# Computational Study of Medium-Sized Cumulenones, $H_2C_nO$ (*n* = 3-7)

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Computations are reported for the very floppy cumulenones $H_2C_nO$ (*n* = 3-7). The structures, harmonic frequencies and dipole moments are computed using the DFT and MP2 methods. $H_2C_6O$ and $H_2C_7O$ are treated for the first time. The carbon skeletons in ground states of these molecules with smaller number of carbon atoms are found to be bent, but very floppy. Those of the cumulenones with higher number of carbon atoms are predicted to be nearly linear. All the molecules are predicted to be of $C_s$ symmetry by the present results. Good agreement with the available experimental observations is obtained.

## Introduction

Carbon clusters with polycumulated double bonds of general structure of $XC_nY$ (X, Y = $H_2$, O, S) received considerable attention recently due to the unusual spectroscopic properties and high reactivity. Some of these molecules are known to be very quasilinear and very floppy.[1] For example, the frequency of the lowest bending mode of the linear molecule $OC_3O$ is only 18 cm$^{-1}$.[2] Determination of the structures and spectroscopic properties of these molecules are considered challenging, due to the large size and the floppiness of the molecules, which are also of astrophysical interests.

Considering the spectroscopic and astrophysical importance of these molecules, we report in the present work the theoretical calculations by employing the density functional theory (DFT),[3,4] which proved[5-9] to give surprisingly accurate spectroscopic properties of medium-sized carbon clusters with much less computational efforts than other correlated *ab initio* methods. The effectiveness of the DFT stems from the fact that computational efforts of the method increase as n$^3$ (n is the number of electrons) with comparable accuracy to the more conventional post-HF techniques, while those of the latter methods are proportional as n$^4 \sim$ n$^7$.[10] In this paper we report the spectroscopic properties of $H_2C_nO$ (*n*=3-7). We employ the BLYP, B3LYP and MP2 methods employing basis sets up to 6-311G\*\*.

## Computational Methods

In this study all the calculations were carried out using the GAUSSIAN 94 set of programs.[11] We find that the density functional theory with the exchange functional of Becke[12] and correlation functional by Lee *et al.*[13] (BLYP) gives the best overall results. Bond lengths, angles, rotational constants and dipole moments are reported along with the zero-point energies and harmonic frequencies.

## Results

The energies, rotational constants, dipole moments, and the zero point energies of the ground states of linear $H_2C_nO$ (*n* = 3-7) are presented in Table 1. In their lowest energy structures, the electronic states are all singlet. The computed rotational constants and dipole moments of $H_2C_3O$ and $H_2C_4O$ agree well with experimental observations[14-17] except one rotational constant (A) about the main axis. For a quasilinear molecule, it is difficult to predict A value which approaches to infinity. Calculated bond lengths and harmonic frequencies are reported in Table 3-Table 7.

Since the focus of the present computations is whether the molecules are of $C_{2v}$ symmetry or not, we present the angles of the $C_\gamma$-$C_\beta$-$C_\alpha$ bonds adjacent to the oxygen atom (we will call it the "kink" angle here) in Table 2. All the computa-

**Table 1**. Total energies (hartree), zero-point energies $E_0$ (kcal/mol), rotational constants $B_e$ (GHz), and dipole moments $\mu$ (debye) of the ground states of $H_2C_nO$ (*n*=3-7) by BLYP/6-311G\*\*

| *n* | Energy | $E_0$ | $B_e$ | | $\mu$ | |
|---|---|---|---|---|---|---|
| | | | Cal. | Exp. | Cal. | Exp. |
| 3 | -190.67176 | 22.6843 | 164.2, 4.290, 4.180 | 153.5, 4.387, 4.258$^a$ | 2.3470 | 2.297$^b$ |
| 4 | -228.76396 | 25.2646 | 280.6, 2.125, 2.110 | 220, 2.16, 2.15$^c$ | 1.9734 | 1.967$^d$ |
| 5 | -266.83571 | 28.4957 | 271.4, 1.234, 1.228 | N/A | 3.1054 | N/A |
| 6 | -304.92459 | 31.6218 | 287.8, 0.785, 0.783 | N/A | 2.5372 | N/A |
| 7 | -342.99985 | 34.9614 | 289.6, 0.529, 0.528 | N/A | 3.6508 | N/A |

$^a$experimental values; Ref. 14., $^b$experimental values; Ref. 15. $^c$experimental values; Ref. 16., For a quasilinear molecule, B(along z-axis) has infinite value. $^d$experimental values; Ref. 17.

**Table 2.** "Kink" angles (in degrees) of $C_\gamma$-$C_\beta$-$C_\alpha$ for $H_2C_nO$ ($n$ = 3-7)

| $n$ | MP2/ 6-311G** | B3LYP/ 6-311G** | BLYP/ 6-311G** | Prediction[a] |
|---|---|---|---|---|
| 3 | 137.7 | 153.1 | 148.1 | 145 ± 3 |
| 4 | 156.2 | 176.5 | 176.0 | 172 ± 8 |
| 5 | 150.1 | 173.9 | 174.4 | 172 ± 8 |
| 6 | 166.5 | 178.6 | 179.9 | N/A |
| 7 | 159.3 | 176.2 | 179.9 | N/A |

[a]Ref. 18.

tional methods employed yield some degree of kinkiness to the molecules. Comparison is also made with the very recent theoretical predictions of East,[18] which are based on computations employing MP2, MP4, QCISD and QCISD(T) methods with 6-31G(d), cc-pVDZ, and augmented cc-pVDZ basis sets. The kinky angles obtained by MP2 method seem to be too small compared with other computed results. The C-C-C bond of $H_2C_3O$ seems to be highly bent with the kinky angle of 140-150°. Since the canonical structure of $H_2C_3O$, $H_2C_\gamma$=$C_\beta$=$C_\alpha$=O, would give $C_{2v}$ structure, there seems to be strong contribution of other resonance structure, notably $H_2C_\gamma$=$C_\beta$-$C_\alpha$≡O, in which the $C_\beta$ atom has a lone pair, as proposed by East.[18] For $H_2C_nO$ with n larger than 4, the kinky angle of $C_\gamma$-$C_\beta$-$C_\alpha$ bond is larger than 120°, indicating that the molecules are nearly of $C_{2v}$ symmetry. The kink angles of $H_2C_6O$ and $H_2C_7O$, which are treated for the first time, are predicted to be nearly 180° by the present computations. For $H_2C_nO$ ($n \geq 4$), the $C_\delta$ atom may also possess a lone pair, and the overall importance of the resonance

structures with the $C_\delta$ =$C_\gamma$=$C_\beta$-$C_\alpha$≡O moiety, with lone pair at $C_\beta$, may decrease, giving structures closer to the $C_{2v}$ structures. Accordingly, the $C_\gamma$=$C_\beta$-$C_\alpha$ bending potential will flatten, and the harmonic frequency of this mode will also decrease, as we will show below.

Table 3-Table 7 present the computed bond angles and bond lengths of the optimized singlet ground states of $H_2C_nO$ ($n$ = 3-7), along with the available experimental data. The C-C bond adjacent to the methylene group is much longer than other C-C bonds in all the molecules studied, as also was predicted by East. Agreement of our computed results with the experimental data is very good. It can be seen that the methylene angles (H-C-H) are less than 120° for all the cumulenones. Lengths of the C=O bond and the C=C bond adjacent to the methylene carbon exhibit oscillatory pattern with respect to the number of carbon atoms n. This pattern was also observed for some bond lengths and stretching frequencies in other carbon clusters bonded with heteroatoms.[5-9]

Table 3-Table 7 also give the harmonic frequencies of the cumulenones treated in this report. It should be noted that no scaling factors were employed here for the harmonic frequencies computed by BLYP and B3LYP to compare with experimental observations. The MP2 method overestimates the harmonic frequencies as usual, and appropriate scaling factors would have to be employed, as was done by East. Overall, the BLYP/6-311* or BLYP/6-311** methods give the results that are in the best agreement with experimental observations. For $H_2C_3O$, harmonic frequencies computed by the BLYP method excellently agree with experimental

**Table 3.** Structures (bond lengths in Å and bond angles in degrees) and harmonic frequencies (cm⁻¹) of $H_2C_3O$

| Method | BLYP | BLYP | BLYP | B3LYP | B3LYP | B3LYP | MP2 | MP2[a] | Exp.[b] |
|---|---|---|---|---|---|---|---|---|---|
| Basis set | 6-31G* | 6-311G* | 6-311G** | 6-31G* | 6-311G* | 6-311G** | 6-311G** | 6-31G* | |
| $R_{CH}$ | 1.0983 | 1.0961 | 1.0953 | 1.0909 | 1.0893 | 1.0887 | 1.0885 | 1.0885 | 1.094 |
| $R_{\beta\gamma}$ | 1.3400 | 1.3338 | 1.3335 | 1.3267 | 1.3215 | 1.3210 | 1.3401 | 1.3401 | 1.3219 |
| $R_{\alpha\beta}$ | 1.3140 | 1.3034 | 1.3026 | 1.2986 | 1.2893 | 1.2886 | 1.3197 | 1.3200 | 1.3198 |
| $R_{CO}$ | 1.1911 | 1.1820 | 1.1824 | 1.1781 | 1.1691 | 1.1695 | 1.1721 | 1.1720 | 1.1631 |
| $A_{HCH}$ | 115.112 | 115.185 | 115.462 | 115.301 | 115.401 | 115.668 | 116.064 | 116.070 | 117.18 |
| $A_{HCC}$ | 121.186 | 121.462 | 121.389 | 121.466 | 121.686 | 121.588 | 120.604 | 120.590 | 120.95 |
| $A_{HCC}$ | 123.701 | 123.352 | 121.389 | 123.233 | 122.913 | 122.745 | 123.332 | 123.350 | 122.47 |
| $A_\beta$ | 144.896 | 147.468 | 148.121 | 150.058 | 152.284 | 153.081 | 137.700 | 137.620 | 144.5 |
| $A_\alpha$ | 167.235 | 169.390 | 169.594 | 169.556 | 171.434 | 171.610 | 167.932 | 167.840 | 169.4 |
| $\nu_9(A')$ | 172(15.5)[†] | 163(17.8) | 161(17.9) | 139(18.9) | 134(20.9) | 131(20.8) | 187(3.7) | 205(17.6) | |
| $\nu_{12}(A'')$ | 264(2.5) | 262(1.4) | 263(1.2) | 265(2.0) | 261(0.8) | 261(0.7) | 274(2.1) | 279(4.6) | |
| $\nu_8(A')$ | 463(12.0) | 480(10.2) | 478(10.2) | 478(14.3) | 503(15.0) | 500(15.0) | 504(11.6) | 515(10.7) | 479 |
| $\nu_{11}(A'')$ | 677(3.6) | 681(12.0) | 681(12.7) | 689(15.4) | 696(19.4) | 696(20.3) | 686(8.9) | 710(8.1) | 674 |
| $\nu_7(A')$ | 927(5.5) | 919(4.1) | 917(4.2) | 955(3.8) | 946(4.3) | 945(4.3) | 898(1.8) | 961(1.6) | 910 |
| $\nu_{10}(A'')$ | 974(1.3) | 974(25.9) | 980(23.2) | 1018(21.9) | 1018(25.5) | 1023(23.1) | 962(25.2) | 1022(27.4) | 988 |
| $\nu_6(A')$ | 1054(12.6) | 1055(12.0) | 1045(11.8) | 1079(12.8) | 1080(11.9) | 1070(11.5) | 1036(23.7) | 1109(22.3) | 1047 |
| $\nu_5(A')$ | 1473(2.4) | 1461(1.7) | 1448(1.7) | 1510(2.5) | 1497(1.6) | 1484(1.5) | 1427(1.2) | 1530(1.4) | 1457 |
| $\nu_4(A')$ | 1703(7.1) | 1699(8.9) | 1698(9.4) | 1785(9.6) | 1778(12.5) | 1777(13.6) | 1629(6.6) | 1735(6.6) | 1685 |
| $\nu_3(A')$ | 2146(642.5) | 2156(728.1) | 2158(723.9) | 2254(847.4) | 2260(939.5) | 2263(932.8) | 2100(677.6) | 2207(617.3) | 2124 |
| $\nu_2(A')$ | 3011(33.5) | 2986(43.9) | 2985(37.6) | 3100(29.4) | 3072(37.9) | 3069(31.6) | 2971(26.4) | 3163(22.8) | 2968.3 |
| $\nu_1(A')$ | 3080(19.4) | 3055(20.8) | 3054(16.2) | 3171(15.4) | 3144(16.4) | 3141(12.2) | 3058(8.8) | 3251(10.3) | 3026.3 |

[†]IR intensities are in parentheses (KM/Mole). [a]Ref. 18. [b]Structure data; Ref. 14., frequency data; Ref. 15.

**Table 4**. Structures (bond lengths in Å and bond angles in degrees) and harmonic frequencies (cm$^{-1}$) of $H_2C_4O$

| Method | BLYP | BLYP | BLYP | B3LYP | B3LYP | B3LYP | MP2 | MP2[a] | Exp[b] |
|---|---|---|---|---|---|---|---|---|---|
| Basis set | 6-31G* | 6-311G* | 6-311G** | 6-31G* | 6-311G* | 6-311G** | 6-311G** | 6-31G* | |
| $R_{CH}$ | 1.094 | 1.091 | 1.0908 | 1.0866 | 1.085 | 1.0842 | 1.0846 | 1.0846 | 1.08 |
| $R_{\gamma\delta}$ | 1.3224 | 1.319 | 1.3177 | 1.3122 | 1.308 | 1.3079 | 1.3199 | 1.3199 | 1.29 |
| $R_{\beta\gamma}$ | 1.2868 | 1.281 | 1.2810 | 1.2789 | 1.2738 | 1.2736 | 1.2846 | 1.2848 | 1.29 |
| $R_{\alpha\beta}$ | 1.2897 | 1.284 | 1.285 | 1.2815 | 1.2778 | 1.2777 | 1.2962 | 1.2965 | 1.30 |
| $R_{CO}$ | 1.1915 | 1.181 | 1.1816 | 1.1767 | 1.1668 | 1.1669 | 1.1716 | 1.1716 | 1.16 |
| $A_{HCH}$ | 117.5 | 117.7 | 117.9 | 117.9 | 117.9 | 118.2 | 119.4 | 119.4 | 121 |
| $A_{HCC}$ | 121.2 | 121.1 | 121.1 | 121.1 | 121.1 | 120.9 | 120.3 | 119.4 | |
| $A_\gamma$ | 179.9 | 179.4 | 179.4 | 179.9 | 179.2 | 173.6 | 177.2 | 177.2 | |
| $A_\beta$ | 179.6 | 176.0 | 176.0 | 179.6 | 174.1 | 176.5 | 156.2 | 155.9 | |
| $A_\alpha$ | 179.8 | 178.7 | 178.7 | 179.8 | 178.3 | 178.9 | 174.0 | 173.9 | |
| $D_{HCCC}$ | 90.035 | 90.200 | 89.999 | 90.201 | 90.019 | 90.026 | 90.115 | 90.650 | |
| $\nu_{10}(A')$ | 111(1.7)[†] | 45(3.3) | 52(3.1) | 105(2.2) | 67(3.7) | 48(3.8) | 77(3.9) | 91(3.6) | |
| $\nu_{15}(A'')$ | 155(0.2) | 136(0.1) | 135(0.1) | 155(0.01) | 137(0.1) | 136(0.1) | 178(0.6) | 193(1.9) | |
| $\nu_{14}(A'')$ | 402(16.8) | 389(0.5) | 386(0.4) | 426(0.7) | 403(0.3) | 400(0.3) | 393(0.2) | 403(0.2) | |
| $\nu_9(A')$ | 416(1.0) | 395(9.0) | 404(8.8) | 447(23.9) | 450(10.4) | 440(9.5) | 468(8.5) | 466(15.8) | |
| $\nu_8(A')$ | 511(0.4) | 478(6.1) | 480(6.3) | 525(0.1) | 510(12.6) | 511(12.5) | 521(14.8) | 502(10.4) | |
| $\nu_{13}(A'')$ | 598(15.9) | 600(18.0) | 599(18.2) | 629(23.2) | 634(25.2) | 632(25.4) | 639(19.3) | 629(19.7) | |
| $\nu_7(A')$ | 673(79.2) | 665(82.1) | 680(77.5) | 734(84.7) | 723(86.7) | 737(81.7) | 682(85.6) | 729(93.6) | 728 |
| $\nu_6(A')$ | 744(2.3) | 740(2.2) | 740(2.2) | 769(2.5) | 765(2.3) | 763(2.3) | 777(1.5) | 805(2.6) | |
| $\nu_{12}(A'')$ | 962(3.6) | 951(3.9) | 938(3.3) | 990(4.1) | 979(4.4) | 966(3.8) | 964(2.5) | 1000(3.8) | |
| $\nu_5(A')$ | 1347(3.0) | 1330(2.1) | 1321(1.1) | 1384(2.5) | 1367(1.7) | 1358(0.9) | 1358(2.2) | 1385(3.0) | |
| $\nu_4(A')$ | 1487(84.3) | 1474(100.7) | 1472(104.5) | 1544(82.7) | 1531(95.5) | 1528(100.7) | 1497(45.0) | 1517(29.9) | 1456 |
| $\nu_3(A')$ | 2008(0.03) | 1998(0.8) | 1999(1.0) | 2084(0.7) | 2073(5.2) | 2073(4.9) | 2053(46.3) | 2064(37.2) | 1996 |
| $\nu_2(A')$ | 2290(1503.6) | 2276(1685.0) | 2276(1696.8) | 2359(1975.4) | 2344(2173.1) | 2345(2193.1) | 2326(1725.9) | 2312(1506.0) | 2242 |
| $\nu_1(A')$ | 3083(9.9) | 3056(8.4) | 3060(12.9) | 3167(12.5) | 3137(10.7) | 3137(16.1) | 3186(21.9) | 3216(21.2) | 3035 |
| $\nu_{11}(A'')$ | 3152(0.2) | 3126(0.1) | 3132(0.8) | 3242(0.6) | 3213(0.4) | 3215(1.6) | 3284(2.1) | 3306(1.5) | 3105 |

[†]IR intensities are in parentheses. [a]Ref. 18. [b]Structure data from Ref. 16; frequency data from Ref. 20.

**Table 5**. Structures (bond lengths in Å and bond angles in degrees) and harmonic frequencies (cm$^{-1}$) of $H_2C_5O$

| Method | BLYP | BLYP | BLYP | B3LYP | B3LYP | B3LYP | MP2 | MP2[a] | Exp[b] |
|---|---|---|---|---|---|---|---|---|---|
| Basis set | 6-31G* | 6-311G* | 6-311G** | 6-31G* | 6-311G* | 6-311G** | 6-311G** | 6-31G* | |
| $R_{CH}$ | 1.0991 | 1.0966 | 1.0955 | 1.0909 | 1.0890 | 1.0884 | 1.0890 | 1.0891 | |
| $R_{\delta\epsilon}$ | 1.3309 | 1.3265 | 1.3268 | 1.3200 | 1.3166 | 1.3164 | 1.3292 | 1.3291 | |
| $R_{\gamma\delta}$ | 1.2817 | 1.2760 | 1.2761 | 1.2737 | 1.2685 | 1.2685 | 1.2768 | 1.2769 | |
| $R_{\beta\gamma}$ | 1.2971 | 1.2924 | 1.2926 | 1.2887 | 1.2842 | 1.2844 | 1.3002 | 1.2999 | |
| $R_{\alpha\beta}$ | 1.2866 | 1.2823 | 1.2827 | 1.2787 | 1.2750 | 1.2752 | 1.3003 | 1.3000 | |
| $R_{CO}$ | 1.1951 | 1.1852 | 1.1850 | 1.1799 | 1.1702 | 1.1702 | 1.1736 | 1.1736 | |
| $A_{HCH}$ | 115.653 | 115.792 | 116.101 | 115.981 | 116.181 | 116.445 | 117.149 | 117.10 | |
| $A_{HCC}$ | 122.173 | 122.097 | 121.937 | 122.022 | 121.904 | 121.770 | 121.376 | 121.39 | |
| $A_{HCC}$ | 122.174 | 122.111 | 121.962 | 121.997 | 121.915 | 121.785 | 121.476 | 121.510 | |
| $A_\delta$ | 179.838 | 179.219 | 179.143 | 179.876 | 179.229 | 179.075 | 174.452 | 174.45 | |
| $A_\gamma$ | 179.890 | 176.281 | 178.981 | 179.985 | 179.146 | 178.986 | 174.275 | 174.28 | |
| $A_\beta$ | 179.071 | 176.840 | 174.424 | 179.982 | 174.897 | 173.916 | 150.049 | 150.35 | |
| $A_\alpha$ | 179.728 | 178.893 | 178.037 | 179.994 | 178.426 | 178.098 | 172.094 | 172.13 | |
| $\nu_{13}(A')$ | 79(1.4)[†] | 27(3.1) | 49(3.0) | 73(1.8) | 53(3.2) | 59(3.1) | 76(4.0) | 83(3.4) | |
| $\nu_{18}(A'')$ | 114(0.0) | 102(0.2) | 104(0.1) | 115(0.01) | 106(0.2) | 106(0.1) | 164(1.2) | 170(2.0) | |
| $\nu_{12}(A')$ | 209(1.3) | 172(2.2) | 171(2.4) | 222(1.3) | 196(2.1) | 197(2.2) | 170(2.8) | 189(2.3) | |
| $\nu_{17}(A'')$ | 301(2.2) | 265(2.1) | 265(2.1) | 301(2.3) | 269(2.1) | 269(2.1) | 264(2.8) | 266(2.4) | |
| $\nu_{11}(A')$ | 390(16.6) | 351(14.1) | 363(14.1) | 428(25.1) | 408(18.3) | 412(17.5) | 396(13.1) | 393(14.4) | |
| $\nu_{10}(A')$ | 490(0.9) | 457(5.0) | 457(6.0) | 503(0.2) | 495(10.6) | 495(11.6) | 507(8.8) | 485(9.0) | |
| $\nu_{16}(A'')$ | 566(7.4) | 566(2.1) | 568(1.0) | 597(9.4) | 595(0.7) | 594(0.3) | 555(2.6) | 566(1.9) | |

**Table 5**. Continued

| Method | BLYP | BLYP | BLYP | B3LYP | B3LYP | B3LYP | MP2 | MP2[a] | Exp[b] |
|---|---|---|---|---|---|---|---|---|---|
| Basis set | 6-31G* | 6-311G* | 6-311G** | 6-31G* | 6-311G* | 6-311G** | 6-311G** | 6-31G* | |
| $\nu_{15}$(A") | 630(3.1) | 617(2.5) | 612(19.0) | 651(3.0) | 645.7(28.1) | 642(28.4) | 626(15.6) | 612(18.1) | |
| $\nu_9$(A') | 689(7.5) | 626(3.1) | 627(3.1) | 697(13.4) | 646.3(3.0) | 647(2.9) | 678(3.7) | 699(3.9) | |
| $\nu_{14}$(A") | 905(31.3) | 901(34.5) | 909(32.1) | 952(33.5) | 947(35.8) | 955(33.7) | 919(34.4) | 945(38.4) | |
| $\nu_8$(A') | 1026(0.1) | 1020(0.1) | 1010(0.1) | 1052(0.1) | 1048(0.1) | 1038(0.2) | 1038(1.0) | 1062(0.3) | |
| $\nu_7$(A') | 1214(22.6) | 1204(25.0) | 1203(24.8) | 1256(23.4) | 1244(24.7) | 1243(24.5) | 1212(4.4) | 1228(3.5) | |
| $\nu_6$(A') | 1468(0.2) | 1451(0.02) | 1439(0.1) | 1506(0.01) | 1488(0.3) | 1477(0.6) | 1483(0.3) | 1512(1.2) | |
| $\nu_5$(A') | 1745(61.4) | 1736(60.0) | 1734(56.5) | 1814(52.2) | 1804(48.5) | 1802(45.8) | 1756(15.3) | 1768(17.8) | 1726 |
| $\nu_4$(A') | 2118(2.0) | 2106(31.1) | 2105(3.1) | 2193(0.004) | 2180(0.7) | 2180(1.0) | 2154(38.4) | 2174(22.7) | 2068 |
| $\nu_3$(A') | 2268(1729.4) | 2255(1901.2) | 2253(1887.5) | 2340(2348.5) | 2326(2541.6) | 2325(2524.8) | 2285(1872.3) | 2280(1742.5) | 2207 |
| $\nu_2$(A') | 3020(23.4) | 2098(29.0) | 3001(21.6) | 3115(15.2) | 3089(19.4) | 3086(13.1) | 3135(10.8) | 3166(9.4) | |
| $\nu_1$(A') | 3080(11.1) | 3059(12.0) | 3063(8.4) | 3183(6.6) | 3159(7.1) | 3156(4.4) | 3223(3.1) | 3248(3.9) | |

[†]IR intensities are in parentheses. [a]Ref. 18. [b]Frequency data ; Ref. 19.

**Table 6**. Structures (bond lengths in Å and bond angles in degrees) and harmonic frequencies (cm$^{-1}$) of $H_2C_6O$

| Method | BLYP | BLYP | BLYP | B3LYP | B3LYP | B3LYP | MP2 |
|---|---|---|---|---|---|---|---|
| Basis Set | 6-31G* | 6-311G* | 6-311G** | 6-31G* | 6-311G* | 6-311G** | 6-311G** |
| $R_{CH}$ | 1.0947 | 1.0928 | 1.0916 | 1.0874 | 1.0858 | 1.0850 | 1.0859 |
| $R_{\varepsilon\zeta}$ | 1.3251 | 1.3211 | 1.3208 | 1.3146 | 1.3108 | 1.3104 | 1.3247 |
| $R_{\delta\varepsilon}$ | 1.2864 | 1.2810 | 1.2810 | 1.2790 | 1.2739 | 1.2738 | 1.2812 |
| $R_{\gamma\delta}$ | 1.2902 | 1.2851 | 1.2851 | 1.2814 | 1.2765 | 1.2765 | 1.2872 |
| $R_{\beta\gamma}$ | 1.2898 | 1.2842 | 1.2842 | 1.2813 | 1.2760 | 1.2759 | 1.2872 |
| $R_{\alpha\beta}$ | 1.2885 | 1.2841 | 1.2841 | 1.2809 | 1.2766 | 1.2766 | 1.2900 |
| $R_{CO}$ | 1.1923 | 1.1825 | 1.1825 | 1.1772 | 1.1673 | 1.1673 | 1.1731 |
| $A_{HCH}$ | 116.975 | 117.200 | 117.515 | 117.486 | 117.6644 | 117.909 | 119.041 |
| $A_{HCC}$ | 121.512 | 121.400 | 121.243 | 121.257 | 121.1677 | 121.046 | 120.479 |
| $A_\varepsilon$ | 179.979 | 179.986 | 179.994 | 179.973 | 179.9738 | 179.972 | 179.168 |
| $A_\delta$ | 179.947 | 179.977 | 179.966 | 179.972 | 179.9523 | 179.944 | 175.208 |
| $A_\gamma$ | 179.995 | 179.873 | 179.967 | 179.981 | 179.8350 | 179.844 | 176.453 |
| $A_\beta$ | 179.999 | 178.928 | 179.996 | 179.927 | 178.6346 | 178.613 | 166.457 |
| $A_\alpha$ | 179.792 | 179.661 | 179.956 | 179.992 | 179.6142 | 179.613 | 176.846 |
| $D_{HCCC}$ | 90.163 | 90.016 | 90.046 | 90.183 | 89.859 | 90.011 | 90.225 |
| $\nu_{21}$(A") | 74(0.2)[†] | 56(0.6) | 53(0.1) | 88(1.3) | 40(1.2) | 34(0.8) | |
| $\nu_{15}$(A') | 82(0.0) | 75(0.1) | 75(0.1) | 109(0.2) | 75(0.1) | 75(0.6) | |
| $\nu_{20}$(A") | 196(0.1) | 159(0.04) | 157(0.04) | 178(0.001) | 156(0.01) | 155(18.7) | |
| $\nu_{14}$(A') | 220(1.5) | 193(0.9) | 191(0.9) | 218(0.7) | 192(0.8) | 190(1.3) | |
| $\nu_{13}$(A') | 403(0.003) | 375(0.6) | 368(0.4) | 402(0.8) | 388(0.7) | 381(0.1) | |
| $\nu_{19}$(A") | 415(13.4) | 412(12.4) | 407(14.0) | 429(15.3) | 424(16.9) | 415(0.01) | |
| $\nu_{18}$(A") | 489(0.2) | 463(5.3) | 464(4.4) | 519(11.1) | 499(10.6) | 498(9.5) | |
| $\nu_{12}$(A') | 547(1.5) | 543(1.5) | 543(1.4) | 552(1.9) | 560(1.6) | 548(0.05) | |
| $\nu_{17}$(A") | 552(10.9) | 548(1.0) | 545(0.3) | 571(0.0006) | 566(0.2) | 560(1.5) | |
| $\nu_{11}$(A') | 647(1.1) | 563(9.8) | 560(7.0) | 611(5.5) | 596(9.8) | 588(2.1) | |
| $\nu_{10}$(A') | 696(6.2) | 622(10.0) | 603(13.2) | 639(22.7) | 635(19.2) | 617(27.7) | |
| $\nu_{16}$(A") | 716(74.3) | 708(73.3) | 720(69.1) | 778(75.4) | 768(76.0) | 781(72.0) | |
| $\nu_9$(A') | 966(1.9) | 958(2.1) | 946(1.7) | 992(2.1) | 988(2.1) | 975(1.7) | |
| $\nu_8$(A') | 1068(39.0) | 1059(45.1) | 1059(45.5) | 1078(48.0) | 1094(43.8) | 1094(44.1) | |
| $\nu_7$(A') | 1391(9.7) | 1372(12.7) | 1361(13.8) | 1409(11.1) | 1409(10.3) | 1399(11.7) | |
| $\nu_6$(A') | 1567(0.5) | 1557(0.1) | 1556(12.5) | 1591(1.2) | 1616(0.04) | 1616(0.01) | |
| $\nu_5$(A') | 1941(255.2) | 1932(302.2) | 1932(310.3) | 1966(358.3) | 2003(310.0) | 2003(320.6) | |
| $\nu_4$(A') | 2164(368.3) | 2151(465.7) | 2151(477.7) | 2179(856.2) | 2217(943.8) | 2218(968.6) | |
| $\nu_3$(A') | 2271(2580.5) | 2260(2795.0) | 2261(2802.7) | 2277(3516.0) | 2329(3558.6) | 2329(3562.2) | |
| $\nu_2$(A') | 3073(5.2) | 3046(3.9) | 3049(8.3) | 3114(5.6) | 3128(5.4) | 3127(10.9) | |
| $\nu_1$(A') | 3141(0.01) | 3115(0.03) | 3120(6.4) | 3189(0.1) | 3204(0.05) | 3204(0.7) | |

[†] IR intensities are in parentheses (KM/Mole)

**Table 7**. Structures (bond lengths in Å and bond angles in degrees) and harmonic frequencies (cm$^{-1}$) of $H_2C_7O$

| Method | BLYP | BLYP | BLYP | B3LYP | B3LYP | B3LYP | MP2 |
|---|---|---|---|---|---|---|---|
| Basis set | 6-31G* | 6-311G* | 6-311G** | 6-31G* | 6-311G* | 6-311G** | 6-311G** |
| $R_{CH}$ | 1.0981 | 1.0957 | 1.0947 | 1.0900 | 1.0882 | 1.0875 | 1.0889 |
| $R_{\zeta\eta}$ | 1.3312 | 1.3271 | 1.3269 | 1.3201 | 1.3165 | 1.3165 | 1.3303 |
| $R_{\epsilon\zeta}$ | 1.2814 | 1.2758 | 1.2758 | 1.2734 | 1.2681 | 1.268 | 1.2761 |
| $R_{\delta\epsilon}$ | 1.2985 | 1.2935 | 1.2936 | 1.2901 | 1.2854 | 1.2858 | 1.2954 |
| $R_{\gamma\delta}$ | 1.2846 | 1.2791 | 1.2791 | 1.276 | 1.2709 | 1.2709 | 1.2807 |
| $R_{\beta\gamma}$ | 1.2943 | 1.2889 | 1.2889 | 1.2856 | 1.2805 | 1.2808 | 1.2908 |
| $R_{\alpha\beta}$ | 1.2877 | 1.2830 | 1.2830 | 1.2798 | 1.2757 | 1.2758 | 1.2929 |
| $R_{CO}$ | 1.1939 | 1.1842 | 1.1842 | 1.1786 | 1.1689 | 1.1690 | 1.1741 |
| $A_{HCH}$ | 115.986 | 116.146 | 116.426 | 116.344 | 116.499 | 116.777 | 117.431 |
| $A_{HCC}$ | 122.018 | 121.928 | 121.794 | 121.830 | 121.758 | 121.635 | 121.307 |
| $A_{HCC}$ | 121.996 | 121.926 | 121.780 | 121.826 | 121.743 | 121.588 | 121.262 |
| $A_{\zeta}$ | 179.970 | 179.932 | 179.802 | 179.928 | 179.858 | 179.854 | 177.993 |
| $A_{\epsilon}$ | 179.946 | 179.974 | 179.907 | 179.952 | 179.946 | 179.926 | 178.107 |
| $A_{\delta}$ | 179.972 | 179.976 | 179.960 | 179.972 | 179.762 | 179.522 | 173.322 |
| $A_{\gamma}$ | 179.998 | 179.999 | 179.957 | 179.982 | 179.507 | 179.495 | 174.434 |
| $A_{\beta}$ | 179.956 | 179.932 | 179.871 | 179.901 | 179.053 | 176.188 | 159.336 |
| $A_{\alpha}$ | 179.970 | 179.970 | 179.929 | 179.899 | 179.098 | 178.803 | 175.089 |
| $\nu_{17}(A')$ | 57(0.3)† | 35(0.8) | 32(0.8) | 54(0.4) | 44(1.0) | 49(0.9) | |
| $\nu_{24}(A'')$ | 64(0.02) | 60(0.2) | 60(0.2) | 65(0.03) | 61(0.2) | 61(0.2) | |
| $\nu_{16}(A')$ | 142(0.5) | 111(0.2) | 110(0.2) | 136(0.3) | 121(0.2) | 126(0.2) | |
| $\nu_{23}(A'')$ | 176(1.6) | 155(1.4) | 155(1.5) | 177(1.7) | 157(1.4) | 158(1.4) | |
| $\nu_{15}(A')$ | 255(2.9) | 224(5.2) | 220(5.2) | 268(3.7) | 247(5.5) | 246(5.1) | |
| $\nu_{22}(A'')$ | 330(0.001) | 300(1.0) | 299(0.9) | 329(0.03) | 303(1.3) | 302(1.3) | |
| $\nu_{14}(A')$ | 399(12.3) | 383(6.4) | 374(6.0) | 440(18.6) | 425(6.5) | 429(3.8) | |
| $\nu_{13}(A')$ | 476(0.2) | 457(7.7) | 453(8.5) | 488(1.4) | 493(5.0) | 492(5.6) | |
| $\nu_{12}(A')$ | 483(1.8) | 479(1.8) | 479(1.7) | 498(1.8) | 497(13.9) | 500(16.4) | |
| $\nu_{21}(A'')$ | 538(10.2) | 536(6.8) | 536(6.0) | 570(12.4) | 559(4.1) | 554(5.0) | |
| $\nu_{20}(A'')$ | 610(1.6) | 578(7.7) | 573(1.5) | 624(4.9) | 593(4.6) | 555(3.2) | |
| $\nu_{11}(A')$ | 655(2.6) | 612(2.5) | 577(8.2) | 653(3.5) | 611(16.5) | 611(16.3) | |
| $\nu_{19}(A'')$ | 780(3.6) | 724(6.5) | 732(6.6) | 780(6.7) | 736(11.5) | 724(12.0) | |
| $\nu_{18}(A'')$ | 873(37.5) | 868(40.8) | 877(37.5) | 921(40.3) | 915(41.9) | 923(39.3) | |
| $\nu_{10}(A')$ | 946(24.4) | 939(27.7) | 939(28.0) | 978(25.3) | 970(27.9) | 970(28.1) | |
| $\nu_{9}(A')$ | 1013(0.002) | 1008(0.002) | 998(0.02) | 1040(0.01) | 1035(0.01) | 1024(0.04) | |
| $\nu_{8}(A')$ | 1354(5.7) | 1343(6.3) | 1340(5.6) | 1396(3.3) | 1383(3.9) | 1379(3.4) | |
| $\nu_{7}(A')$ | 1475(28.2) | 1458(22.9) | 1450(21.6) | 1518(26.1) | 1502(20.3) | 1494(18.3) | |
| $\nu_{6}(A')$ | 1753(42.5) | 1744(52.5) | 1744(54.9) | 1819(43.9) | 1810(51.9) | 1808(53.6) | |
| $\nu_{5}(A')$ | 2054(142.1) | 2045(152.3) | 2044(146.9) | 2127(121.6) | 2117(129.6) | 2116(121.5) | |
| $\nu_{4}(A')$ | 2141(539.8) | 2128(593.0) | 2128(572.3) | 2204(1027.7) | 2192(1115.8) | 2190(1086.5) | |
| $\nu_{3}(A')$ | 2260(2644.0) | 2251(2887.0) | 2251(2891.1) | 2330(3531.4) | 2320(3795.1) | 2319(3799.7) | |
| $\nu_{2}(A')$ | 3031(18.6) | 3008(23.4) | 3010(5.6) | 3124(9.7) | 3098(13.1) | 3096(6.6) | |
| $\nu_{1}(A')$ | 3094(6.9) | 3073(7.5) | 3075(4.7) | 3195(3.6) | 3170(3.9) | 3169(1.9) | |

†IR intensities are in parentheses (KM/Mole)

frequencies to within 30 cm$^{-1}$. The CH$_2$ symmetric and anti-symmetric stretching frequencies are very high, in the range of 3000-3100 cm$^{-1}$. The B3LYP method seems to give too large values for high frequency stretching modes, as we observed before.[5-9] It can be seen that the floppy modes involving the C$_\beta$ carbon atom is in-plane for H$_2$C$_3$O, H$_2$C$_5$O, and H$_2$C$_7$O, while those for H$_2$C$_4$O and H$_2$C$_6$O are out of plane (Figure 1). The harmonic frequencies for this floppy mode of H$_2$C$_n$O ($n \geq 4$) are predicted to be much smaller
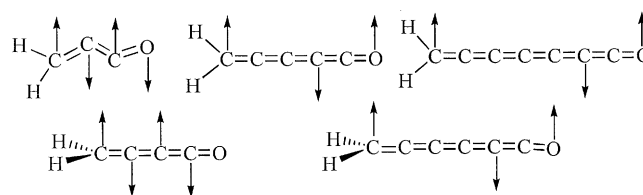


**Figure 1**. Floppy vibrational modes of cumulenones.

than that of $H_2C_3O$, in accordance with the trend of the kinky angle discussed above, and they stabilize to about 50 cm$^{-1}$ ($\nu$ = 161, 52, 49, 53, 32 cm$^{-1}$ for $n$ = 3-7). Again, agreement of the BLYP results with the experimentally measured (matrix IR)[19,20] frequencies is very good.

It must be stressed that most of the present computation were performed on a personal computer. Bigger molecules such as $H_2C_6O$ and $H_2C_7O$ presumabley cannot be treated using personal computers by employing more conventional correlated *ab initio* methods. Our present work therefore showed that the density functional theory can give results that are comparable to or better than the conventional methods (except CCSD or CCSD(T)) in much more economical fashion.

## Conclusion

We presented the density functional theory calculations on cumulenones $H_2C_nO$ ($n$ = 3-7). Good agreement between the computed properties and the experimental observations indicates the efficiency of the BLYP method for medium-sized carbon clusters. We hope that the present calculations would stimulate further investigations on these interesting molecules.

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