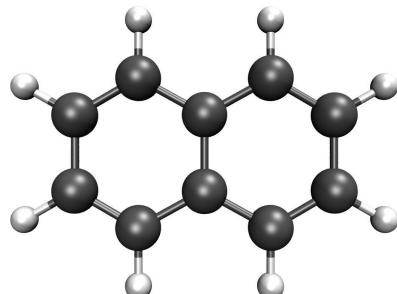




A Report On The Calculation Of The Optimised Structure, Vibrational Frequencies And Excited States Of Naphthalene At The PBE1PBE/6-31G(d,p) Level

osl - 07th June 2022



Abstract

The calculation of optimised structure, vibrational frequencies and excited states for the system 'Naphthalene' is presented, accompanied by automated analysis and image generation provided by the Silico software package. The calculations were performed using the Gaussian software package(s) at the PBE1PBE/6-31G(d,p) level of theory. The total self-consistent field (SCF) energy of the system was found to be -10488.99 eV after 5 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -6.13 and -0.92 eV respectively, corresponding to a HOMO-LUMO band gap of 5.21 eV. The permanent dipole moment (PDM) was calculated to be 0.00 D. The most intense vibrational frequencies were calculated to be at 487, 806, 1294, 1580 and 3224 cm⁻¹, and there were zero negative frequencies. In total, 20 excited states were calculated with singlet and triplet multiplicity. The most intense absorption peaks were calculated to be at 194 and 261 nm. The lowest energy singlet and triplet excited states (S_1 and T_1) were calculated to be 4.65 and 3.03 eV (266 and 409 nm) respectively, corresponding to a singlet/triplet splitting energy (ΔE_{ST}) of 1.62 eV.

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. [d]: Pressure used for thermochemistry analysis.

| Calculation no. | Date ^[a] | Duration ^[b] | Success (Converged) | Computational package | Level of theory | Calculations | Wavefunction | Multiplicity | T ^[c] / K | P ^[d] / atm |
|-----------------|------------------------|-------------------------|---------------------|-----------------------|--------------------|---|--------------|--------------|----------------------|------------------------|
| Combined | 07/06/2022 17:37:23 | 16 m, 7 s | True (True) | Gaussian (2016+C.01) | PBE1PBE/6-31G(d,p) | Optimisation, Frequencies, Excited States | restricted | 1 (singlet) | N/A | N/A |
| 1 | 07/06/2022 16:39:10 | 4 m, 57 s | True (True) | Gaussian (2016+C.01) | PBE1PBE/6-31G(d,p) | Optimisation, Frequencies | restricted | 1 (singlet) | 298.15 | 1.0 |
| 2 | 07/06/2022 16:48:19 | 4 m, 21 s | True (N/A) | Gaussian (2016+C.01) | PBE1PBE/6-31G(d,p) | Excited States | restricted | 1 (singlet) | N/A | N/A |
| 3 | 07/06/2022 17:37:23 | 6 m, 49 s | True (True) | Gaussian (2016+C.01) | PBE1PBE/6-31G(d,p) | Optimisation, Excited States | restricted | 1 (singlet) | N/A | N/A |

Summary Of Results

Scf Energy

Table 2: Summary of SCF energy properties.

| | |
|--------------|---------------------------------|
| No. of steps | 5 |
| Final energy | -10488.9903 eV |
| Final energy | -1,012,034 kJ·mol ⁻¹ |

Geometry

Table 3: Summary of geometry properties.

| | |
|------------------|--------------------------------|
| Formula | C ₁₀ H ₈ |
| Exact mass | 128.0626 g·mol ⁻¹ |
| Molar mass | 128.1705 g·mol ⁻¹ |
| Alignment method | Minimal |
| X extension | 6.74 Å |
| Y extension | 4.97 Å |
| Z extension | 0.00 Å |
| Linearity ratio | 0.26 |
| Planarity ratio | 1.00 |

Molecular Orbitals

Table 4: Summary of HOMO & LUMO properties.

| | |
|------------------------|----------|
| E _{HOMO,LUMO} | 5.21 eV |
| E _{HOMO} | -6.13 eV |

E_{LUMO} -0.92 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 ° |

S₁ Transition Dipole Moment

Table 6: Summary of the transition (S₁) dipole moment (TDM) properties μ : Electric TDM. m : Magnetic TDM. $\theta_{\mu,x}$ and $\theta_{m,x}$: Angle between μ or m and the x-axis. $\theta_{\mu,xy}$ and $\theta_{m,xy}$: Angle between μ or m and the xy-plane. $\theta_{\mu,m}$: Angle between the electric and magnetic TDM. g_{lum} : Dissymmetry factor.

| | |
|----------------------|------------------------------|
| μ | 0.07 D |
| $\theta_{\mu,x}$ | 0.00 ° |
| $\theta_{\mu,xy}$ | 0.00 ° |
| $m^{[d]}$ | 0.00 a.u. |
| $\theta_{m,x}$ | 0.00 ° |
| $\theta_{m,xy}$ | 0.00 ° |
| μ (Gaussian-CGS) | 6.74e-20 esu·cm |
| m (Gaussian-CGS) | 0.00e+00 erg·G ⁻¹ |
| | 90.00 ° |

| | |
|------------------------|-------|
| $\theta_{\mu,m}$ | |
| $\cos(\theta_{\mu,m})$ | 0.00 |
| g_{lum} | 0.000 |

Vibrations

Table 7: Summary of the properties of the calculated vibration frequencies.

| | |
|--------------------------|--|
| No. frequencies | 48 |
| Simulated peaks | 487, 806, 1294, 1580 and 3224 ... cm ⁻¹ |
| No. negative frequencies | 0 |
| Negative frequencies | N/A |

Excited States

Table 8: Summary of the calculated excited states. E_x : The energy of excited state x . λ_x : The wavelength of a photon of equivalent energy to excited state x . f_x : The oscillator strength of the excited state transition x . ΔE_{xy} : The difference in energy between the lowest excited states of multiplicity x and y .

| | |
|-------------------------------|-------------------------------------|
| No. calculated singlets | 10 |
| E_{S_1} | 4.65 eV |
| λ_{S_1} (colour, CIE) | 266 nm (Ultraviolet ■ (0.00, 0.00)) |
| f_{S_1} | < 0.01 |
| No. calculated triplets | 10 |
| E_{T_1} | 3.03 eV |
| λ_{T_1} (colour, CIE) | 409 nm (Violet ■ (0.17, 0.00)) |
| f_{T_1} | 0.00 |
| ΔE_{ST} | 1.62 eV |
| Simulated Absorption Peaks | 194 and 261 nm |

Adiabatic S₁ Emission

Table 9: Summary of the adiabatic emission from the S₁ state.

| | |
|---|-------------------------------------|
| Excited energy | -10484.45 eV |
| Excited multiplicity | Singlet |
| Ground energy | -10488.99 eV |
| Ground multiplicity | Singlet |
| Emission type | Fluorescence |
| S ₁ energy | 4.54 eV |
| S ₁ wavelength (colour, CIE) | 273 nm (Ultraviolet ■ (0.00, 0.00)) |
| S ₁ oscillator strength | 0.00 |
| S ₁ rate | 3.13e+05 /s ¹ |

Vertical S₁ Emission

Table 10: Summary of the vertical emission from the S₁ state.

| | |
|----------------------|--------------|
| Excited energy | -10484.45 eV |
| Excited multiplicity | Singlet |
| Ground energy | -10488.88 eV |
| Ground multiplicity | Singlet |
| Emission type | Fluorescence |

| | |
|---|-------------------------------------|
| S ₁ energy | 4.44 eV |
| S ₁ wavelength (colour, CIE) | 279 nm (Ultraviolet ■ (0.00, 0.00)) |
| S ₁ oscillator strength | 0.00 |
| S ₁ rate | 2.91e+05 /s ¹ |

Methodology

Metadata

This report was generated from the combined results of three individual calculations. The individual metadata for each separate calculation are presented in the following sections, and the overall calculation 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 **07th June 2022** after a total duration of **16 m, 7 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals. The full calculation metadata is tabulated in table 1.

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 **07th June 2022** after a total duration of **4 m, 57 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

The calculation of the excited states 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 **07th June 2022** after a total duration of **4 m, 21 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

The calculation of the optimised structure and excited states 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 **07th June 2022** after a total duration of **6 m, 49 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

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 Commission internationale de l'éclairage (CIE) coordinates, along with visual representations of the equivalent colour, were calculated using the Colour Science library.³ Emission rate constants (k_e) were calculated according to the method developed by Shizu and Kaji⁴ as described by formula 1, where ΔE_e is the energy of emission, ϵ_0 is the vacuum permittivity constant, \hbar is the reduced Planck constant (the Dirac constant), c is the speed of light and μ_e is the transition dipole moment of the emission.

$$k_e = \frac{4 \Delta E_e}{3 \epsilon_0 \hbar^4 c^3} \mu_e \quad 1$$

Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using Visual Molecular Dynamics (VMD)⁵ and the Tachyon ray-tracer.⁶ Finally, two-dimensional graphs were plotted using the Matplotlib library,⁷ while this report itself was prepared using the Mako template library⁸ and the Weasyprint library⁹, 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 -10488.99 eV, corresponding to -1,012,034 KJmol⁻¹. A plot of the total SCF electron density is shown in figure 2.

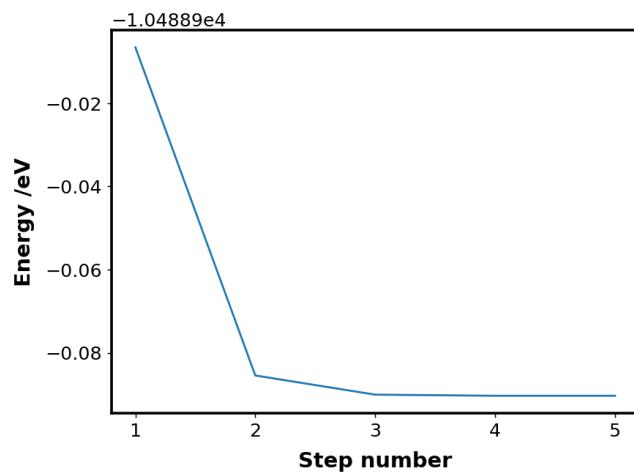


Figure 1: Graph of calculated energies at the self-consistent field (SCF) level.

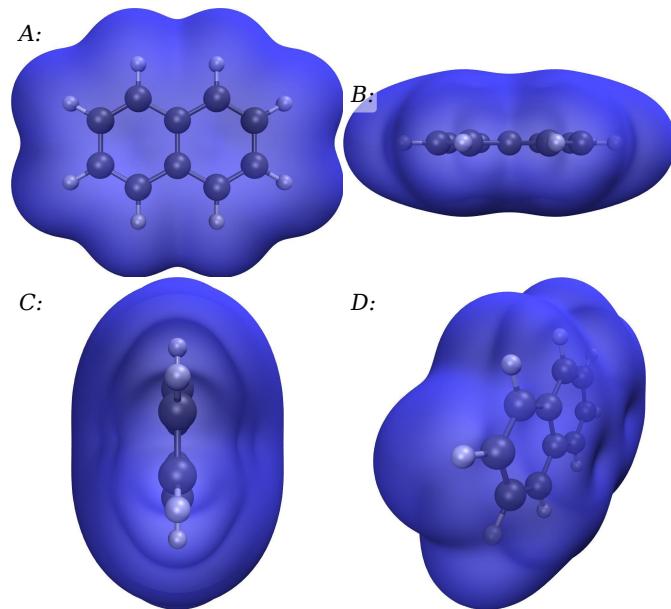


Figure 2: Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Geometry

The **empirical formula** of the studied system was C₁₀H₈, corresponding to a **molecular mass** of 128.17 gmol⁻¹ and an **exact mass**, considering only specific atomic isotopes, of 128.06 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 6.74, 4.97 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 0.26 and 1.00 respectively.

Permanent Dipole Moment

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

Transition (S₁) Dipole Moment

The calculated **electric (TEDM, μ)** and **magnetic (TMDM, m)** transition dipole moments between the ground state and the S₁ excited state were 0.07 D and 0.00 au respectively. The corresponding vector components (x,y,z) were $\mu = 0.07, -0.00, -0.00$ D and $m = 0.00, 0.00, 0.00$ au. In comparison to the molecular geometry, the angle between each dipole moment and the longest axis of the molecule (the x-axis) was $\theta_{\mu,x} = 0.00^\circ$ and $\theta_{m,x} = 0.00^\circ$, while the angle between each dipole moment and the xy-plane was $\theta_{\mu,xy} = 0.00^\circ$ and $\theta_{m,xy} = 0.00^\circ$. In Gaussian-CGS units, in which the magnetic and electric transition dipole moments can be directly compared, the magnitude of each dipole moment was $\mu = 6.74e-20$ esu·cm and $m = 0.00e+00$ erg·G⁻¹, while the **angle between the two dipole moments** was $\theta_{\mu,m} = 90.00^\circ$. Correspondingly, the cosine of the angle was $\cos(\theta_{\mu,m}) = 0.00$, and the **dissymmetry factor** of the excited state transition was $g_{lum} = 0.000$. A plot of the electric and magnetic transition dipole moments is shown in figure 3.

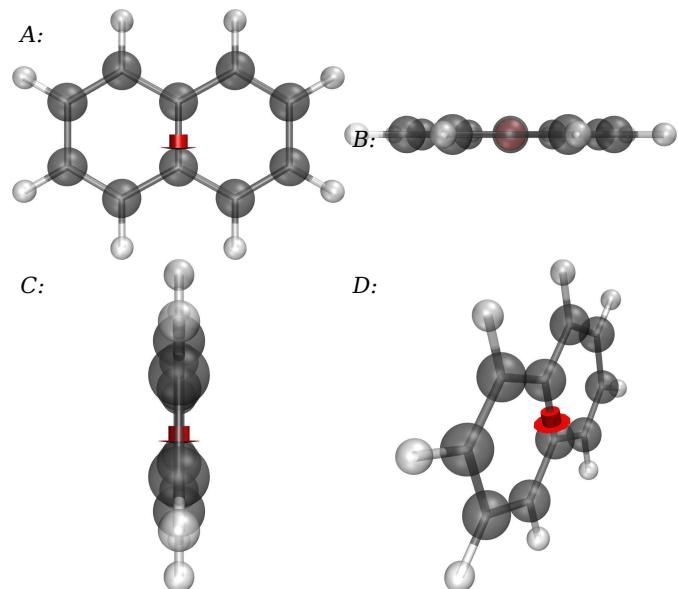


Figure 3: The electric (red arrow) and magnetic (green arrow) transition (S₁) dipole moment plotted against the aligned molecular geometry with a scale of 1 Å = 0.2 D = 0.1 au. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Molecular Orbitals

In total, 190 doubly occupied molecular orbitals were calculated, divided into 34 occupied orbitals and 156 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO** and **LUMO** were -6.13 and -0.92 eV respectively,

corresponding to a **HOMO-LUMO band gap** of 5.21 eV (figure 15). Plots of the orbital density for the HOMO-5, HOMO-4, HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+4 are shown in figures 4-10 and 12-14 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 11.

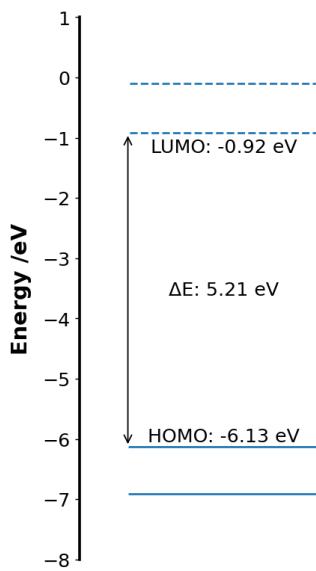


Figure 15: Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.

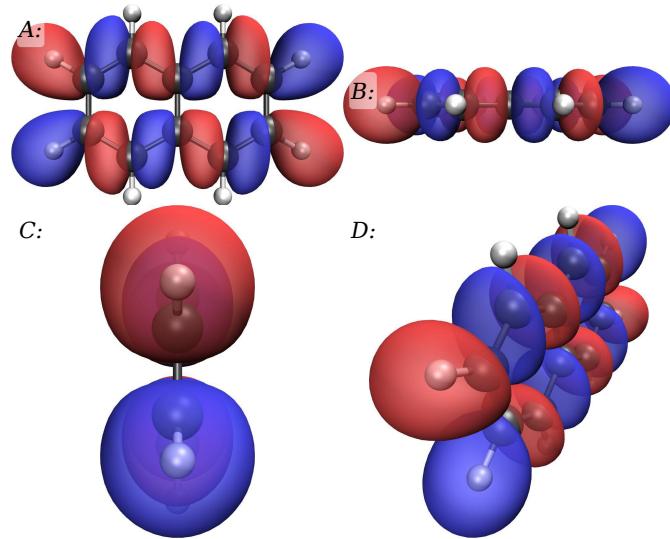


Figure 4: Orbital density plots of the HOMO-5, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

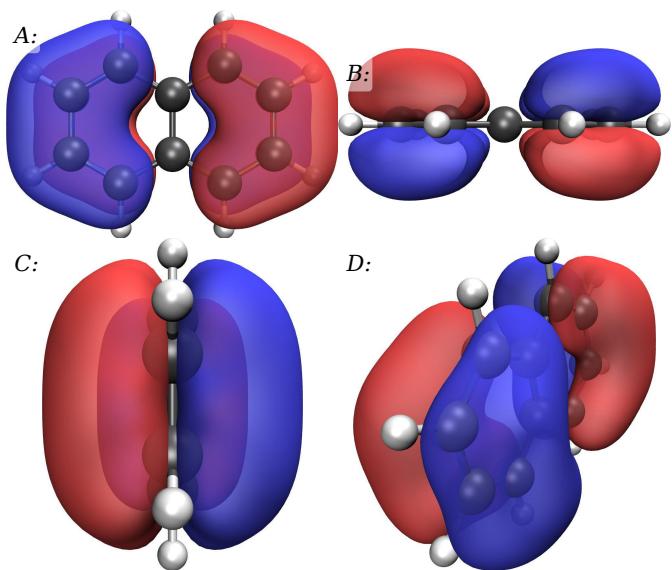


Figure 5: Orbital density plots of the HOMO-4, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

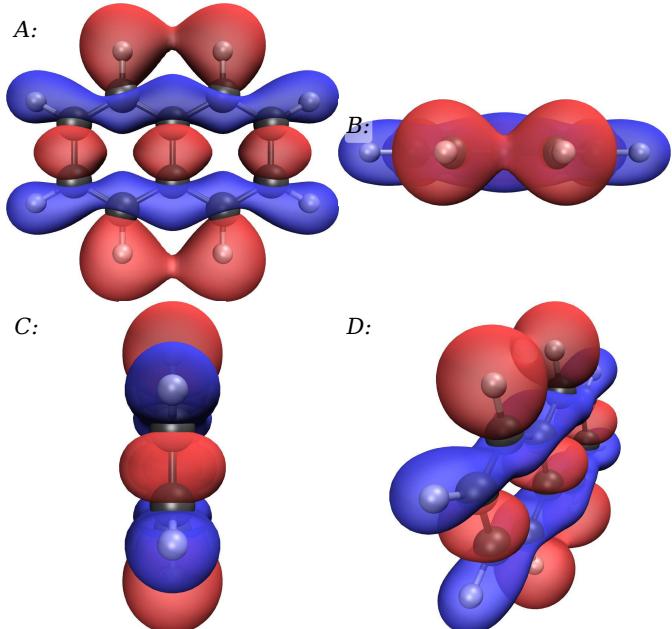


Figure 6: Orbital density plots of the HOMO-3, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

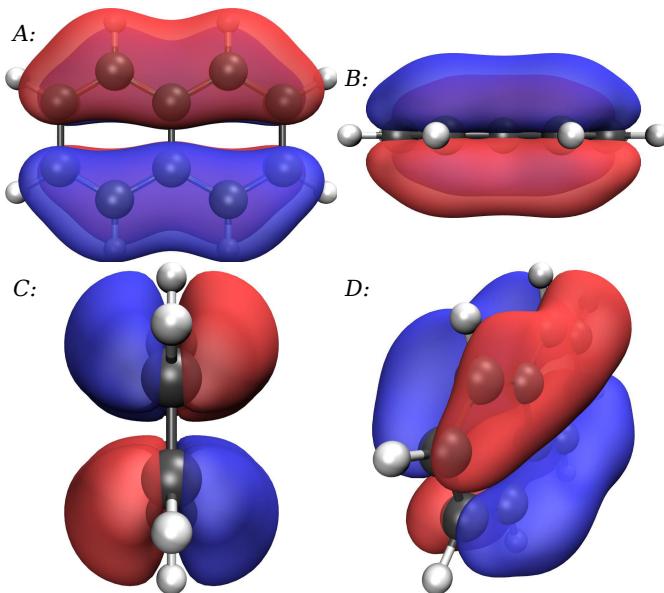


Figure 7: Orbital density plots of the HOMO-2, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

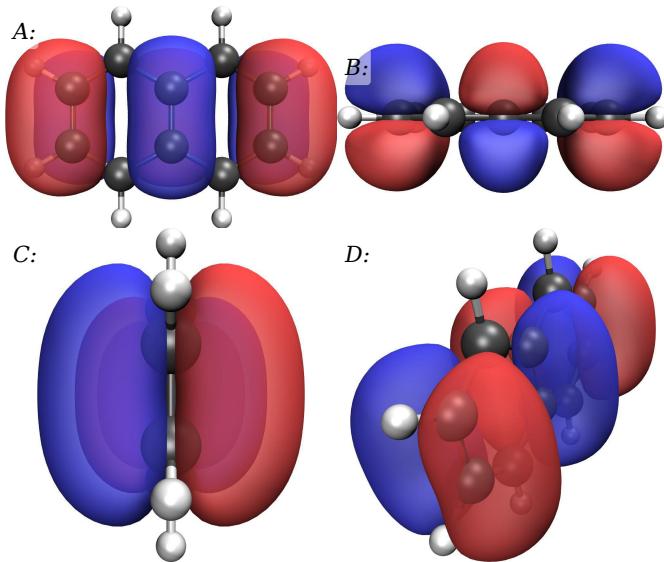


Figure 8: Orbital density plots of the HOMO-1, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

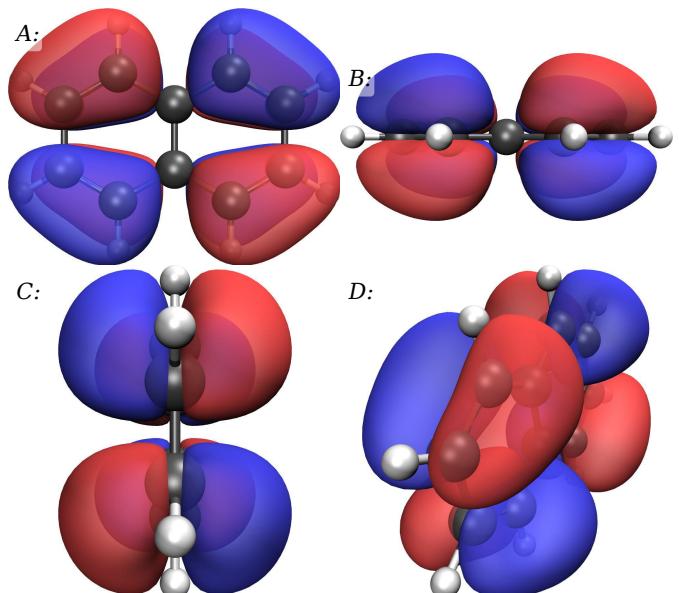


Figure 9: Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

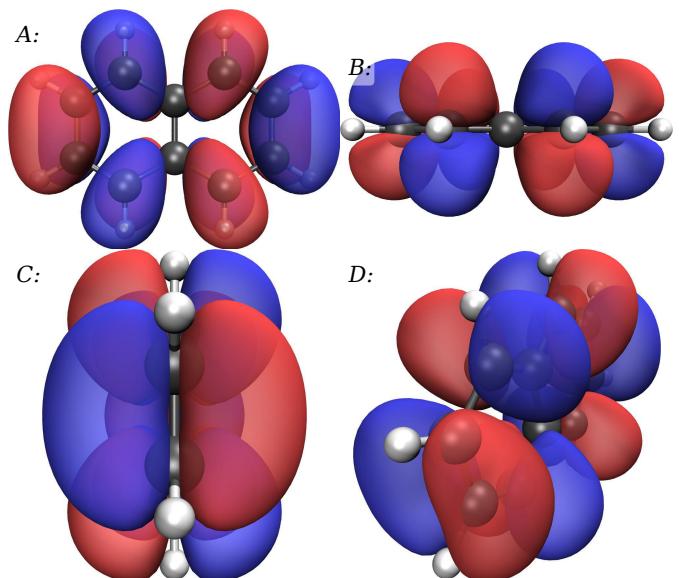


Figure 10: Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

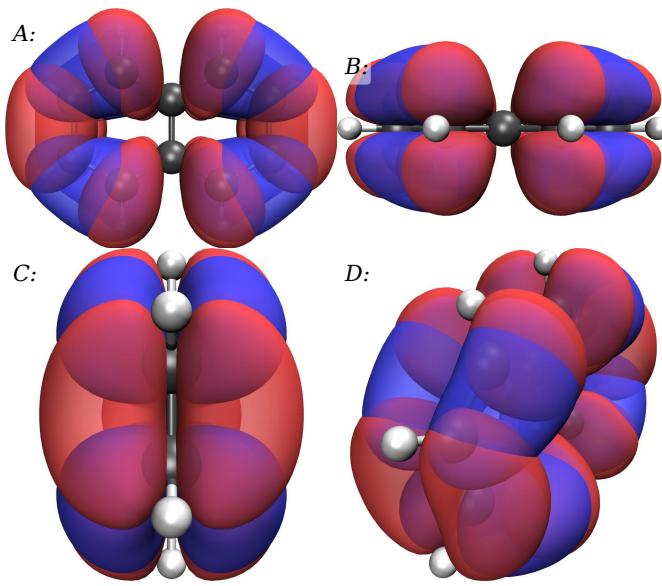


Figure 11: Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

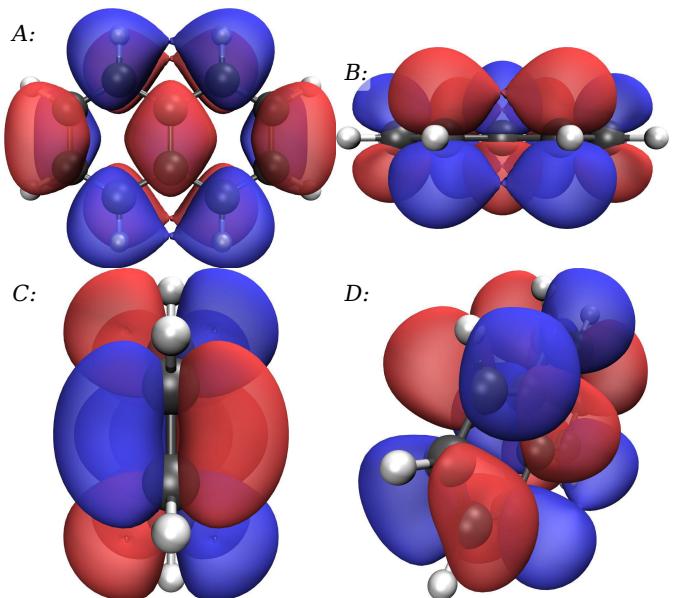


Figure 13: Orbital density plots of the LUMO+2, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

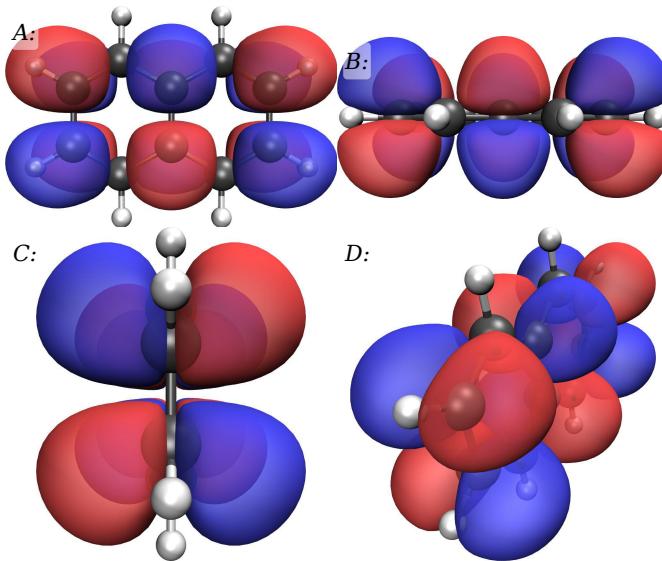


Figure 12: Orbital density plots of the LUMO+1, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

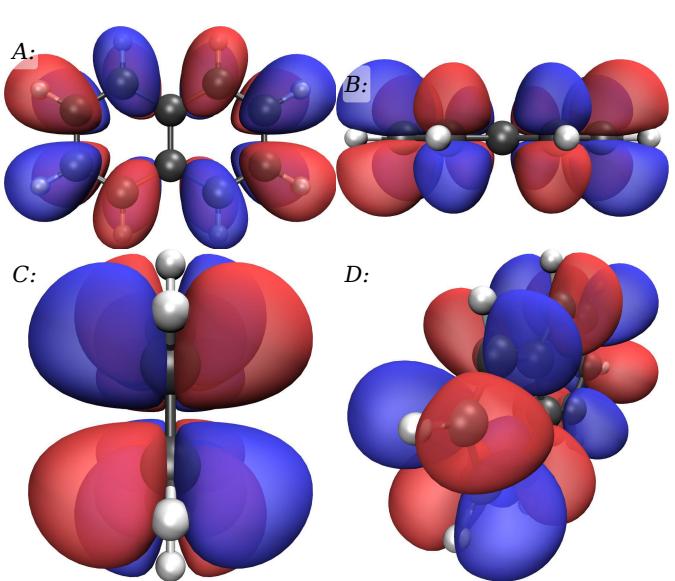


Figure 14: Orbital density plots of the LUMO+4, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Vibrational Frequencies

The energies of a total of 48 vibrational transitions were calculated and vibrational absorption peaks were simulated using a gaussian function with full-width at half maximum (FWHM) of 80 cm⁻¹. From this analysis the **five most intense vibrational peaks** were found at 487, 806, 1294, 1580 and 3224 cm⁻¹. The full simulated vibrational frequency spectrum is shown in figure 16. Finally there were zero **calculated negative frequencies**.

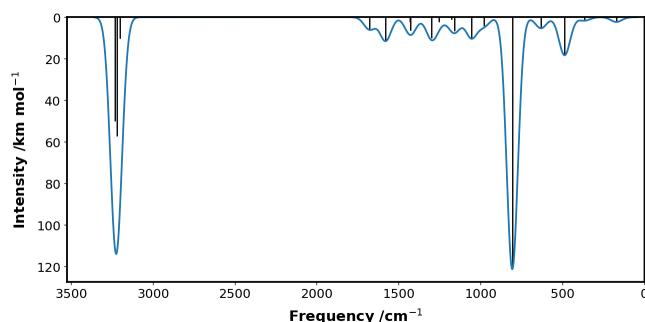


Figure 16: Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vertical black bars while simulated peaks with a gaussian function with FWHM: 80 cm^{-1} are shown as a blue line. Peaks can be found at: 170, 368, 487, 631, 806, 1053, 1160, 1294, 1427, 1580, 1673 and 3224 cm^{-1} .

Excited States

In total, the energies of 20 electronic excited states were calculated (figure 17), consisting of 10 states with a multiplicity of singlet and 10 of multiplicity triplet. The energy of the lowest **singlet excited state (S_1)** was 4.65 eV, corresponding to absorption by a photon with a wavelength of 266 nm, an ultraviolet 'color' ■ and CIE coordinates of (0.00, 0.00), while the energy of the T_1 was 3.03 eV (409 nm, violet ■, CIE: (0.17, 0.00)). The difference in energy between the S_1 and T_1 excited states (ΔE_{ST}) was therefore 1.62 eV. A complete table of the calculated excited state properties is available in table 11. In addition, an electronic transition spectrum was simulated using a gaussian function with full-width at half maximum (FWHM) of 0.40 eV, from which the **two most intense peaks** were found at 194 and 261 nm. The full simulated absorption spectrum is shown in figure 18. Finally, **natural transition orbitals (NTOs)** were calculated for the S_1 , S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , S_8 , S_9 and S_{10} excited states and are shown in figures 19-28.

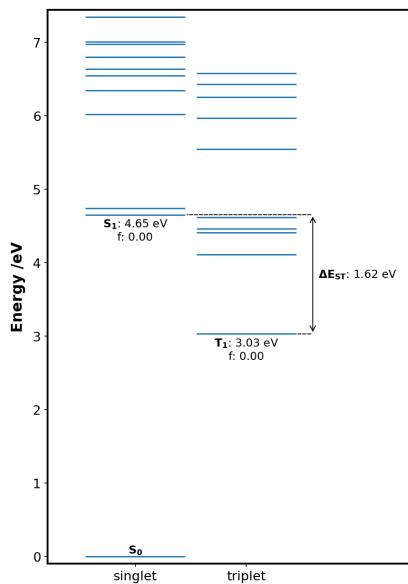


Figure 17: Graph of the calculated excited states. f : oscillator strength of the relevant ground to excited state transition.

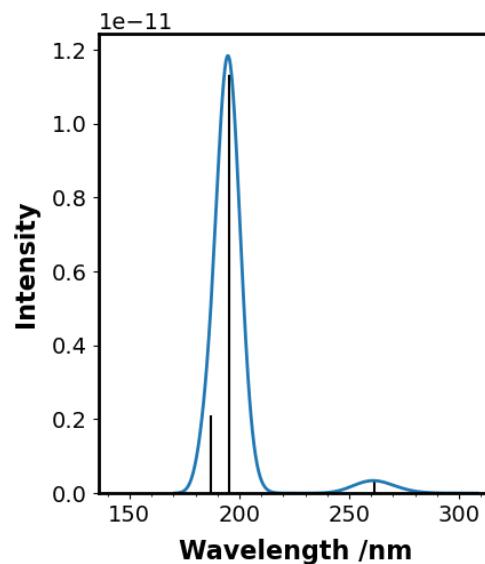


Figure 18: Graph of the simulated absorption spectrum. Excited states are shown as vertical black lines, while peaks simulated with a gaussian function with FWHM: 0.40 eV are shown as a blue line. Peaks can be found at: 194 and 261 nm.

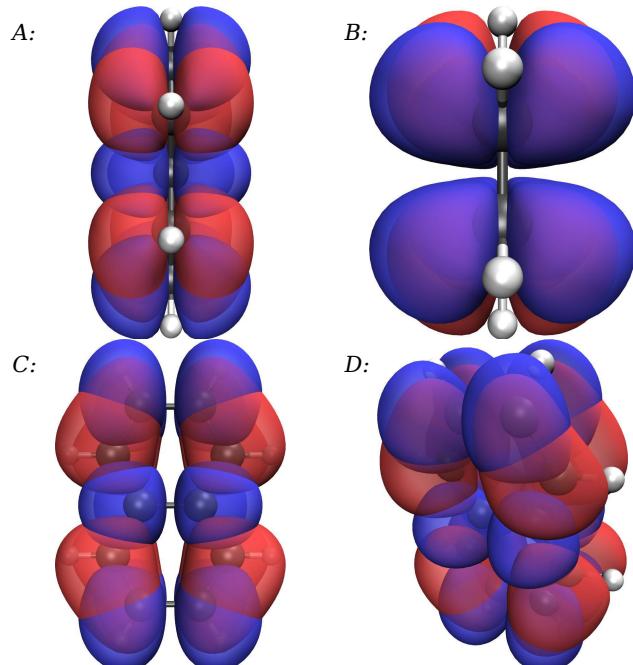


Figure 19: Density plot of the NTO hole (blue) & electron (red) of the S_1 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

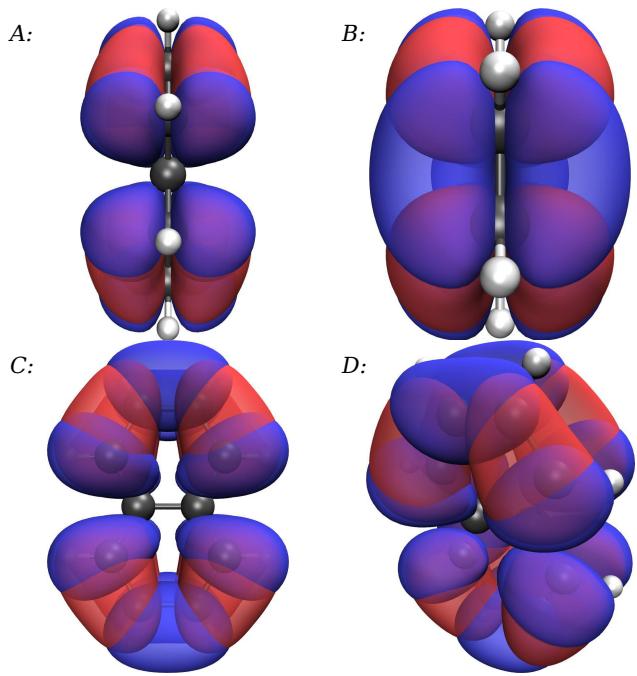


Figure 20: Density plot of the NTO hole (blue) & electron (red) of the S_2 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

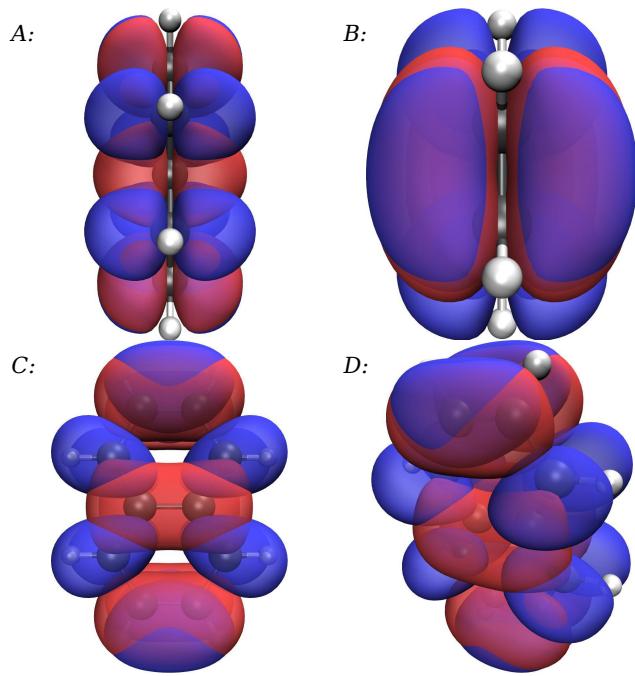


Figure 22: Density plot of the NTO hole (blue) & electron (red) of the S_4 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

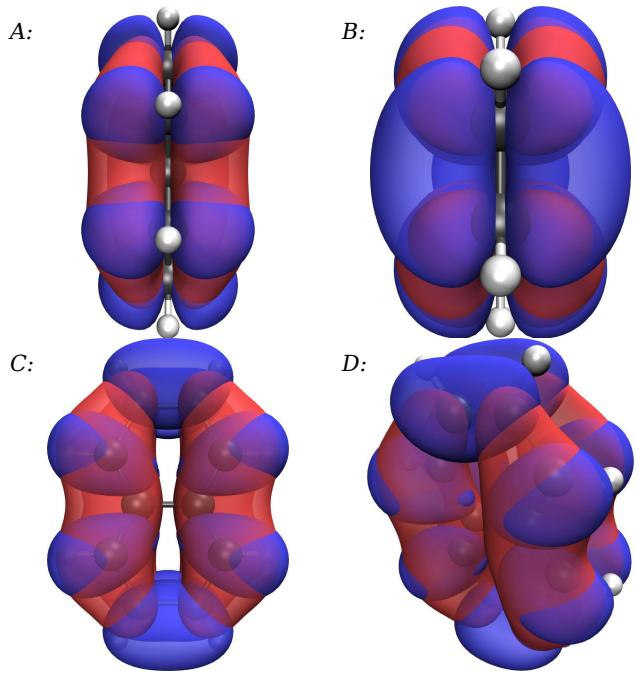


Figure 21: Density plot of the NTO hole (blue) & electron (red) of the S_3 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

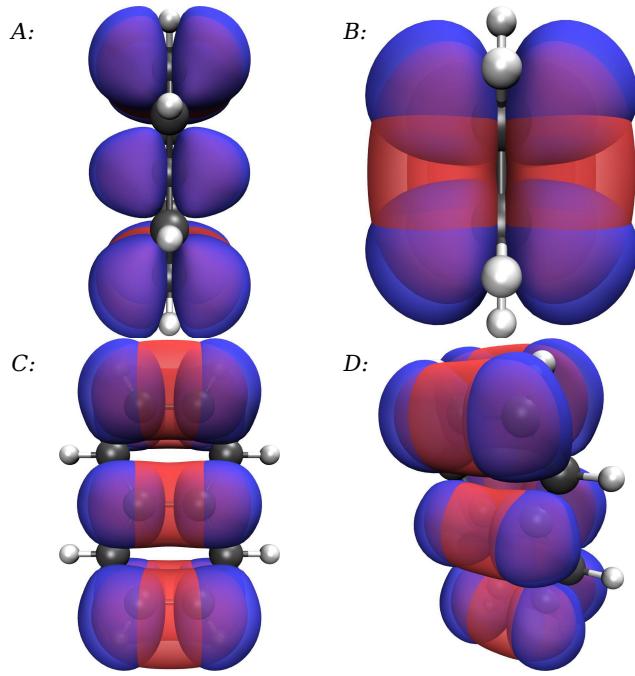


Figure 23: Density plot of the NTO hole (blue) & electron (red) of the S_5 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

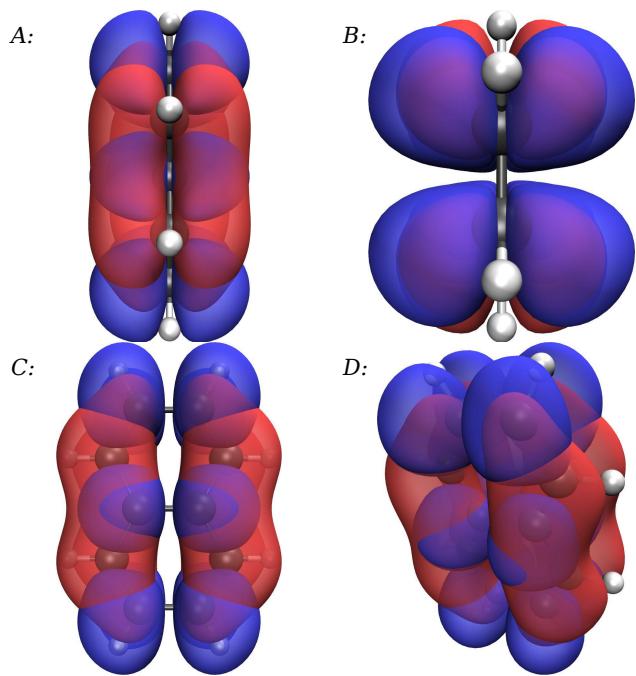


Figure 24: Density plot of the NTO hole (blue) & electron (red) of the S_6 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

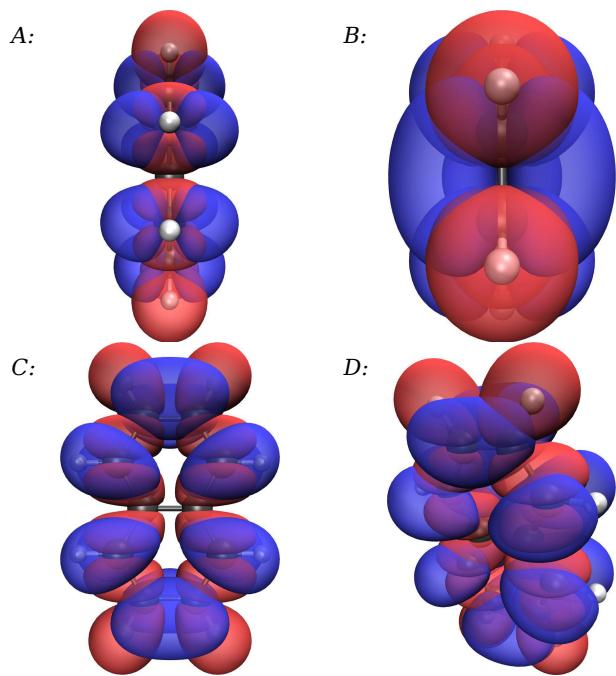


Figure 26: Density plot of the NTO hole (blue) & electron (red) of the S_8 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

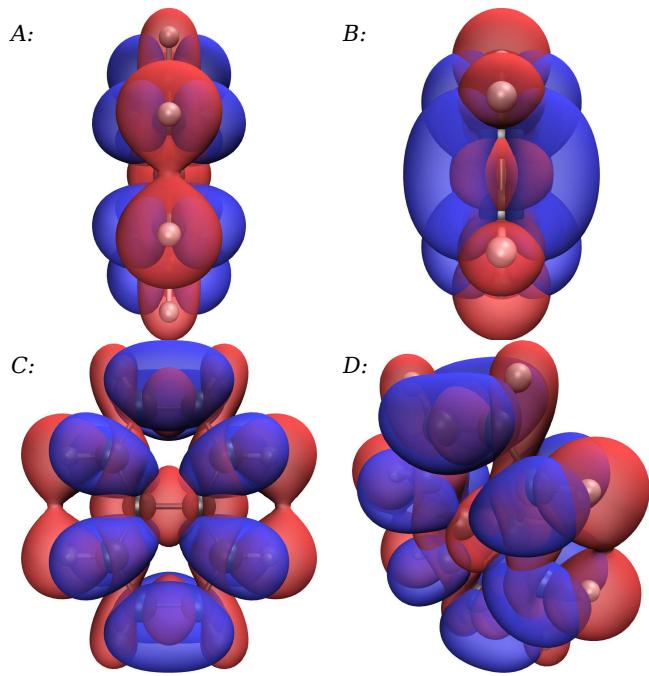


Figure 25: Density plot of the NTO hole (blue) & electron (red) of the S_7 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

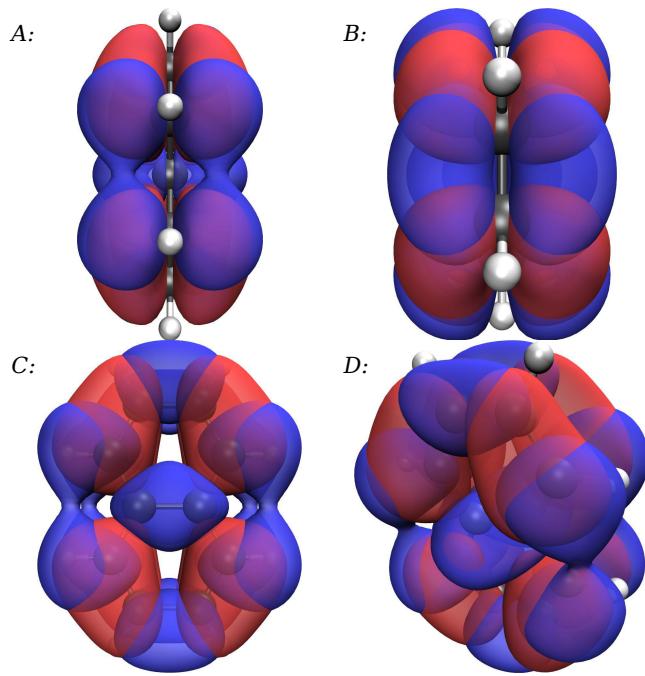


Figure 27: Density plot of the NTO hole (blue) & electron (red) of the S_9 state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

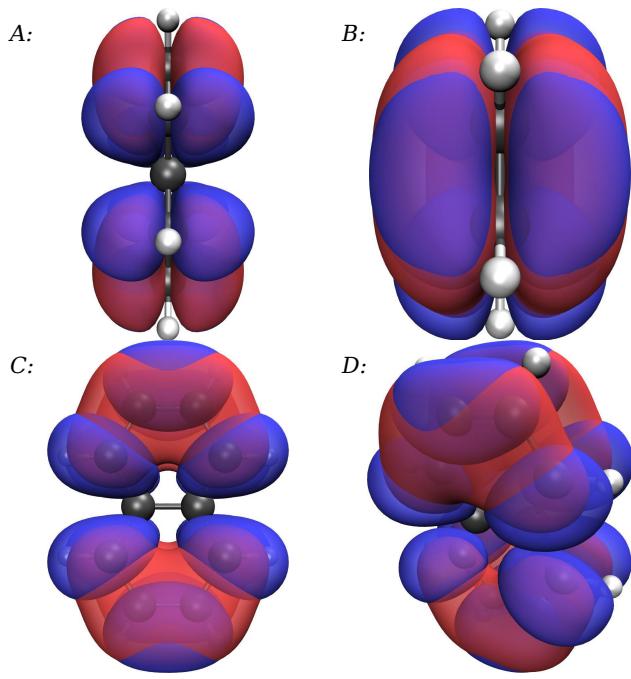


Figure 28: Density plot of the NTO hole (blue) & electron (red) of the S_{10} state, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Adiabatic Emission Energy

The adiabatic emission energy, corresponding to the difference in energy between an excited state at an excited state geometry, and the ground state at the ground state geometry, from the **S_1 state** to the ground state was calculated and found to be 4.54 eV. This energy is equivalent to emission of a photon with a wavelength of 273 nm, corresponding to a colour of Ultraviolet ■ and CIE coordinates (x,y) of (0.00, 0.00). The excited state had a total energy of -10484.45 eV and a multiplicity of one, while the ground state had a total energy of -10488.99 eV and a multiplicity of one. This emission is therefore a fluorescence type process, because both the ground and excited state have the same multiplicity. Finally, the rate constant of the emission was calculated to be $3.13 \times 10^5 \text{ s}^{-1}$

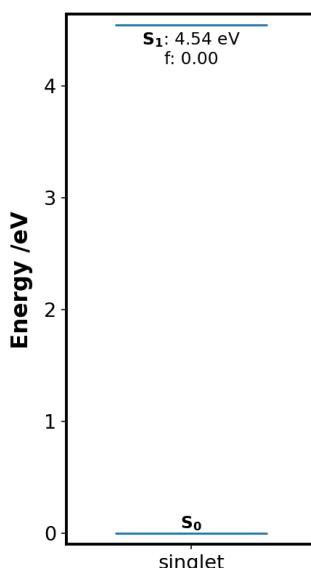


Figure 29: Graph of the calculated adiabatic S_1 emission energy.

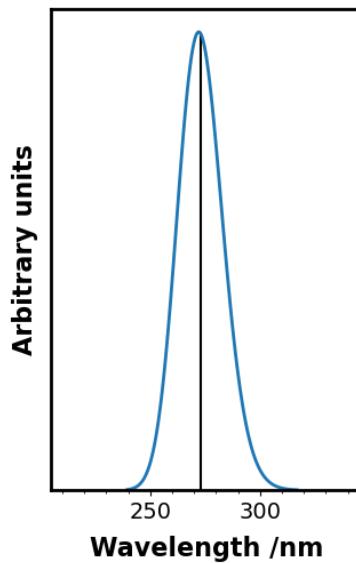


Figure 30: Graph of the simulated adiabatic S_1 emission spectrum. Excited states are shown as vertical black lines, while peaks simulated with a gaussian function with FWHM: 0.4 eV are shown as a blue line. The oscillator strength of each excited state has arbitrarily been set to 1 because all oscillator strengths were 0. Peaks can be found at: 272 nm.

Vertical Emission Energy

The vertical emission energy, corresponding to the difference in energy between an excited state at an excited state geometry, and the ground state at the ground state geometry, from the **S_1 state** to the ground state was calculated and found to be 4.44 eV. This energy is equivalent to emission of a photon with a wavelength of 279 nm, corresponding to a colour of Ultraviolet ■ and CIE coordinates (x,y) of (0.00, 0.00). The excited state had a total energy of -10484.45 eV and a multiplicity of one, while the ground state had a total energy of -10488.88 eV and a multiplicity of one. This emission is therefore a fluorescence type process, because both the ground and excited state have the same multiplicity. Finally, the rate constant of the emission was calculated to be $2.91 \times 10^5 \text{ s}^{-1}$

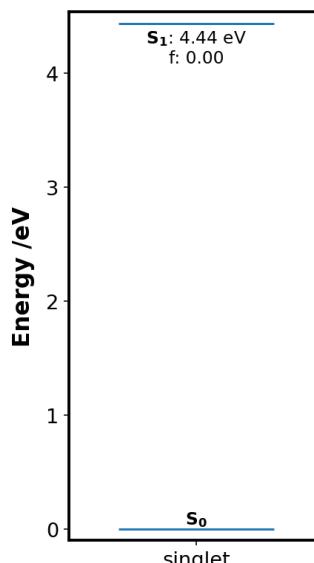


Figure 31: Graph of the calculated vertical S_1 emission energy.

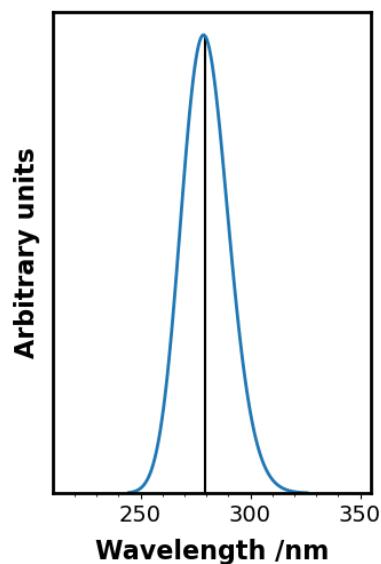


Figure 32: Graph of the simulated vertical S_1 emission spectrum. Excited states are shown as vertical black lines, while peaks simulated with a gaussian function with FWHM: 0.4 eV are shown as a blue line. The oscillator strength of each excited state has arbitrarily been set to 1 because all oscillator strengths were 0. Peaks can be found at: 278 nm.

Tables Of Results

Atom Coordinates

Table 12: 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 | -1.2404550 | -1.3991360 | -0.0000000 | | | | |
| C | -2.4260000 | -0.7066350 | -0.0000000 | | | | |
| C | -2.4260000 | 0.7066350 | 0.0000010 | | | | |
| C | -1.2404550 | 1.3991360 | 0.0000010 | | | | |
| C | 0.0000000 | 0.7142260 | -0.0000010 | | | | |
| C | 0.0000000 | -0.7142260 | -0.0000010 | | | | |
| C | 1.2404550 | -1.3991360 | 0.0000010 | 1 | A | 170.6603 | 2.3323 |
| C | 1.2404550 | 1.3991360 | -0.0000000 | 2 | A | 186.3677 | 0.0000 |
| C | 2.4260000 | 0.7066350 | -0.0000000 | 3 | A | 365.1609 | 1.6874 |
| C | 2.4260000 | -0.7066350 | 0.0000010 | 4 | A | 393.2304 | 0.0000 |
| H | -1.2366960 | -2.4861970 | -0.0000030 | 5 | A | 477.4391 | 0.0000 |
| H | -3.3696970 | -1.2439660 | 0.0000010 | 6 | A | 486.8646 | 18.3491 |
| H | -3.3696970 | 1.2439660 | -0.0000010 | 7 | A | 516.9575 | 0.0000 |
| H | -1.2366960 | 2.4861970 | 0.0000000 | 8 | A | 522.9547 | 0.0000 |
| H | 1.2366960 | -2.4861970 | 0.0000000 | 9 | A | 631.0734 | 5.3597 |
| H | 1.2366960 | 2.4861970 | -0.0000030 | 10 | A | 636.2303 | 0.0000 |
| H | 3.3696970 | 1.2439660 | 0.0000010 | 11 | A | 734.4453 | 0.0000 |
| H | 3.3696970 | -1.2439660 | -0.0000010 | 12 | A | 783.2293 | 0.0000 |
| | | | | 13 | A | 787.4275 | 0.0000 |
| | | | | 14 | A | 806.2853 | 121.0015 |
| | | | | 15 | A | 809.4087 | 0.2244 |

Molecular Orbitals

Table 13: Energies of the calculated molecular orbitals.

| Level | Label | Symmetry | Energy /eV | | | | |
|-------|-------------|----------|----------------|----|---|-----------|---------|
| 50 | LUMO+15 | A | 8.6396 | 18 | A | 947.6833 | 0.0000 |
| 49 | LUMO+14 | A | 7.9114 | 19 | A | 961.3577 | 0.0000 |
| 48 | LUMO+13 | A | 6.9152 | 20 | A | 978.7553 | 4.2681 |
| 47 | LUMO+12 | A | 6.0692 | 21 | A | 999.1135 | 0.0000 |
| 46 | LUMO+11 | A | 5.7949 | 22 | A | 1006.5492 | 0.0000 |
| 45 | LUMO+10 | A | 5.3487 | 23 | A | 1055.4957 | 10.0015 |
| 44 | LUMO+9 | A | 5.1506 | 24 | A | 1066.4428 | 0.0000 |
| 43 | LUMO+8 | A | 5.0034 | 25 | A | 1158.3757 | 6.7028 |
| 42 | LUMO+7 | A | 4.9519 | 26 | A | 1178.7603 | 1.0658 |
| 41 | LUMO+6 | A | 3.6912 | 27 | A | 1179.8776 | 0.0000 |
| 40 | LUMO+5 | A | 3.4207 | 28 | A | 1188.4321 | 0.0000 |
| 39 | LUMO+4 | A | 2.9674 | 29 | A | 1254.2980 | 2.4273 |
| 38 | LUMO+3 | A | 2.9127 | 30 | A | 1274.8273 | 0.0000 |
| 37 | LUMO+2 | A | 1.0612 | 31 | A | 1299.2065 | 10.0549 |
| 36 | LUMO+1 | A | -0.1010 | 32 | A | 1426.1623 | 6.3760 |
| 35 | LUMO | A | -0.9244 | 33 | A | 1430.5870 | 2.2480 |
| 34 | HOMO | A | -6.1307 | 34 | A | 1451.2573 | 0.0000 |
| 33 | HOMO-1 | A | -6.9087 | 35 | A | 1508.0715 | 0.0000 |
| 32 | HOMO-2 | A | -8.0747 | 36 | A | 1510.3663 | 0.0000 |
| 31 | HOMO-3 | A | -9.1879 | 37 | A | 1579.8388 | 11.4633 |
| 30 | HOMO-4 | A | -9.2562 | 38 | A | 1655.4851 | 0.0000 |
| 29 | HOMO-5 | A | -9.4032 | 39 | A | 1677.4730 | 5.9807 |
| 28 | HOMO-6 | A | -10.2679 | 40 | A | 1714.4767 | 0.0000 |
| 27 | HOMO-7 | A | -11.0274 | 41 | A | 3201.3483 | 0.0000 |
| 26 | HOMO-8 | A | -11.1363 | 42 | A | 3202.4466 | 10.2646 |

| | | | | | | | |
|----|---|-----------|--------|----|---|-----------|---------|
| 43 | A | 3204.6890 | 0.2493 | 46 | A | 3220.5827 | 57.2959 |
| 44 | A | 3207.0173 | 0.0000 | 47 | A | 3232.8358 | 49.9545 |
| 45 | A | 3220.0583 | 0.0000 | 48 | A | 3233.8528 | 0.0000 |

Excited States

Table 11: Energies and other properties of the calculated excited states.

| Number | Symbol | Symmetry | Energy /eV | Wavelength /nm | Colour (CIE x,y) | Oscillator Strength | Transitions (Probability) |
|--------|-----------------|-------------|------------|----------------|----------------------------|---------------------|--|
| 1 | T ₁ | Triplet-B1U | 3.0294 | 409.27 | Violet ■ (0.17, 0.00) | 0.0000 | HOMO → LUMO (0.92) HOMO-2 → LUMO+2 (0.03) HOMO-1 → LUMO+1 (0.03) |
| 2 | T ₂ | Triplet-B2U | 4.1078 | 301.83 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-1 → LUMO (0.58) HOMO → LUMO+1 (0.40) |
| 3 | T ₃ | Triplet-B2U | 4.4060 | 281.40 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO → LUMO+1 (0.59) HOMO-1 → LUMO (0.41) |
| 4 | T ₄ | Triplet-B3G | 4.4608 | 277.94 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-2 → LUMO (0.51) HOMO → LUMO+2 (0.46) |
| 5 | T ₅ | Triplet-B1U | 4.6180 | 268.48 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-1 → LUMO+1 (0.94) HOMO → LUMO (0.04) |
| 6 | S ₁ | Singlet-B2U | 4.6525 | 266.49 | Ultraviolet ■ (0.00, 0.00) | 0.0001 | HOMO-1 → LUMO (0.50) HOMO → LUMO+1 (0.49) |
| 7 | S ₂ | Singlet-B1U | 4.7387 | 261.64 | Ultraviolet ■ (0.00, 0.00) | 0.1168 | HOMO → LUMO (0.90) HOMO-1 → LUMO+1 (0.07) |
| 8 | T ₆ | Triplet-AG | 5.5459 | 223.56 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-1 → LUMO+2 (0.31) HOMO-4 → LUMO (0.30) HOMO-2 → LUMO+1 (0.26) HOMO → LUMO+4 (0.13) |
| 9 | T ₇ | Triplet-B3G | 5.9643 | 207.88 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO → LUMO+2 (0.53) HOMO-2 → LUMO (0.47) |
| 10 | S ₃ | Singlet-B3G | 6.0185 | 206.01 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO → LUMO+2 (0.51) HOMO-2 → LUMO (0.49) |
| 11 | T ₈ | Triplet-AG | 6.2558 | 198.19 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-2 → LUMO+1 (0.62) HOMO-1 → LUMO+2 (0.30) HOMO-4 → LUMO (0.06) |
| 12 | S ₄ | Singlet-B2U | 6.3419 | 195.50 | Ultraviolet ■ (0.00, 0.00) | 2.1780 | HOMO → LUMO+1 (0.48) HOMO-1 → LUMO (0.47) |
| 13 | T ₉ | Triplet-AG | 6.4283 | 192.87 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-4 → LUMO (0.38) HOMO-1 → LUMO+2 (0.36) HOMO → LUMO+4 (0.12) HOMO-2 → LUMO+1 (0.07) HOMO-7 → LUMO+2 (0.04) |
| 14 | S ₅ | Singlet-AG | 6.5463 | 189.40 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-2 → LUMO+1 (0.49) HOMO-1 → LUMO+2 (0.46) HOMO-4 → LUMO (0.04) |
| 15 | T ₁₀ | Triplet-B1G | 6.5767 | 188.52 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-3 → LUMO (0.98) |
| 16 | S ₆ | Singlet-B1U | 6.6348 | 186.87 | Ultraviolet ■ (0.00, 0.00) | 0.3684 | HOMO-1 → LUMO+1 (0.86) HOMO-2 → LUMO+2 (0.07) HOMO → LUMO (0.04) |
| 17 | S ₇ | Singlet-B1G | 6.7955 | 182.45 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-3 → LUMO (0.99) |
| 18 | S ₈ | Singlet-B2G | 6.9759 | 177.73 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-5 → LUMO (0.98) |
| 19 | S ₉ | Singlet-B3G | 7.0061 | 176.97 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-2 → LUMO (0.48) HOMO → LUMO+2 (0.45) |
| 20 | S ₁₀ | Singlet-AG | 7.3438 | 168.83 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-4 → LUMO (0.63) HOMO-1 → LUMO+2 (0.27) HOMO-2 → LUMO+1 (0.07) |

Transition Dipole Moments

Table 15: Properties of the calculated transition dipole moments. [a]: The electric transition dipole moment (TEDM), in Debye (D). [b]: Angle between the TEDM and the x-axis of the molecule. [c]: Angle between the TEDM and xy-plane of the molecule. [d]: The magnetic transition dipole moment (TMDM), in atomic units (au). [e]: Angle between the TMDM and the x-axis of the molecule. [f]: Angle between the TMDM and xy-plane of the molecule. [g]: The TEDM, in Gaussian CGS (centimetre, gram, second) units. [h]: The TMDM, in Gaussian CGS (centimetre, gram, second) units. [i]: The angle between the electric and magnetic transition dipole moments, in Gaussian CGS units. [j]: The cosine of the angle between the electric and magnetic transition dipole moments, in Gaussian CGS units. [k]: The dissymmetry factor of the transition dipole moment.

| Excited State | $\mu^{[a]}$ Vector /D | $\mu^{[a]}$ /D | $\theta_{\mu,x}^{[b]}$ /° | $\theta_{\mu,xy}^{[c]}$ /° | m ^[d] Vector /au | m ^[d] /au | $\theta_{m,x}^{[e]}$ /° | $\theta_{m,xy}^{[f]}$ /° | $\mu^{[g]}$ /esu·cm | m ^[h] /erg·G ⁻¹ | $\theta_{\mu,m}^{[i]}$ /° | $\cos(\theta_{\mu,m})^{[j]}$ | $g_{lum}^{[k]}$ |
|----------------|-----------------------|----------------|---------------------------|----------------------------|-----------------------------|----------------------|-------------------------|--------------------------|---------------------|---------------------------------------|---------------------------|------------------------------|-----------------|
| T ₁ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₂ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₃ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |

| | | | | | | | | | | | | | |
|-----------------|--------------------|------|-------|------|-------------------|------|-------|-------|----------|----------|-------|------|-------|
| T ₄ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₅ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₁ | 0.07, -0.00, -0.00 | 0.07 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 6.74e-20 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₂ | 0.00, 2.55, -0.00 | 2.55 | 90.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 2.55e-18 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₆ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₇ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₃ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.43 | 0.43 | 90.00 | 90.00 | 0.00e+00 | 3.98e-21 | 90.00 | 0.00 | 0.000 |
| T ₈ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₄ | 9.52, -0.00, -0.00 | 9.52 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 9.52e-18 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₉ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₅ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| T ₁₀ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₆ | 0.00, -3.83, 0.00 | 3.83 | 90.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 3.83e-18 | 0.00e+00 | 90.00 | 0.00 | 0.000 |
| S ₇ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.27, -0.00 | 0.27 | 90.00 | 0.00 | 0.00e+00 | 2.50e-21 | 90.00 | 0.00 | 0.000 |
| S ₈ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | -0.10, 0.00, 0.00 | 0.10 | 0.00 | 0.00 | 0.00e+00 | 9.67e-22 | 90.00 | 0.00 | 0.000 |
| S ₉ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 1.28 | 1.28 | 90.00 | 90.00 | 0.00e+00 | 1.19e-20 | 90.00 | 0.00 | 0.000 |
| S ₁₀ | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00, 0.00, 0.00 | 0.00 | 0.00 | 0.00 | 0.00e+00 | 0.00e+00 | 90.00 | 0.00 | 0.000 |

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