

Supporting Information for “Splitting of Degenerate Superatomic Molecular Orbitals Determined by Point Group Symmetry”

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Computational details

For the exploration of the geometric and electronic structures of superatoms, the density functional theory (DFT) can greatly save computational resources while ensuring reasonable calculation results of superatomic electronic structures. Therefore, the DFT method were selected in this work. These studied systems of neutral C_{20} and its dianionic C_{20}^{2-} were fully optimized by using the third-generation dispersion-corrected B3LYP functional (B3LYP-D3)[1,2] with the cc-pVDZ[3] basis set. They are single ground state and quintuple ground state, and the point symmetries of these two superatoms are judged to be D_{3d} and I_h symmetries under an atomic coordinate tolerance of 0.001, respectively. To simulate axial expansion and compression behaviors, the relative displacement of the two five-membered rings (perpendicular to the symmetry axis of C_5/S_{10} and marked by the black circles in Fig. 2(a)) was expanded (or compressed) at intervals of 0.1 Å. The deflection ($\Delta/2R$) is used to describe the axial expansion (or compression) process, corresponding to the deflection value varying from 0.0 to 0.097 (or -0.097). Then, the restrictive optimizations of the dianionic C_{20}^{2-} structures corresponding to each deflection value were performed under the condition of fixing the carbon atoms on the five-membered rings. The above calculations were performed using the Gaussian 16[4] program.

Table S1. Atomic coordinates for neutral C_{20} (C_{3v} symmetry) and its dianionic C_{20}^{2-} (I_h symmetry) clusters.

| Numbering | C_{20} (C_{3v}) | | | C_{20}^{2-} (I_h) | | |
|-----------|-----------------------|-----------|-----------|-------------------------|-----------|-----------|
| | x (Å) | y (Å) | z (Å) | x (Å) | y (Å) | z (Å) |
| 1 | 0.760184 | 1.824964 | 0.657318 | -0.882926 | 0.637091 | -1.741287 |
| 2 | -0.760184 | 1.824964 | 0.657318 | 0.412980 | 1.291984 | -1.541807 |
| 3 | 1.200373 | 1.570821 | -0.657318 | -1.728136 | 0.943594 | -0.583878 |
| 4 | 0.000000 | 1.358586 | -1.449709 | -0.954649 | 1.788134 | 0.330749 |
| 5 | -1.200373 | 1.570821 | -0.657318 | 0.368713 | 2.003323 | -0.261338 |
| 6 | 1.960557 | 0.254143 | -0.657318 | -2.026881 | -0.315164 | 0.104868 |
| 7 | 1.176570 | -0.679293 | -1.449709 | -1.437783 | -0.248665 | 1.445239 |
| 8 | 0.000000 | 0.000000 | -1.950428 | -0.775117 | 1.051111 | 1.584741 |

| | | | | | | |
|----|-----------|-----------|-----------|-----------|-----------|-----------|
| 9 | 1.960557 | -0.254143 | 0.657318 | -1.366003 | -1.399625 | -0.626848 |
| 10 | 1.200373 | -1.570821 | 0.657318 | -0.368713 | -2.003323 | 0.261338 |
| 11 | 0.760184 | -1.824964 | -0.657318 | -0.412980 | -1.291983 | 1.541807 |
| 12 | 1.176570 | 0.679293 | 1.449709 | -0.659020 | -0.811064 | -1.767740 |
| 13 | 0.000000 | 0.000000 | 1.950428 | 0.775118 | -1.051112 | -1.584742 |
| 14 | 0.000000 | -1.358586 | 1.449709 | 0.954649 | -1.788134 | -0.330748 |
| 15 | -1.176570 | 0.679293 | 1.449709 | 1.437783 | 0.248664 | -1.445239 |
| 16 | -1.960557 | -0.254143 | 0.657318 | 2.026881 | 0.315164 | -0.104869 |
| 17 | -1.200373 | -1.570821 | 0.657318 | 1.728136 | -0.943594 | 0.583878 |
| 18 | -0.760184 | -1.824964 | -0.657318 | 0.882926 | -0.637091 | 1.741287 |
| 19 | -1.176570 | -0.679293 | -1.449709 | 0.659020 | 0.811064 | 1.767740 |
| 20 | -1.960557 | 0.254143 | -0.657318 | 1.366003 | 1.399625 | 0.626848 |

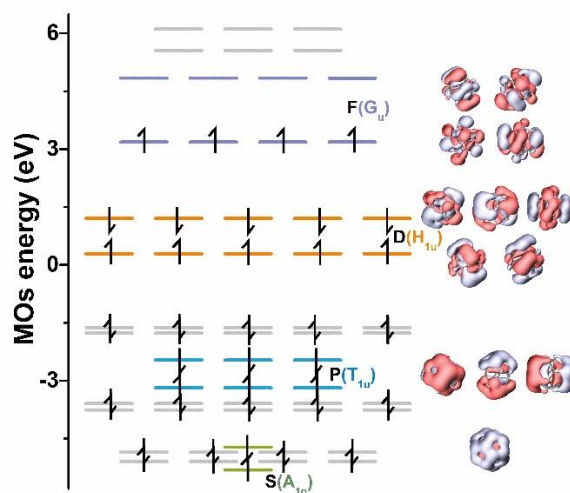


Fig. S1. Energy level diagram of the dianionic C_{20}^{2-} with I_h symmetry at B3LYP-D3/aug-cc-pVDZ level. The angular momentum types of SAMOs are labeled and the parentheses are their irreducible representations. Their corresponding SAMOs shapes are shown to the left. The result is corresponding to that at B3LYP-D3/cc-pVDZ level.

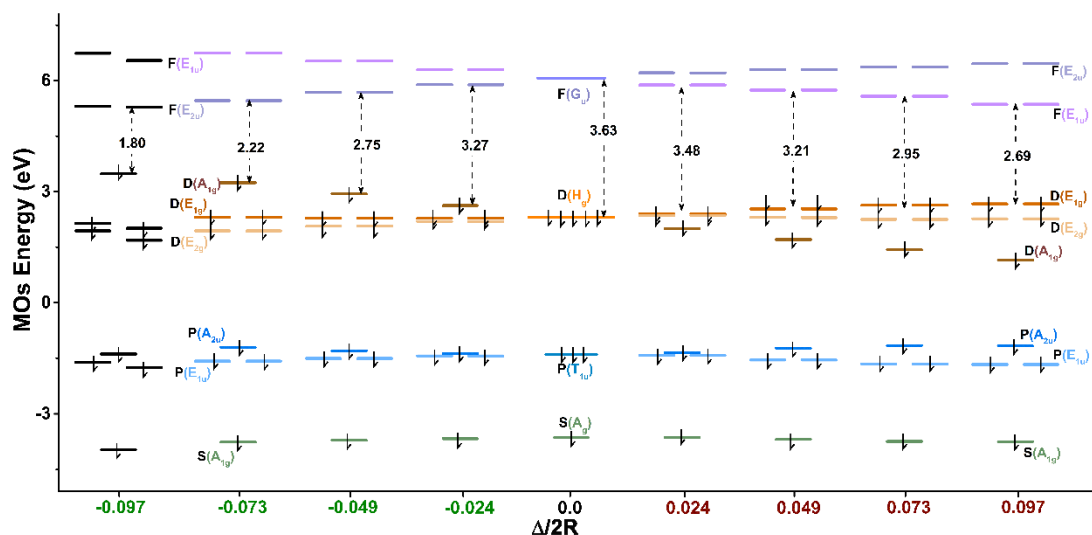


Fig. S2. Evolution characteristics during axial expansion and compression for spin-down electrons. The angular momentum types of SAMOs are labeled and the parentheses are their irreducible representations.

Table S2. The C-C bond lengths during the expansion and compression of dianionic C_{20}^{2-} clusters. Upon the expansion and compression, the C_{20}^{2-} structures are D_{5d} symmetry (except the structure with the deflection of -0.097), and thus there are three C-C bond lengths (b_1 , b_2 , b_3). The bold italic data represents the average bond length of the C-C bonds at the corresponding position in the structure C_s (-0.097). And the D_{5d}^* (-0.097) structure in Fig. 2 is constructed according to the C-C bond lengths of C_s (-0.097) structure.

| $\Delta/2R$ | C-C bond lengths | | |
|-------------|---------------------|---------------------|-------|
| | b_1 | b_2 | b_3 |
| 0.097 | 1.577 | 1.436 | 1.466 |
| 0.073 | 1.539 | 1.439 | 1.466 |
| 0.049 | 1.509 | 1.446 | 1.466 |
| 0.024 | 1.486 | 1.456 | 1.466 |
| 0.0 | 1.466 | 1.466 | 1.466 |
| -0.024 | 1.448 | 1.475 | 1.466 |
| -0.049 | 1.431 | 1.485 | 1.466 |
| -0.073 | 1.417 | 1.498 | 1.466 |
| -0.097 | <i>1.418</i> | <i>1.554</i> | 1.466 |

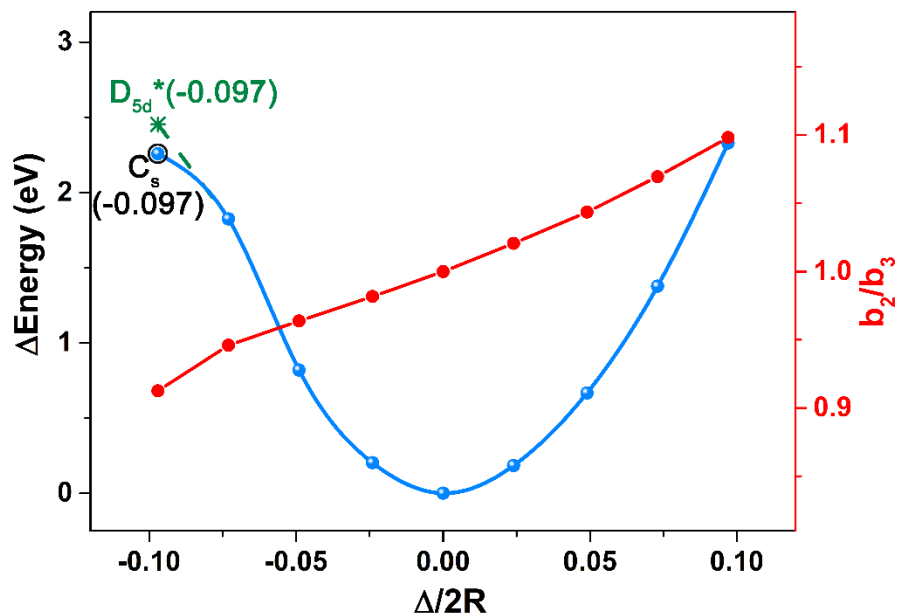


Fig. S3. The total energy of the dianionic C_{20}^{2-} structures during axial expansion and compression. When the deflection is greater than -0.073 and is not 0.0, the structures during expansion and compression all have D_{5d} symmetry. Red line displays the magnitude of b_2 to b_3 ratio (b_2/b_3), and the value increases as the deflection increases. It may be used as an important parameter to modulate the splitting spacing of molecular orbitals in Fig. 2(a).

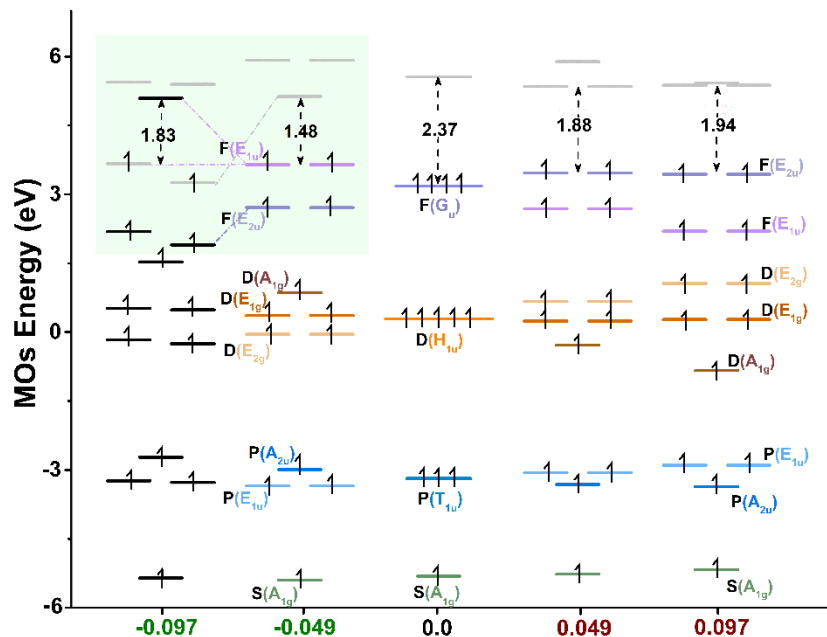


Fig. S4. Evolution characteristics of electronic structures during axial expansion and compression at B3LYP-D3/aug-cc-pVDZ level. The angular momentum types of SAMOs are labeled and the parentheses are their irreducible representations. The initial structure ($\Delta/2R=0.0$) has I_h symmetry. As the deflections are 0.049, 0.097 and -0.049, the structures have D_{5d} symmetry, while the structure symmetry with a deflection of -0.097 is C_s . The result is corresponding to that at B3LYP-D3/cc-pVDZ level.

References

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