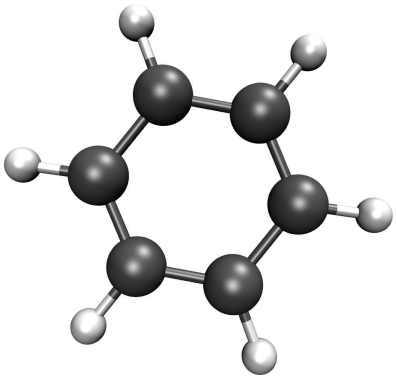
A Report On The Calculation Of The Optimised Structure And Vibrational Frequencies Of Benzene At The PBE0/6-31G** Level

osl - 24th 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 Turbomole software package at the PBE0/6-31G** level of theory. The total self-consistent field (SCF) energy of the system was found to be -6310.46 eV after 24 steps. The alpha and beta highest-occupied molecular orbitals (HOMO) were calculated to be 3.83 and 0.00 eV respectively, while the alpha and beta lowest-unoccupied molecular orbitals (LUMO) were 6.28 and 6.39 eV. These values correspond to a calculated HOMO-LUMO band gap of 2.45 and 6.38 eV for the alpha and beta case respectively. The permanent dipole moment (PDM) was calculated to be 0.04 D. The most intense vibrational frequencies were calculated to be at 329, 575, 931, 1516 and 3165 cm^{-1}, and there were zero 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
24/06/2022 12:21:56	2 m, 12 s	**True** (**True**)	Turbomole (7.5.0)	PBE0/6-31G**	Optimisation, Frequencies	unrestricted	2 (doublet)	N/A	N/A

Summary Of Results

Scf Energy

Table 2: *Summary of SCF energy properties.*

No. of steps	24
Final energy	-6310.4572 eV
Final energy	-608,867 $kJ \cdot mol^{-1}$

Geometry

Table 3: *Summary of geometry properties.*

Formula	$C_6H_6^-$
Molar mass	78.1118 $g \cdot mol^{-1}$
Alignment method	Minimal
X extension	4.98 Å
Y extension	4.72 Å
Z extension	0.05 Å
Linearity ratio	0.05
Planarity ratio	0.99

Alpha Orbitals

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

$E_{HOMO,LUMO}$	2.45 eV
E_{HOMO}	3.83 eV
E_{LUMO}	6.28 eV

Beta Orbitals

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

$E_{HOMO,LUMO}$	6.38 eV
E_{HOMO}	0.00 eV
E_{LUMO}	6.39 eV

Permanent Dipole Moment

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

Total	0.04 D
X axis angle	49.10 °
XY plane angle	4.17 °

Vibrations

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

No. frequencies	30
Simulated peaks	329, 575, 931, 1516 and 3165 ... cm^{-1}
No. negative frequencies	**0**
Negative frequencies	N/A

Methodology

Metadata

The calculation of the optimised structure and vibrational frequencies was performed using the **Turbomole (7.5.0)** program, the **DFT** method with the **PBE0** functional and the **6-31G**** basis set. It was completed on the **24th June 2022** after a total duration of **2 m, 12 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 24 steps, the results of which are displayed in figure 1. The energy calculated by the final step was -6310.46 eV, corresponding to -608,867 KJmol^{-1}. A plot of the total SCF electron density is shown in figure 2.

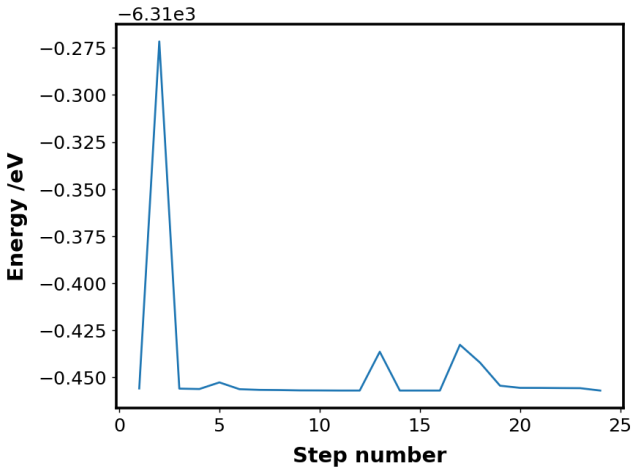


Figure 1: *Graph of calculated energies at the self-consistent field (SCF) level.*

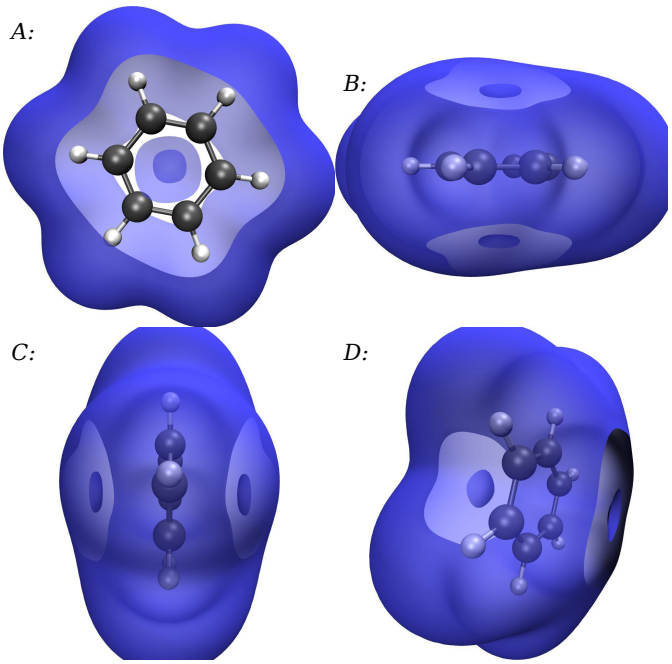


Figure 2: *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

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.

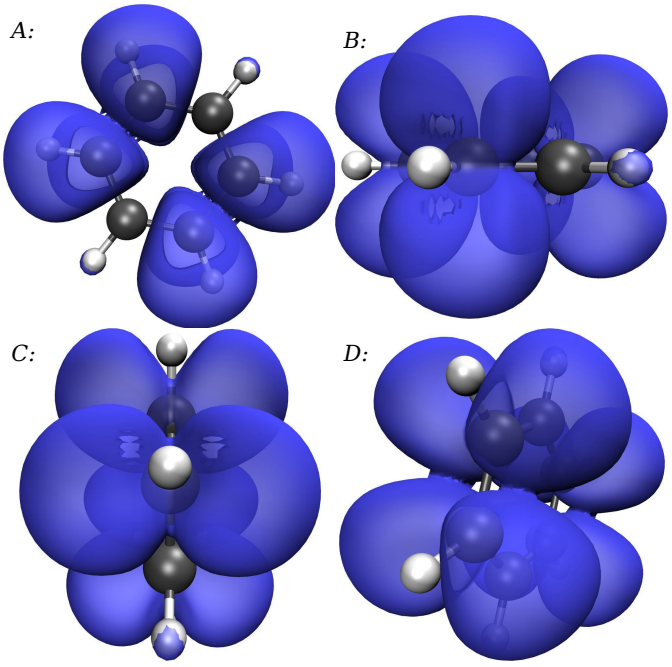


Figure 3: *Plot of the positive difference in spin density (alpha, electron), plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

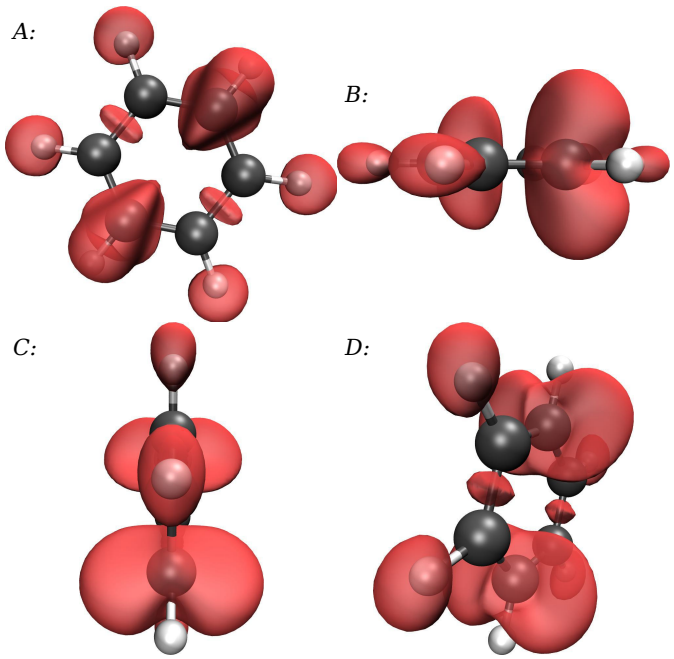


Figure 4: *Plot of the negative difference in spin density (beta, hole), plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

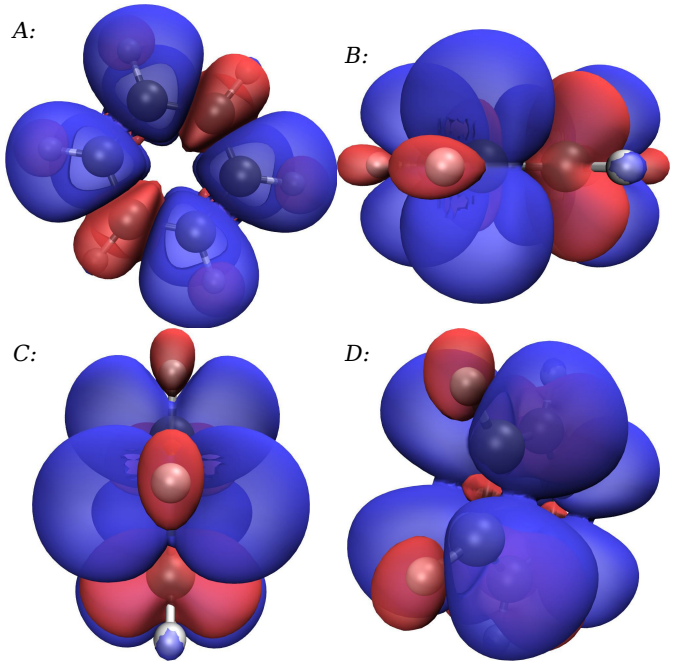


Figure 5: *Plot of the positive (alpha, electron, blue) and negative (beta, hole, red) difference in spin density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Geometry

The **empirical formula** of the studied system was $C_6H_6^-$, corresponding to a **molecular mass** of 78.11 $gmol^{-1}$. 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 4.98, 4.72 and 0.05 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 0.05 and 0.99 respectively.

Permanent Dipole Moment

The calculated **permanent dipole moment** was 0.04 D, with a vector (x,y,z) of -0.02, 0.03, -0.00 D. The angle between the dipole moment vector and the x-axis was 49.10 °, while the angle between the dipole moment and the xy-plane was 4.17 °. A plot of the permanent dipole moment is shown in figure 6.

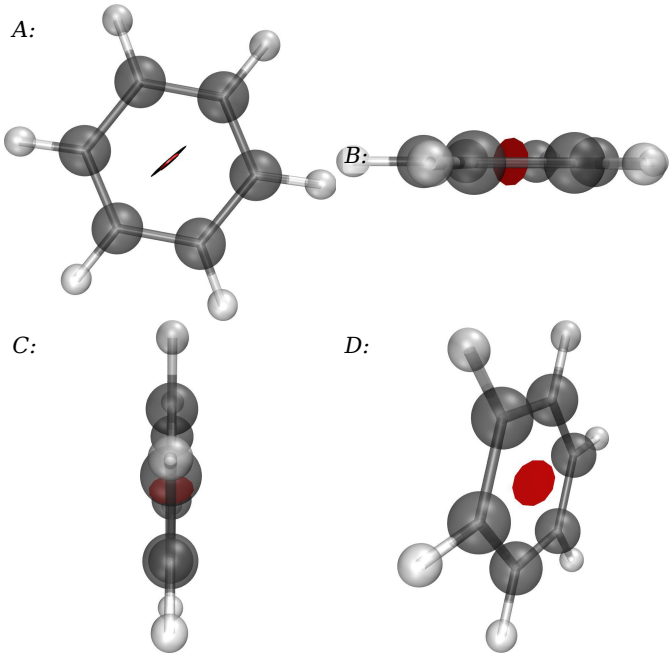


Figure 6: *The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Molecular Orbitals

In total, 228 singly occupied molecular orbitals were calculated, divided into 22 alpha occupied orbitals, 21 beta occupied orbitals, 92 alpha unoccupied (or virtual) orbitals and 93 beta unoccupied orbitals. The calculated energies of the **alpha and beta HOMOs** were 3.83 and 0.00 eV respectively, while the energies of the **alpha and beta LUMOs** were 6.28 and 6.39 eV. These values correspond to a calculated **HOMO-LUMO band gap** of 2.45 and 6.38 eV for the alpha and beta case respectively (figures 13). Plots of the orbital density for the HOMO (beta), HOMO (alpha), LUMO (alpha) and LUMO (beta) are shown in figures 7-10 respectively, while the orbital overlap between the HOMO and LUMO is shown in figures 11 and 12 (alpha and beta respectively).

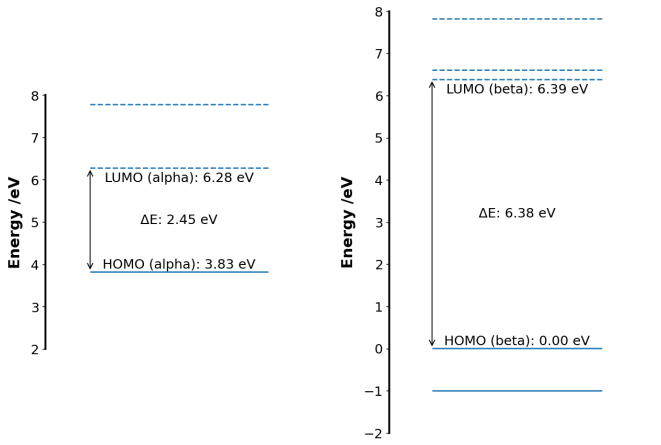


Figure 13: *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*

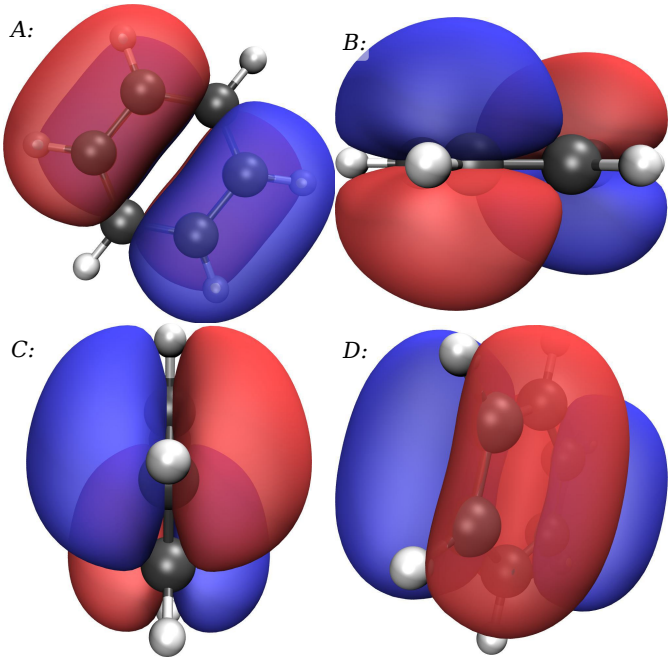


Figure 7: *Orbital density plots of the HOMO (beta), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

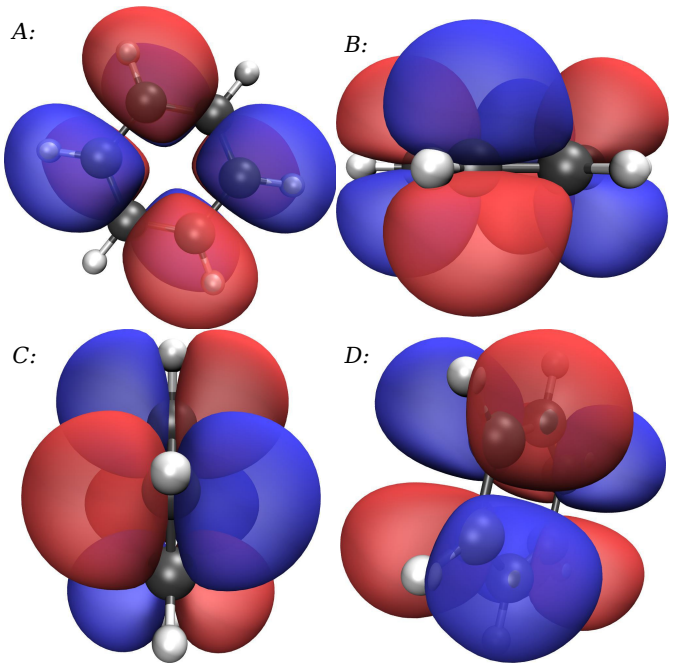


Figure 8: *Orbital density plots of the HOMO (alpha), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

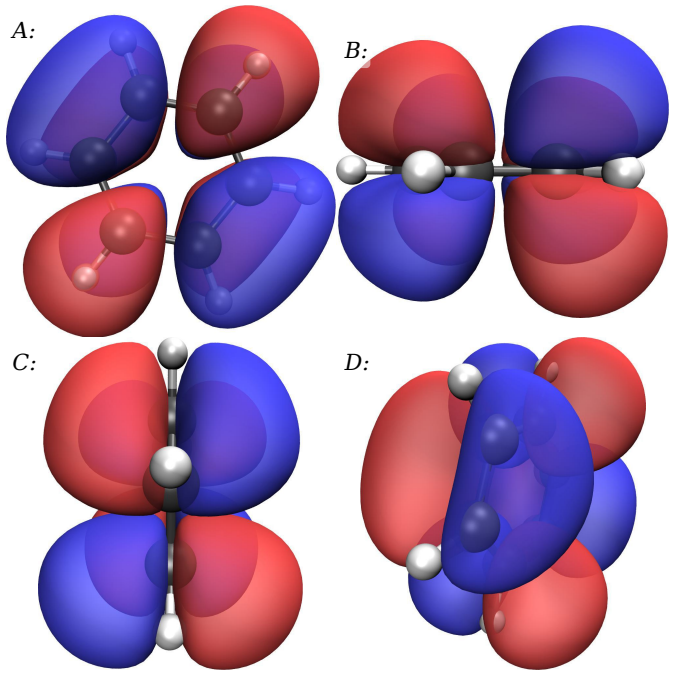


Figure 9: *Orbital density plots of the LUMO (alpha), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

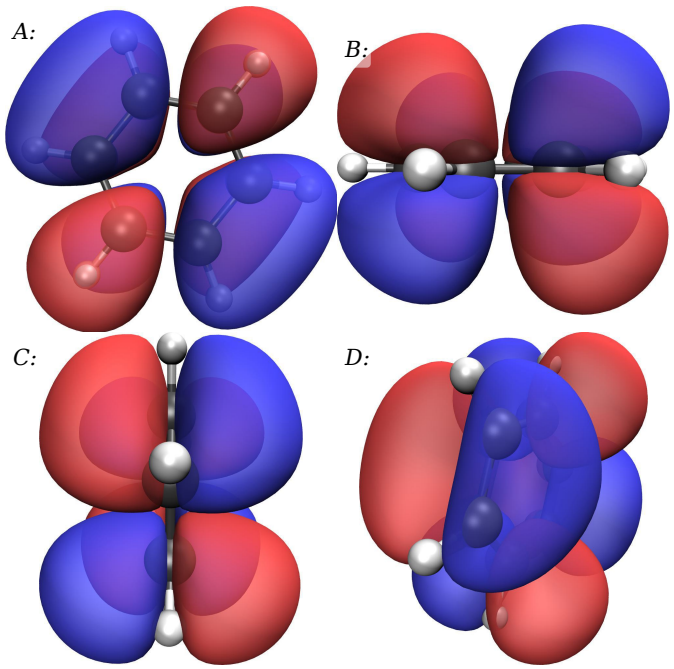


Figure 10: *Orbital density plots of the LUMO (beta), plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

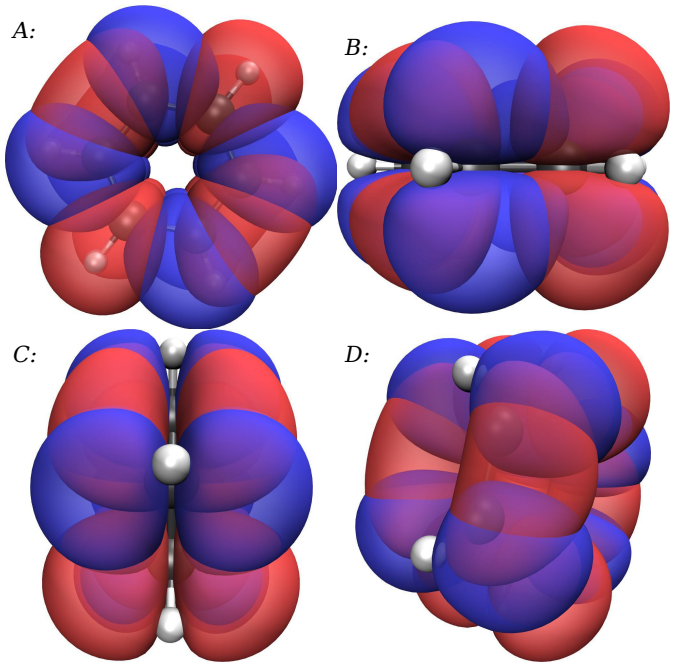


Figure 11: *Orbital density plots of the alpha HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

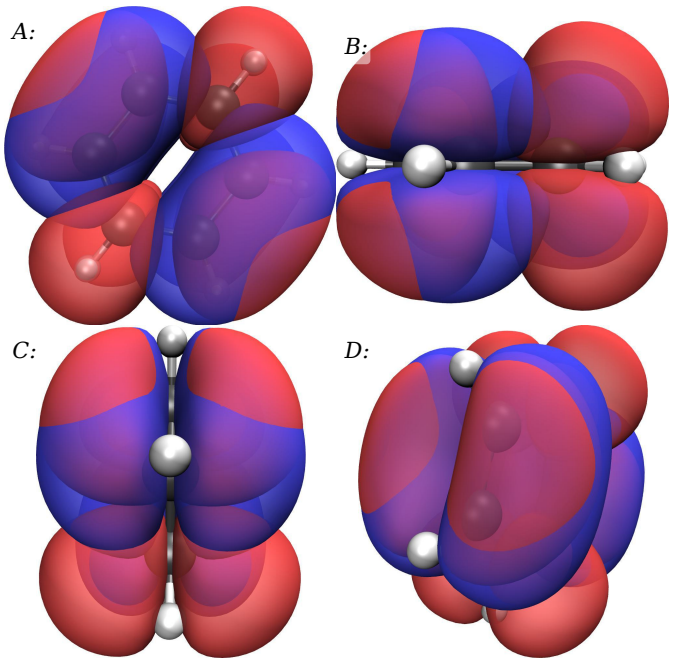


Figure 12: *Orbital density plots of the beta HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

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 329, 575, 931, 1516 and 3165 cm^{-1}. The full simulated vibrational frequency spectrum is shown in figure 14. Finally there were zero **calculated negative frequencies**.

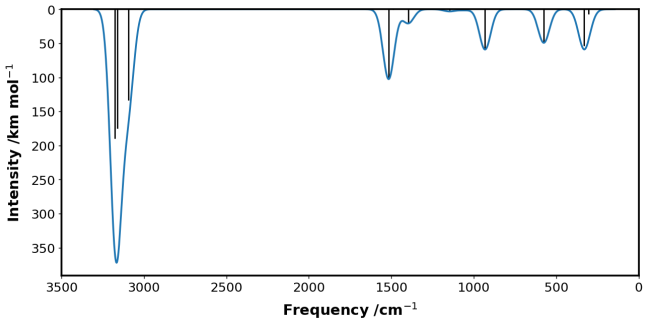


Figure 14: *Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vetical black bars while simulated peaks with a gaussian function with FHWM: 80 cm^{-1} are shown as a blue line. Peaks can be found at: 329, 575, 931, 1060, 1145, 1399, 1516 and 3165 cm^{-1}.*

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	1.4169241	-0.2092420	0.0058053
C	0.5002493	-1.3420930	-0.0092482
C	-0.8696348	-1.0889060	-0.0138056
C	-1.4073637	0.1982578	-0.0046956
C	-0.4906871	1.3311115	0.0101902
C	0.8791979	1.0779217	0.0148167
H	2.4949251	-0.3614925	0.0095117
H	0.8751772	-2.3642463	-0.0163120
H	-1.5571891	-1.9411002	-0.0250246
H	-2.4853611	0.3505124	-0.0092797
H	-0.8656171	2.3532591	0.0179698
H	1.5667493	1.9301175	0.0261019

Molecular Orbitals

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

Level	Label	Symmetry	Energy / eV	Label	Symmetry	Energy / eV
38	LUMO+15 (alpha)	A	20.8419	LUMO+16 (beta)	A	20.9823
37	LUMO+14 (alpha)	A	20.6414	LUMO+15 (beta)	A	20.9339
36	LUMO+13 (alpha)	A	20.4394	LUMO+14 (beta)	A	20.7688
35	LUMO+12 (alpha)	A	18.8435	LUMO+13 (beta)	A	18.9156
34	LUMO+11 (alpha)	A	14.5989	LUMO+12 (beta)	A	14.6539
33	LUMO+10 (alpha)	A	14.0413	LUMO+11 (beta)	A	14.1639
32	LUMO+9 (alpha)	A	14.0251	LUMO+10 (beta)	A	14.0768
31	LUMO+8 (alpha)	A	13.5835	LUMO+9 (beta)	A	13.7651
30	LUMO+7 (alpha)	A	10.1823	LUMO+8 (beta)	A	10.7969
29	LUMO+6 (alpha)	A	10.1712	LUMO+7 (beta)	A	10.2684
28	LUMO+5 (alpha)	A	10.0530	LUMO+6 (beta)	A	10.2415
27	LUMO+4 (alpha)	A	9.8948	LUMO+5 (beta)	A	10.2233
26	LUMO+3 (alpha)	A	9.3798	LUMO+4 (beta)	A	9.4586
25	LUMO+2 (alpha)	A	9.0680	LUMO+3 (beta)	A	9.0742
24	LUMO+1 (alpha)	A	7.7818	LUMO+2 (beta)	A	7.8245
23	**LUMO (alpha)**	**A**	**6.2757**	LUMO+1 (beta)	A	6.6032
22	**HOMO (alpha)**	**A**	**3.8253**	**LUMO (beta)**	**A**	**6.3875**
21	HOMO-1 (alpha)	A	-1.1278	**HOMO (beta)**	**A**	**0.0035**
20	HOMO-2 (alpha)	A	-1.3676	HOMO-1 (beta)	A	-0.9948
19	HOMO-3 (alpha)	A	-3.2454	HOMO-2 (beta)	A	-3.1799
18	HOMO-4 (alpha)	A	-3.7915	HOMO-3 (beta)	A	-3.6112
17	HOMO-5 (alpha)	A	-4.1658	HOMO-4 (beta)	A	-3.7183
16	HOMO-6 (alpha)	A	-5.4369	HOMO-5 (beta)	A	-5.3397
15	HOMO-7 (alpha)	A	-5.7879	HOMO-6 (beta)	A	-5.7684
14	HOMO-8 (alpha)	A	-5.9674	HOMO-7 (beta)	A	-5.8700
13	HOMO-9 (alpha)	A	-7.1742	HOMO-8 (beta)	A	-7.0124
12	HOMO-10 (alpha)	A	-8.4458	HOMO-9 (beta)	A	-8.3708
11	HOMO-11 (alpha)	A	-10.4704	HOMO-10 (beta)	A	-10.4269
10	HOMO-12 (alpha)	A	-10.9305	HOMO-11 (beta)	A	-10.5491
9	HOMO-13 (alpha)	A	-14.3088	HOMO-12 (beta)	A	-13.9481
8	HOMO-14 (alpha)	A	-14.7385	HOMO-13 (beta)	A	-14.6226
7	HOMO-15 (alpha)	A	-17.2797	HOMO-14 (beta)	A	-17.0821
6	HOMO-16 (alpha)	A	-271.9499	HOMO-15 (beta)	A	-271.8150

Vibrational Frequencies

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

Number	Symmetry	Frequency /cm^{-1}	Intensity /km mol^{-1}
1	A	263.6800	0.0000
2	A	271.7900	0.0200
3	A	302.7500	7.5100
4	A	332.2100	53.6200
5	A	457.5000	0.0000
6	A	489.4700	0.0000
7	A	575.0600	49.2700
8	A	613.8100	0.0000
9	A	639.2500	0.0000
10	A	692.3400	0.0000
11	A	880.0000	0.1400
12	A	905.0800	0.0000
13	A	931.3800	59.0500
14	A	984.1200	0.0000
15	A	995.8600	0.1300
16	A	1057.9600	1.4800
17	A	1146.9700	3.1400
18	A	1150.1900	0.0000
19	A	1290.4800	0.0000
20	A	1340.5200	0.0000
21	A	1397.2500	20.6200
22	A	1489.6200	0.6200
23	A	1516.0100	102.0900
24	A	1568.0200	0.0000

25	A	3094.2700	133.9900	28	A	3162.1900	174.8000
26	A	3097.0400	0.0000	29	A	3174.7500	190.1700
27	A	3145.4900	0.0000	30	A	3189.1200	0.0000

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