufu Normal University
273165, P.R. China

Supplementary Material

*Corresponding author. E-mail address: varandas@uc.pt.

Table S1: Structural parameters (R_i), total interaction energies (E_{C_κ}) and harmonic vibrational frequencies (w_i) of the global minima predicted from the $V^{(2+3+4)}$ PESs of C_κ (κ=2-10).

Cluster[a]	R_1/a$_0$	R_2/a$_0$	R_3/a$_0$	R_4/a$_0$	R_5/a$_0$	E_{C_κ}[b]/kJ mol^{-1}	w_i[a]/cm^{-1}
C_2	2.483 (2.485[c]; 2.479[d])					−610.0 (−605.8[c]; −610.0±2.1[d])	1638.3(σ_g)
ℓ-C_3	2.445 (2.453[c]; 2.445[e])					−1372.5 (−1342.6[c]; −1324.1±13.0[f])	42.8(π_u); 1206.7(σ_g); 2101.3(σ_u)
ℓ-C_4	2.524 (2.483[c])	2.435 (2.444[c]; 2.458[g])				−1860.5 (−1829.5[c]; −1826.8±17.0[f])	120.0(π_u); 360.1(π_g); 1134.7(σ_g); 1156.4(σ_u); 1987.7(σ_g)
ℓ-C_5	2.575 (2.444[c])	2.539 (2.430[c]; 2.425[g])				−2228.6 (−2546.1[c]; −2524.6±17.0[f])	163.8(π_u); 304.8(π_g); 520.5(π_u); 832.6(σ_u); 881.4(σ_g); 1122.0(σ_g); 1686.2(σ_u)
ℓ-C_6	2.483 (2.466[c])	2.485 (2.439[c])	2.536 (2.415[c]; 2.432[g])			−3155.9 (−3061.4[c]; −3015.8±20.0[f])	83.7(π_u); 153.1(π_g); 296.0(π_g); 452.4(π_u); 660.1(σ_u); 1067.3(σ_u); 1092.0(σ_g); 1594.9(σ_g); 1841.4(σ_g)
ℓ-C_7	2.478 (2.444[c])	2.459 (2.438[c])	2.584 (2.411[c]; 2.419[g])			−3732.7 (−3747.3[c]; −3729.1±20.0[f])	89.2(π_u); 160.9(π_g); 232.2(π_g); 341.8(π_g); 481.2(π_g); 598.7(σ_g); 903.8(σ_u); 1064.3(σ_g); 1085.9(σ_u); 1719.8(σ_g); 1868.5(σ_u)
ℓ-C_8	2.488 (2.458[c])	2.456 (2.442[c])	2.534 (2.413[c])	2.668 (2.425[c])		−4310.3 (−4278.4[c]; −4203.7±43.5[c])	62.0(π_u); 121.7(π_g); 189.7(π_g); 291.5(π_g); 388.9(π_u); 486.8(σ_g); 497.5(π_g); 881.3(σ_u); 891.2(σ_g); 1065.4(σ_u); 1177.8(σ_g); 1771.5(σ_u); 1856.0(σ_g)
ℓ-C_9	2.488 (2.443[c])	2.467 (2.443[c])	2.530 (2.408[c])	2.607 (2.419[c])		−4884.5 (−4952.0[c]; −4932.7±43.5[c])	67.6(π_u); 112.9(π_g); 164.2(π_g); 247.9(π_u); 335.4(π_u); 428.4(π_u); 445.4(σ_g); 513.4(π_u); 762.5(σ_u); 864.1(σ_g); 953.2(σ_u); 1101.6(σ_g); 1232.9(σ_u); 1772.8(σ_g); 1823.6(σ_u)
ℓ-C_{10}	2.484 (2.434[c])	2.465 (2.432[c])	2.549 (2.398[c])	2.596 (2.413[c])	2.554 (2.400[c])	−5459.4 (−5502.1[c]; −5488.0±43.5[h])	76.1(π_u); 122.1(π_g); 169.4(π_g); 226.1(π_g); 298.7(π_u); 371.6(π_g); 410.7(σ_g); 457.1(π_u); 523.7(π_u); 701.0(σ_u); 829.3(σ_g); 840.1(σ_u); 1037.8(σ_g); 1109.4(σ_g); 1293.4(σ_u); 1788.3(σ_g); 1820.0(σ_g)

[a] This work. See text for the references here adressed. [b] Energies given with respect to the infinitely separated κ C(^3P) atoms. [c] Karton *et al.* (Ref. 55). Equilibrium geometries obtained at CCSD(T)/VQZ level. Energies predicted from the W4 theory via Eq. (12). [d] Experimental values taken from Rocha and Varandas (Ref. 33). [e] Experimental value of Breier *et al.* (Ref. 59) [f] Experimental energies retrieved from Gingerich *et al.* (Ref. 56) via Eq. (12). [g] Experimentally averaged C=C bond lengths of van Orden and Saykally (Ref. 6). [e]This work. Total interaction energy predicted from a fit to the experimental data using a straight line; see text.