***Supporting Information***

*(Total of 9 pages)*

for

# Spectral lineshape in nonlinear electronic spectroscopy

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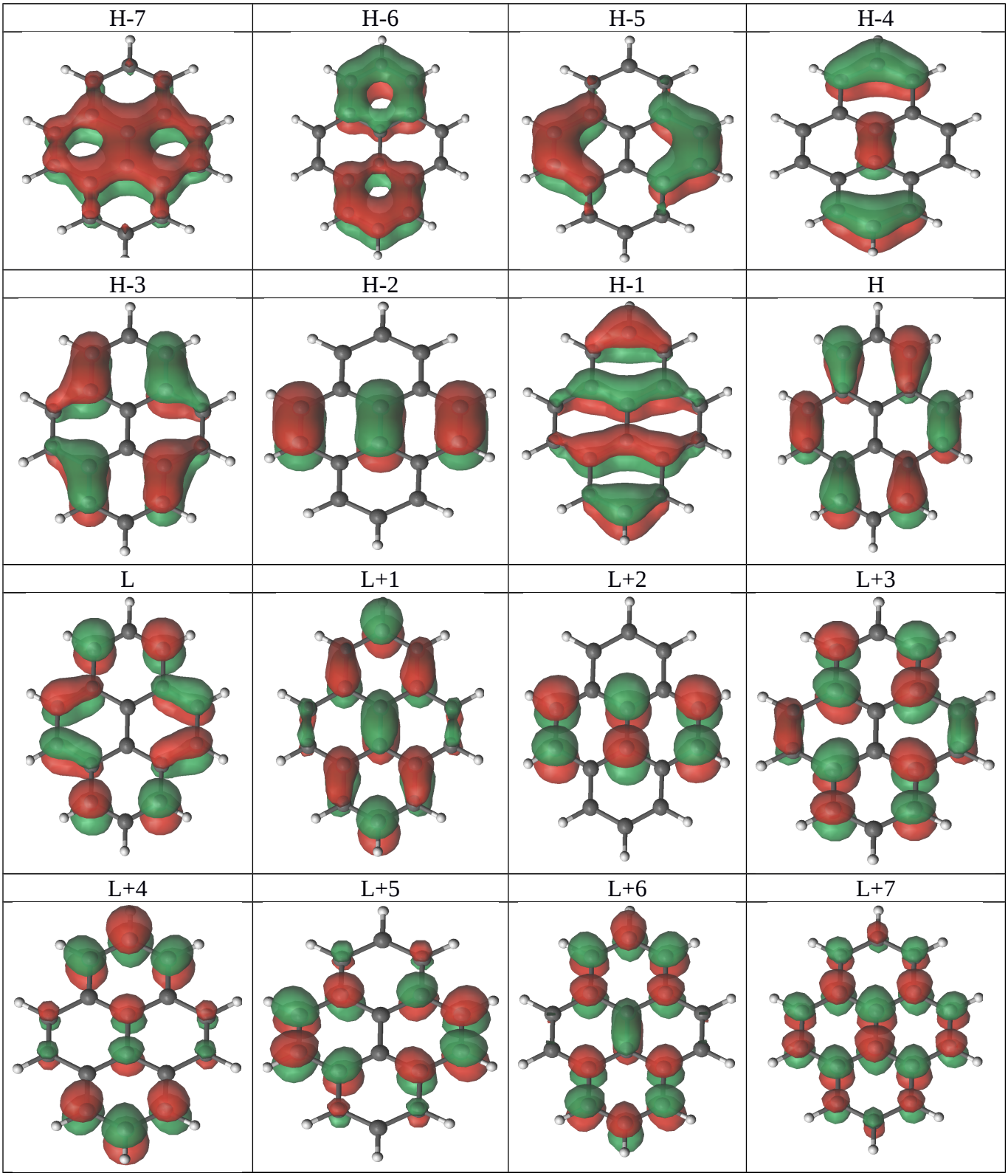


**Figure S1.** Valence π orbitals of pyrene.

| Geometry / State | $^1(gs)_{min}$ | $^1(Lb)_{min}$ | $^1(La)_{min}$ | $(^1La/^1Lb)_{CI}$ |
|---|---|---|---|---|
| gs | 0.00 | -0.13 | -0.12 | 0.18 |
| Lb | 3.42 (<0.01) | 2.93 | 3.05 | 3.45 |
| La | 3.77 (0.15) | 3.33 | 3.24 | 3.43 |

**Table S1.** SA-RASSCF(4,8|0,0|4,8)/SS-RASPT2/ANO-L(321,21) energies (eV) for the ground, the $L_b$ and the $L_a$ states of pryene at relevant characterized geometries. All the reported values are referred to the ground state minimum. In parenthesis are reported the oscillator strength for the ground state → $L_b$ and ground state → $L_a$ electronic transitions at the $^1(gs)_{min.}$

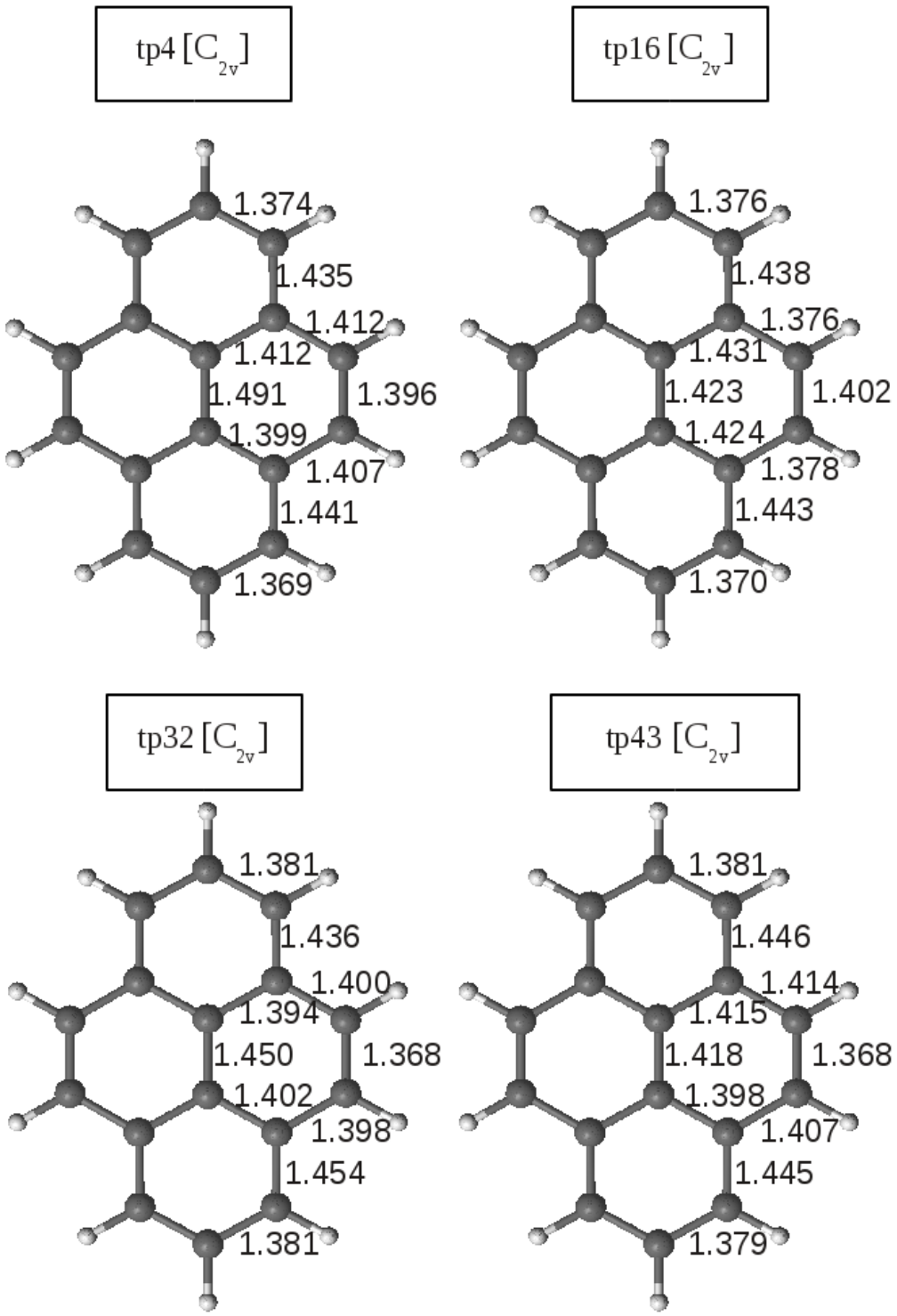


**Figure S2.** Example of geometries along the $L_a$ CAS(2,2) dynamics, at which high-level computations reveal an inversion of the energetic order of the $L_b$ and $L_a$ states. Bond lengths are reported (in Ångstrom).

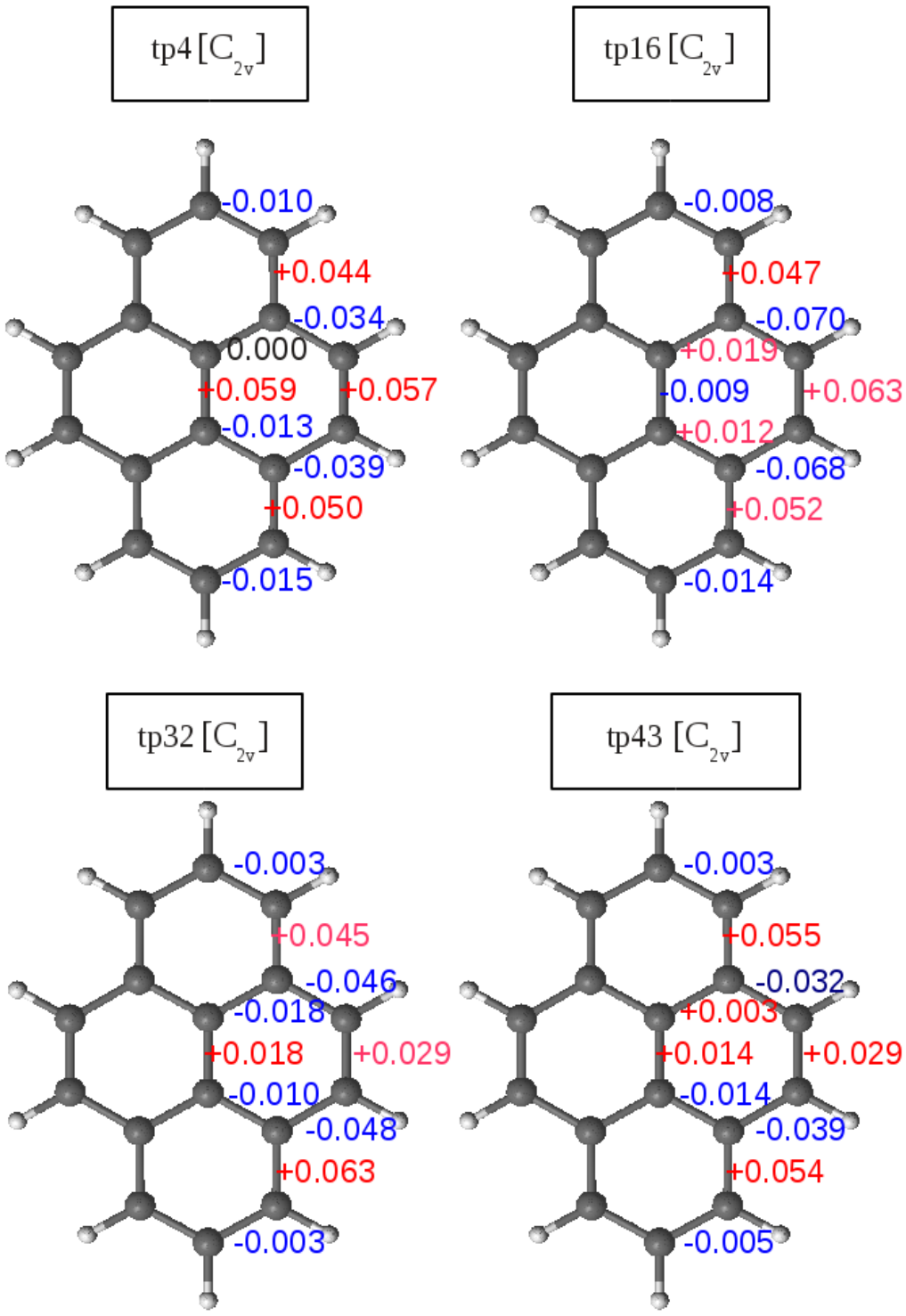


**Figure S3.** Example of geometries along the $L_a$ CAS(2,2) dynamics, at which high-level computations reveal an inversion of the energetic order of the $L_b$ and $L_a$ states. Bond lengths are reported (in Ångstrom). Bond length differences with respect to the $^1(gs)_{min}$ structure are reported.

**Table S2.** Cartesian coordinates x, y, z (in Å) of the optimized structures for the pyrene molecule.

| | $^1(gs)_{min}$ | | |
|---|---|---|---|
| C | -0.20367148 | -2.45661691 | -0.19293374 |
| C | -1.15218720 | -1.36569775 | -0.16127474 |
| C | 1.11391082 | -2.23811492 | -0.09219851 |
| C | -0.66333621 | -0.04904205 | -0.02044630 |
| C | 1.64641965 | -0.90166291 | 0.05303075 |
| C | 0.74567760 | 0.18459827 | 0.08755353 |
| H | -0.58298686 | -3.45747048 | -0.30093173 |
| C | -2.52415228 | -1.57257875 | -0.26467841 |
| C | -1.56397310 | 1.03709385 | 0.01410574 |
| C | 1.23448527 | 1.50111615 | 0.22831859 |
| C | -2.92921112 | 0.78999208 | -0.09191119 |
| C | -3.40240879 | -0.50328052 | -0.23007049 |
| H | -2.90147587 | -2.57432892 | -0.37186583 |
| C | -1.03156727 | 2.37347110 | 0.15963529 |
| H | -3.61952409 | 1.61469118 | -0.06606173 |
| H | -4.46017855 | -0.67880794 | -0.31059401 |
| C | 3.01146383 | -0.65464812 | 0.15913424 |
| C | 2.60665406 | 1.70799436 | 0.33156437 |
| C | 3.48475560 | 0.63879744 | 0.29732821 |
| H | 1.80579958 | -3.06144253 | -0.11829752 |
| C | 0.28610722 | 2.59195559 | 0.26030152 |
| H | -1.72349580 | 3.19676486 | 0.18572456 |
| H | 2.98395575 | 2.70975344 | 0.43867846 |
| H | 4.54248439 | 0.81420607 | 0.37843797 |
| H | 0.66531333 | 3.59285845 | 0.36827421 |
| H | 3.70188457 | -1.47928984 | 0.13367630 |

$^{1}(Lb)_{min}$

| | | | |
|---|---|---|---|
| C | -0.690801 | -2.464193 | 0.000000 |
| C | 0.690801 | -2.464193 | 0.000000 |
| C | -0.690801 | 2.464193 | 0.000000 |
| C | 0.690801 | 2.464193 | 0.000000 |
| C | -1.428491 | -1.252226 | 0.000000 |
| C | 1.428491 | -1.252226 | 0.000000 |
| C | -1.428491 | 1.252226 | 0.000000 |
| C | 1.428491 | 1.252226 | 0.000000 |
| C | -0.689856 | 0.000000 | 0.000000 |
| C | 0.689856 | 0.000000 | 0.000000 |
| H | -1.228780 | -3.401488 | 0.000000 |
| H | 1.228780 | -3.401488 | 0.000000 |
| H | -1.228780 | 3.401488 | 0.000000 |
| H | 1.228780 | 3.401488 | 0.000000 |
| C | -2.836767 | -1.221816 | 0.000000 |
| C | 2.836767 | -1.221816 | 0.000000 |
| C | -2.836767 | 1.221816 | 0.000000 |
| C | 2.836767 | 1.221816 | 0.000000 |
| C | -3.537580 | 0.000000 | 0.000000 |
| C | 3.537580 | 0.000000 | 0.000000 |
| H | -3.382568 | -2.154006 | 0.000000 |
| H | 3.382568 | -2.154006 | 0.000000 |
| H | -3.382568 | 2.154006 | 0.000000 |
| H | 3.382568 | 2.154006 | 0.000000 |
| H | -4.617256 | 0.000000 | 0.000000 |
| H | 4.617256 | 0.000000 | 0.000000 |

$^{1}(La)_{min}$

| | | | |
|---|---|---|---|
| C | -0.695341 | -2.441510 | 0.000000 |
| C | 0.695341 | -2.441510 | 0.000000 |
| C | -0.695341 | 2.441510 | 0.000000 |
| C | 0.695341 | 2.441510 | 0.000000 |
| C | -1.424307 | -1.237006 | 0.000000 |
| C | 1.424307 | -1.237006 | 0.000000 |
| C | -1.424307 | 1.237006 | 0.000000 |
| C | 1.424307 | 1.237006 | 0.000000 |
| C | -0.705545 | 0.000000 | 0.000000 |
| C | 0.705545 | 0.000000 | 0.000000 |
| H | -1.230954 | -3.379741 | 0.000000 |
| H | 1.230954 | -3.379741 | 0.000000 |
| H | -1.230954 | 3.379741 | 0.000000 |
| H | 1.230954 | 3.379741 | 0.000000 |
| C | -2.849178 | -1.210583 | 0.000000 |
| C | 2.849178 | -1.210583 | 0.000000 |
| C | -2.849178 | 1.210583 | 0.000000 |
| C | 2.849178 | 1.210583 | 0.000000 |
| C | -3.534693 | 0.000000 | 0.000000 |
| C | 3.534693 | 0.000000 | 0.000000 |
| H | -3.391350 | -2.144258 | 0.000000 |
| H | 3.391350 | -2.144258 | 0.000000 |
| H | -3.391350 | 2.144258 | 0.000000 |
| H | 3.391350 | 2.144258 | 0.000000 |
| H | -4.615518 | 0.000000 | 0.000000 |
| H | 4.615518 | 0.000000 | 0.000000 |

$(^1La/^1L_b)_{CI}$

| | | | |
|---|---|---|---|
| C | -0.2305326175 | -2.4206838723 | -0.1918497284 |
| C | -1.1530987141 | -1.3625179316 | -0.1610115102 |
| C | 1.1319087499 | -2.1923208553 | -0.0871788596 |
| C | -0.6783860304 | -0.0516374927 | -0.0214391440 |
| C | 1.6434173421 | -0.8934155008 | 0.0535462693 |
| C | 0.7480954709 | 0.1849161063 | 0.0877045945 |
| H | -0.6089695627 | -3.4200337348 | -0.2995290832 |
| C | -2.5873415287 | -1.5844268474 | -0.2695426679 |
| C | -1.5637501300 | 1.0335947293 | 0.0140028912 |
| C | 1.2344475170 | 1.4922627535 | 0.2277249535 |
| C | -2.9926845498 | 0.7809119427 | -0.0967575843 |
| C | -3.4639212238 | -0.5134722103 | -0.2347649111 |
| H | -2.9669052283 | -2.5845349177 | -0.3765440093 |
| C | -1.0449268000 | 2.3310427890 | 0.1550598984 |
| H | -3.6843399335 | 1.6035593500 | -0.0711467165 |
| H | -4.5215494399 | -0.6890051045 | -0.3158384527 |
| C | 3.0773222004 | -0.6483594002 | 0.1638112460 |
| C | 2.6707075351 | 1.7232113461 | 0.3370032907 |
| C | 3.5461748031 | 0.6488868712 | 0.3017727837 |
| H | 1.8335491420 | -3.0039272924 | -0.1116789793 |
| C | 0.3181038589 | 2.5547209120 | 0.2592108618 |
| H | -1.7353960504 | 3.1533498102 | 0.1807182495 |
| H | 3.0511799539 | 2.7200221296 | 0.4440380240 |
| H | 4.6057709120 | 0.8246446852 | 0.3828813012 |
| H | 0.7100646794 | 3.5478867511 | 0.3671548736 |
| H | 3.7692607519 | -1.4671544358 | 0.1389568107 |