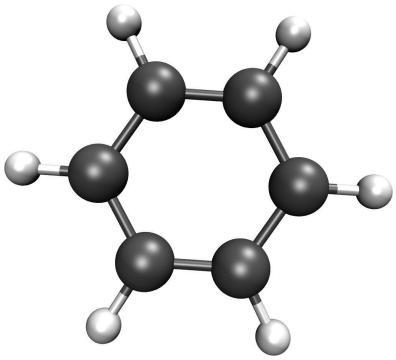
A Report On The Calculation Of The Optimised Structure And Vibrational Frequencies Of Benzene At The PBE1PBE/ 6-31G(d,p) Level

osl - 20th June 2022



Abstract

The calculation of optimised structure and vibrational frequencies for the system 'Benzene' is presented, accompanied by automated analysis and image generation provided by the Silico software package. The calculation was performed using the Gaussian software package at the PBE1PBE/ 6-31G(d,p) level of theory. The total self-consistent field (SCF) energy of the system was found to be -6310.54 eV after 5 steps. The alpha and beta highest-occupied molecular orbitals (HOMO) were calculated to be 3.83 and -0.02 eV respectively, while the alpha and beta lowest-unoccupied molecular orbitals (LUMO) were 6.27 and 6.34 eV. These values correspond to a calculated HOMO-LUMO band gap of 2.44 and 6.36 eV for the alpha and beta case respectively. The permanent dipole moment (PDM) was calculated to be 0.00 D. The most intense vibrational frequencies were calculated to be at -220, 646, 940, 1402 and 3141 cm^{-1}, and there were two negative frequencies.

Table 1: *Summary of overall calculation metadata. [a]: The date and time at which the calculation was completed. [b]: Total combined duration in real-time (wall-time) for all components of the calculation. [c]: Temperature used for thermochemistry analysis. [b]: Pressure used for thermochemistry analysis.*

Date[a]	Duration[b]	Success (Converged)	Computational package	Level of theory	Calculations	Wavefunction	Multiplicity	T[c] / K	p[d] / atm
20/06/2022 17:16:54	2 m, 13 s	True (True)	Gaussian (2016+C.01)	PBE1PBE/ 6-31G(d,p)	Optimisation, Frequencies	unrestricted	2 (doublet)	298.15	1.0

Summary Of Results

Scf Energy

Table 2: *Summary of SCF energy properties.*

No. of steps	5
Final energy	-6310.5381 eV
Final energy	-608,874 $kJ \cdot mol^{-1}$

Geometry

Table 3: *Summary of geometry properties.*

Formula	$C_6H_6^-$
Exact mass	78.0469 $g \cdot mol^{-1}$
Molar mass	78.1118 $g \cdot mol^{-1}$
Alignment method	Minimal
X extension	5.04 Å
Y extension	4.51 Å
Z extension	0.00 Å
Linearity ratio	0.11
Planarity ratio	1.00

Alpha Orbitals

Table 4: *Summary of HOMO & LUMO (alpha) properties.*

$E_{HOMO,LUMO}$	2.44 eV
E_{HOMO}	3.83 eV
E_{LUMO}	6.27 eV

Beta Orbitals

Table 4: *Summary of HOMO & LUMO (beta) properties.*

$E_{HOMO,LUMO}$	6.36 eV
E_{HOMO}	-0.02 eV
E_{LUMO}	6.34 eV

Permanent Dipole Moment

Table 5: *Summary of the permanent dipole moment properties.*

Total	0.00 D
X axis angle	0.00 °
XY plane angle	0.00 °

Vibrations

Table 6: *Summary of the properties of the calculated vibration frequencies.*

No. frequencies	30
Simulated peaks	-220, 646, 940, 1402 and 3141 ... cm^{-1}
No. negative frequencies	2
Negative frequencies	-299.12 and -220.12 cm^{-1}

Methodology

Metadata

The calculation of the optimised structure and vibrational frequencies was performed using the **Gaussian (2016+C.01)** program, the **DFT** method with the **PBE1PBE** functional and the **6-31G(d,p)** basis set. It was completed on the **20th June 2022** after a total duration of **2 m, 13 s** and **finished successfully**. The base multiplicity of the system under study was **2 (doublet)**. Finally, an **unrestricted wavefunction** was used, resulting in two sets of singly occupied orbitals, designated as either alpha or beta, to account separately for both spin up and spin down electrons. The full calculation metadata is tabulated in table 1.

Analysis

The report presented here was generated using the Silico software package. This toolset relies upon a number of third-party applications and libraries which should be cited appropriately in derivative works. In particular, the calculation results described within were parsed by the cclib library.[1] Scientific constants which were used, among other things, for the interconversion of scientific units were provided by SciPy.[2] Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using Visual Molecular Dynamics (VMD)[3] and the Tachyon ray-tracer.[4] Finally, two-dimensional graphs were plotted using the MatPlotlib library,[5] while this report itself was prepared using the Mako template library[6] and the Weasyprint library[7], the latter of which was responsible for generation of the PDF file.

Discussion

Total SCF Energy

The total energy of the system was calculated at the **self-consistent field (SCF)** level, corresponding to the energy calculated by the density-functional theory (DFT) method, over a total of five steps, the results of which are displayed in figure 1. The energy calculated by the final step was -6310.54 eV, corresponding to -608,874 KJmol^{-1}. A plot of the total SCF electron density is shown in figure 2.

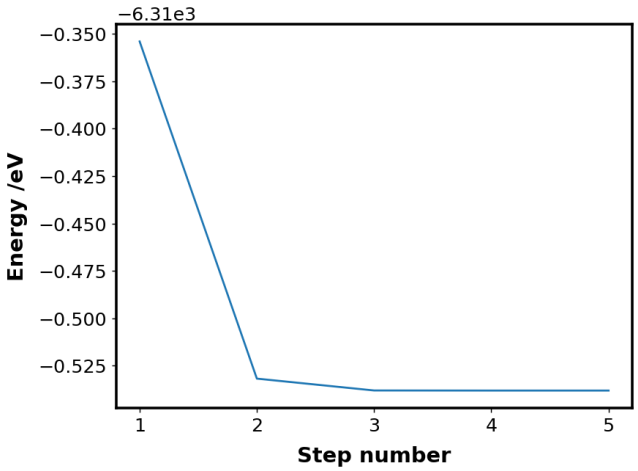


Figure 1: *Graph of calculated energies at the self-consistent field (SCF) level.*

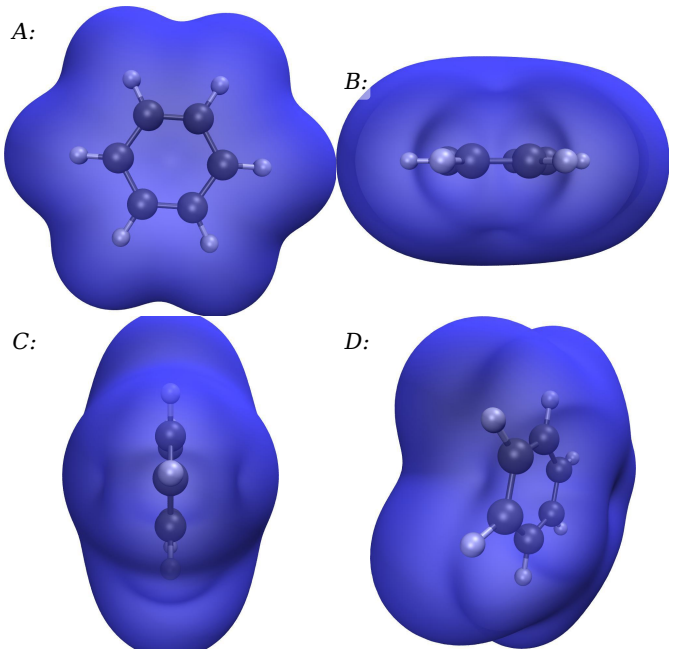


Figure 2: *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Spin Density

The calculated difference in spin density between the alpha and beta cases is shown in figure 3 for the positive difference and figure 4 for the negative difference. A combined plot of both the positive and negative difference is shown in figure 5.

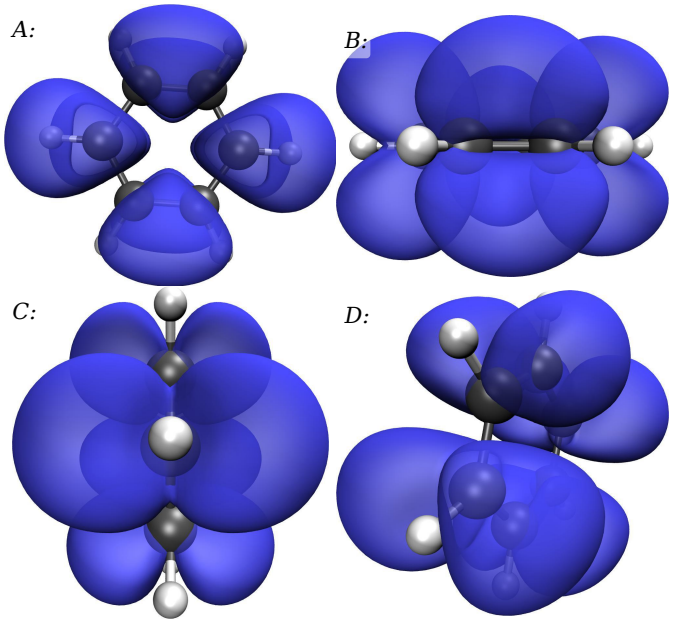


Figure 3: *Plot of the positive difference in spin density (alpha, electron), plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

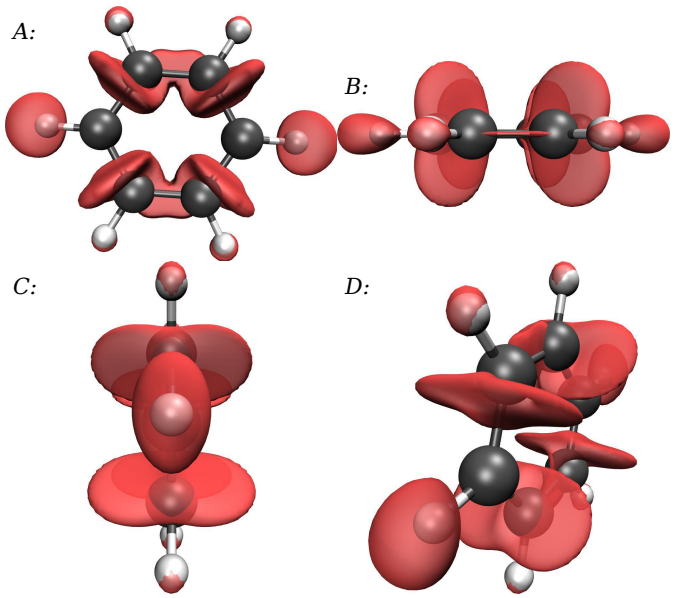


Figure 4: *Plot of the negative difference in spin density (beta, hole), plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

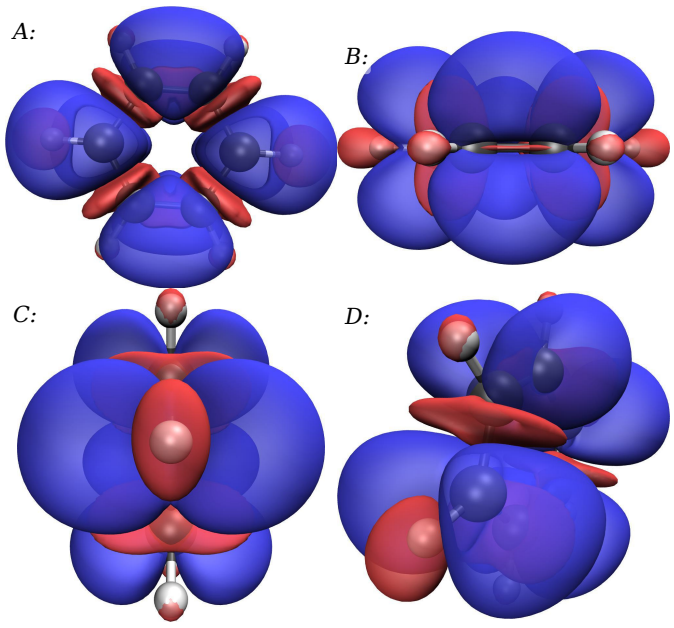


Figure 5: *Plot of the positive (alpha, electron, blue) and negative (beta, hole, red) difference in spin density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Geometry

The **empirical formula** of the studied system was $C_6H_6^-$, corresponding to a **molecular mass** of 78.11 $gmol^{-1}$ and an **exact mass**, considering only specific atomic isotopes, of 78.05 $gmol^{-1}$. The molecular geometry was aligned to the cartesian (X, Y and Z) axes by the **Minimal (MIN)** method. Using this method, the **extent of the molecular system** in the X, Y and Z axes (L_X, L_Y and L_Z, corresponding to the molecular width, length and height respectively) was determined to be 5.04, 4.51 and 0.00 Å respectively. These extensions give rise to a **molecular linearity ratio** (1-(L_Y/L_X)) and **planarity ratio** (1-(L_X/L_Y)) of 0.11 and 1.00 respectively.

Permanent Dipole Moment

The calculated **permanent dipole moment** was exactly 0 D.

Molecular Orbitals

In total, 240 singly occupied molecular orbitals were calculated, divided into 22 alpha occupied orbitals, 21 beta occupied orbitals, 98 alpha unoccupied (or virtual) orbitals and 99 beta unoccupied orbitals. The calculated energies of the **alpha and beta HOMOs** were 3.83 and -0.02 eV respectively, while the energies of the **alpha and beta LUMOs** were 6.27 and 6.34 eV. These values correspond to a calculated **HOMO-LUMO band gap** of 2.44 and 6.36 eV for the alpha and beta case respectively (figures 12). Plots of the orbital density for the HOMO (beta), HOMO (alpha), LUMO (alpha) and LUMO (beta) are shown in figures 6-9 respectively, while the orbital overlap between the HOMO and LUMO is shown in figures 10 and 11 (alpha and beta respectively).

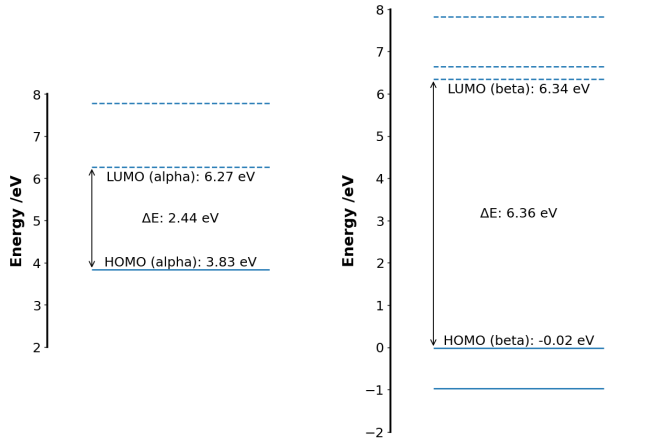


Figure 12: *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*

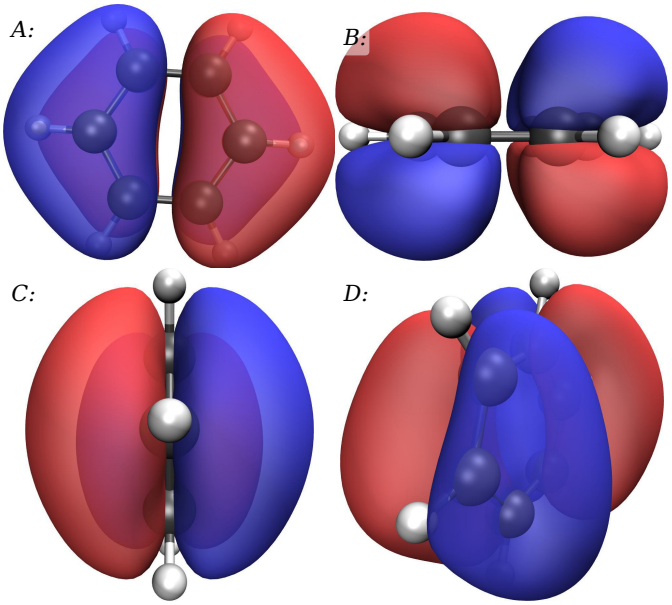


Figure 6: *Orbital density plots of the HOMO (beta), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

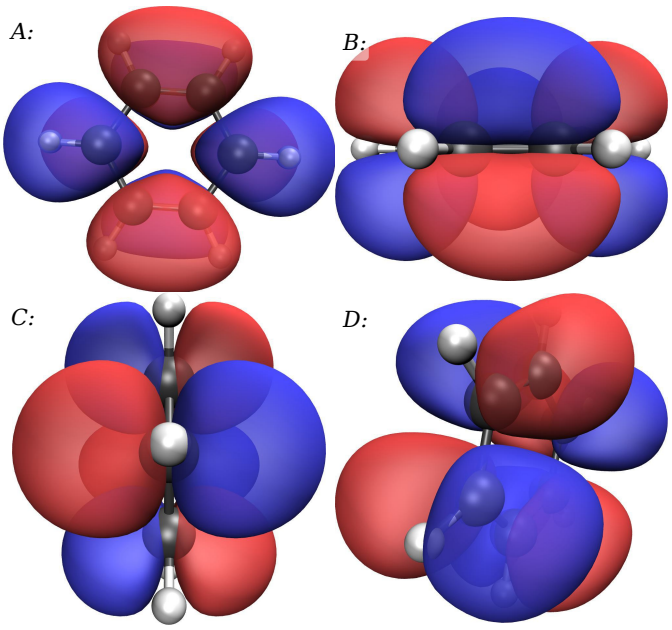


Figure 7: *Orbital density plots of the HOMO (alpha), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

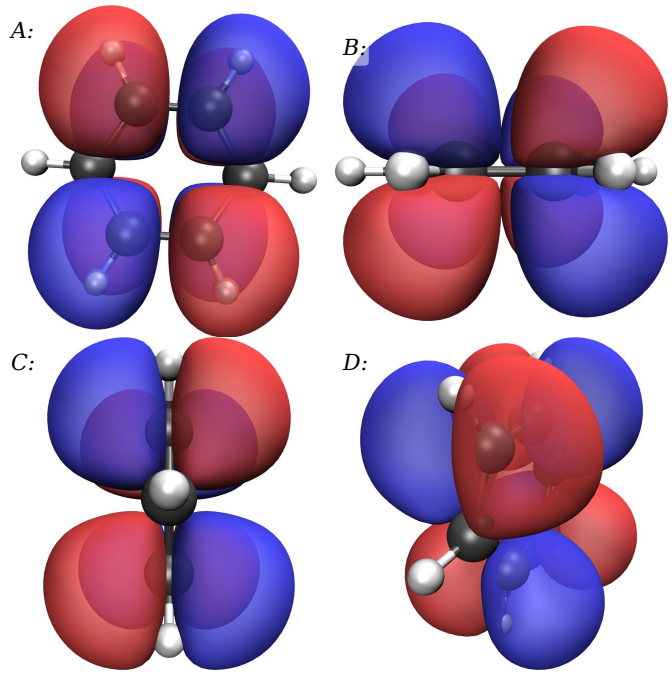


Figure 8: *Orbital density plots of the LUMO (alpha), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

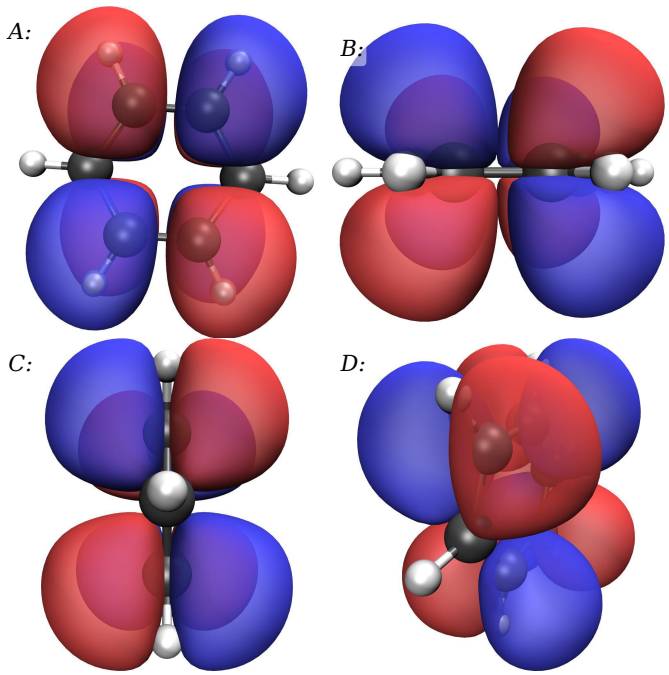


Figure 9: *Orbital density plots of the LUMO (beta), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

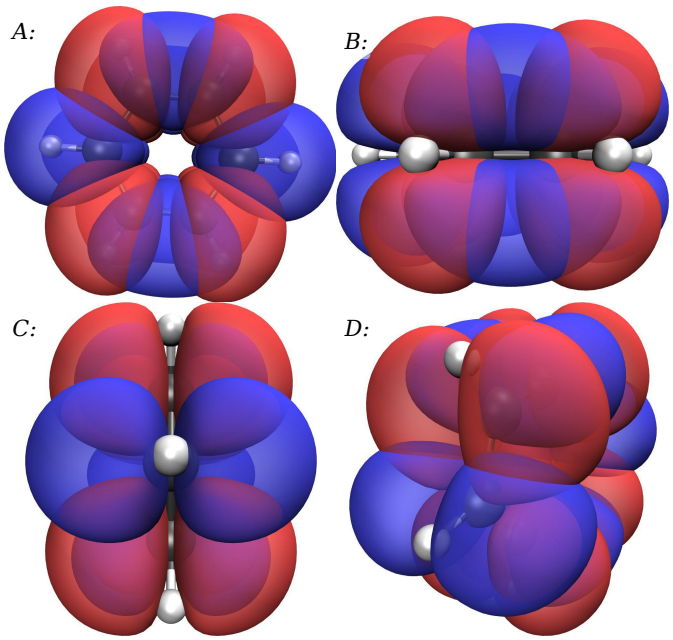


Figure 10: *Orbital density plots of the alpha HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

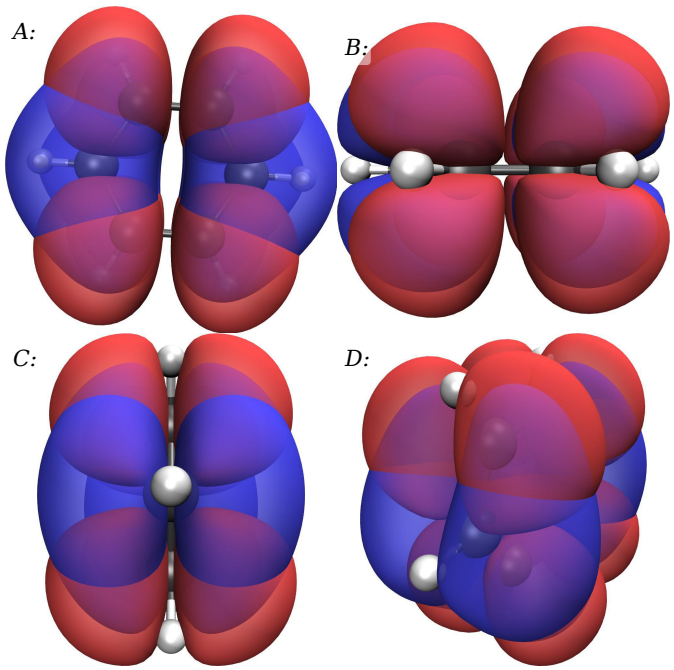


Figure 11: *Orbital density plots of the beta HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Vibrational Frequencies

The energies of a total of 30 vibrational transitions were calculated and vibrational absorption peaks were simulated using a gaussian function with full-width at half maximum (FHWM) of 80 cm^{-1}. From this analysis the **five most intense vibrational peaks** were found at -220, 646, 940, 1402 and 3141 cm^{-1}. The full simulated vibrational frequency spectrum is shown in figure 13. Finally there were two **calculated negative frequencies**.

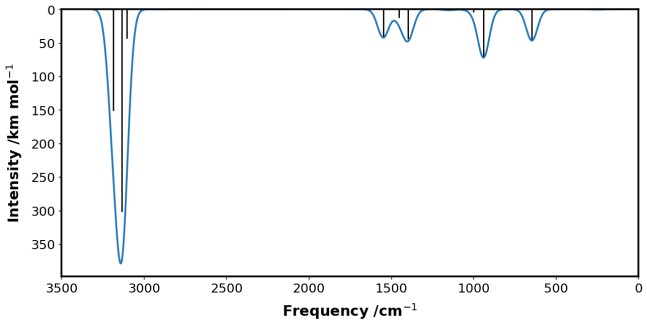


Figure 13: *Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vetical black bars while simulated peaks with a gaussian function with FHWM: 80 cm^{-1} are shown as a blue line. Peaks can be found at: -220, 242, 646, 940, 1149, 1402, 1548 and 3141 cm^{-1}.*

Tables Of Results

Atom Coordinates

Table 7: *Coordinates of the atoms of the system under study, as aligned to the cartesian axes by the Minimal method.*

Element	X Coord /Å	Y Coord /Å	Z Coord /Å
C	-1.4360800	0.0964170	-0.0000050
C	-0.7678990	-1.1729720	-0.0000330
C	0.6034130	-1.2662280	0.0000420
C	1.4360800	-0.0964130	-0.0000160
C	0.7679010	1.1729710	-0.0000340
C	-0.6034150	1.2662260	0.0000430
H	-2.5203110	0.1691460	-0.0001060
H	-1.3622100	-2.0901160	-0.0000400
H	1.0688330	-2.2548880	0.0001390
H	2.5203100	-0.1691580	-0.0000640
H	1.3622030	2.0901200	-0.0000390
H	-1.0688250	2.2548910	0.0001390

Molecular Orbitals

Table 8: *Energies of the calculated molecular orbitals.*

Level	Label	Symmetry	Energy / eV	Label	Symmetry	Energy / eV
38	LUMO+15 (alpha)	A	20.8573	LUMO+16 (beta)	A	20.9495
37	LUMO+14 (alpha)	A	20.6385	LUMO+15 (beta)	A	20.9473
36	LUMO+13 (alpha)	A	20.4352	LUMO+14 (beta)	A	20.7661
35	LUMO+12 (alpha)	A	18.8390	LUMO+13 (beta)	A	18.9111
34	LUMO+11 (alpha)	A	14.6035	LUMO+12 (beta)	A	14.6601
33	LUMO+10 (alpha)	A	14.0237	LUMO+11 (beta)	A	14.1611
32	LUMO+9 (alpha)	A	13.9929	LUMO+10 (beta)	A	14.0343
31	LUMO+8 (alpha)	A	13.6315	LUMO+9 (beta)	A	13.8076
30	LUMO+7 (alpha)	A	10.1686	LUMO+8 (beta)	A	10.7997
29	LUMO+6 (alpha)	A	10.1605	LUMO+7 (beta)	A	10.2669
28	LUMO+5 (alpha)	A	10.0720	LUMO+6 (beta)	A	10.2473
27	LUMO+4 (alpha)	A	9.8935	LUMO+5 (beta)	A	10.2149
26	LUMO+3 (alpha)	A	9.3822	LUMO+4 (beta)	A	9.4530
25	LUMO+2 (alpha)	A	9.0628	LUMO+3 (beta)	A	9.0747
24	LUMO+1 (alpha)	A	7.7748	LUMO+2 (beta)	A	7.8181
23	**LUMO (alpha)**	**A**	**6.2681**	LUMO+1 (beta)	A	6.6480
22	**HOMO (alpha)**	**A**	**3.8325**	**LUMO (beta)**	**A**	**6.3427**
21	HOMO-1 (alpha)	A	-1.1374	**HOMO (beta)**	**A**	**-0.0158**
20	HOMO-2 (alpha)	A	-1.3600	HOMO-1 (beta)	A	-0.9791
19	HOMO-3 (alpha)	A	-3.2548	HOMO-2 (beta)	A	-3.1897
18	HOMO-4 (alpha)	A	-3.7837	HOMO-3 (beta)	A	-3.6115
17	HOMO-5 (alpha)	A	-4.1682	HOMO-4 (beta)	A	-3.7103
16	HOMO-6 (alpha)	A	-5.4964	HOMO-5 (beta)	A	-5.4034
15	HOMO-7 (alpha)	A	-5.6777	HOMO-6 (beta)	A	-5.6268
14	HOMO-8 (alpha)	A	-6.0235	HOMO-7 (beta)	A	-5.9549
13	HOMO-9 (alpha)	A	-7.1770	HOMO-8 (beta)	A	-7.0140
12	HOMO-10 (alpha)	A	-8.4516	HOMO-9 (beta)	A	-8.3768
11	HOMO-11 (alpha)	A	-10.4867	HOMO-10 (beta)	A	-10.4541
10	HOMO-12 (alpha)	A	-10.9207	HOMO-11 (beta)	A	-10.5300
9	HOMO-13 (alpha)	A	-14.2971	HOMO-12 (beta)	A	-13.9548
8	HOMO-14 (alpha)	A	-14.7608	HOMO-13 (beta)	A	-14.6269
7	HOMO-15 (alpha)	A	-17.2893	HOMO-14 (beta)	A	-17.0904
6	HOMO-16 (alpha)	A	-271.8910	HOMO-15 (beta)	A	-271.7030

Vibrational Frequencies

Table 9: *Energies of the calculated vibrational frequencies.*

Number	Symmetry	Frequency /cm^{-1}	Intensity /km mol^{-1}
1	A	-299.1199	0.0006
2	A	-220.1211	64.4413
3	A	157.4867	0.0000
4	A	242.2175	0.4047
5	A	444.8093	0.0072
6	A	565.2478	0.0000
7	A	622.3455	0.0000
8	A	646.6220	46.6961
9	A	651.6166	0.0010
10	A	717.1228	0.0000
11	A	863.0493	0.0000
12	A	863.6642	0.0006
13	A	939.5250	71.2484
14	A	985.5880	0.0000
15	A	1000.6886	4.1103
16	A	1042.7355	0.0149
17	A	1149.3141	1.3956
18	A	1190.9143	0.0000
19	A	1268.9169	0.0000
20	A	1340.3245	0.0000
21	A	1398.2403	44.4296
22	A	1453.7231	12.4799
23	A	1548.7904	41.9984
24	A	1685.9705	0.0000

25	A	3098.0460	0.0000	28	A	3135.3627	301.9398
26	A	3104.1485	43.6269	29	A	3188.4116	150.9304
27	A	3133.5420	0.0000	30	A	3197.2484	0.0000

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