# Controlling the Mechanism of Fulvene $S_1/S_0$ Decay: Switching Off the Stepwise Population Transfer

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# SUPPLEMENTARY MATERIAL

**Contents**



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- **Cartesian coordinates and energies of all optimized geometries**

**CASSCF(6,6)/6-31G(d) optimized Cartesian coordinates in Å.**

**$S_0(A_1)$ $C_{2V}$ minimum (Energy: -230.7230983 a.u)**

| Atom | X | Y | Z |
|---|---|---|---|
| C | 1.175903 | -0.111998 | 0.000000 |
| C | 0.000000 | 0.778381 | 0.000000 |
| C | -1.175903 | -0.111998 | 0.000000 |
| C | 0.740038 | -1.394395 | 0.000000 |
| C | -0.740038 | -1.394396 | 0.000000 |
| C | 0.000000 | 2.126984 | 0.000000 |
| H | -0.916423 | 2.689184 | 0.000000 |
| H | 0.916423 | 2.689184 | 0.000000 |
| H | -2.193338 | 0.227518 | 0.000000 |
| H | 2.193338 | 0.227518 | 0.000000 |
| H | -1.349886 | -2.277167 | 0.000000 |
| H | 1.349886 | -2.277167 | 0.000000 |

**$S_0(A_1)$/ $S_1(B_2)$ $C_{2V}$ conical intersection (Energy: -230.6173706 a.u)**

| Atom | X | Y | Z |
|---|---|---|---|
| C | 1.104403 | -0.066203 | 0.000000 |
| C | 0.000000 | 0.743625 | 0.000000 |
| C | -1.104403 | -0.066203 | 0.000000 |
| C | 0.658689 | -1.527182 | 0.000000 |
| C | -0.658689 | -1.527182 | 0.000000 |
| C | 0.000000 | 2.318608 | 0.000000 |
| H | -0.926697 | 2.854235 | 0.000000 |
| H | 0.926697 | 2.854235 | 0.000000 |
| H | -2.130491 | 0.252015 | 0.000000 |
| H | 2.130491 | 0.252015 | 0.000000 |
| H | -1.327882 | -2.364831 | 0.000000 |
| H | 1.327882 | -2.364831 | 0.000000 |

- **Initial momentum vector**

**Components of the initial momentum in the normal mode coordinate set (dimensionless)**

| Coordinate | Normal mode of vibration | Value (dimensionless) |
|---|---|---|
| Q1 | B1 | 0.00000 |
| Q2 | B2 | 0.00000 |
| Q3 | A2 | -2.02794 |
| Q4 | B1 | 0.00001 |
| Q5 | A1 | -1.99872 |
| Q6 | A2 | -2.80784 |
| Q7 | A2 | -4.11536 |
| Q8 | B1 | -0.00026 |
| Q9 | B2 | -0.00002 |
| Q10 | B1 | 0.00000 |
| Q11 | A2 | -0.18238 |
| Q12 | B1 | -0.00031 |
| Q13 | A1 | -0.88109 |
| Q14 | B2 | 0.00000 |
| Q15 | A1 | -0.82133 |
| Q16 | B2 | -0.00027 |
| Q17 | A1 | 1.43731 |
| Q18 | B2 | 0.00000 |
| Q19 | B2 | 0.00006 |
| Q20 | A1 | -1.66280 |
| Q21 | A1 | 0.72868 |
| Q22 | A1 | 3.13010 |
| Q23 | B2 | -0.00009 |
| Q24 | A1 | -0.69194 |
| Q25 | A1 | 5.81317 |
| Q26 | B2 | -0.00009 |
| Q27 | A1 | 0.14509 |
| Q28 | B2 | 0.00000 |
| Q29 | B2 | 0.00001 |
| Q30 | A1 | 0.15218 |

The twelve modes that mainly contribute to the vector are highlighted.

**Cartesian coordinates giving the direction of the induced geometrical displacement with respect to Franck-Condon point given above (arbitrary unit)**

| Atom | X | Y | Z |
|---|---|---|---|
| C | 1.129511 | -0.083075 | -0.028529 |
| C | 0.000001 | 0.755718 | 0.000000 |
| C | -1.129513 | -0.083076 | 0.028522 |
| C | 0.684267 | -1.471303 | -0.017719 |
| C | -0.684268 | -1.471304 | 0.017715 |
| C | -0.000001 | 2.234938 | 0.000000 |
| H | -0.437498 | 2.788274 | -0.808915 |
| H | 0.437501 | 2.788269 | 0.808914 |
| H | -2.151303 | 0.242415 | 0.062184 |
| H | 2.151303 | 0.242408 | -0.062180 |
| H | -1.329263 | -2.327573 | 0.036598 |
| H | 1.329272 | -2.327582 | -0.036596 |