Supplemental Material for

On the Performance of DFT/MRCI-R and MR-MP2 in Spin–Orbit Coupling Calculations in Diatomics and Polyatomic Organic Molecules

Vladimir Jovanović, Igor Lyskov, Martin Kleinschmidt, and Christel M. Marian

Institute of Theoretical and Computational Chemistry, Heinrich-Heine-University Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

(May 29, 2016)
S1. On the calculation of SOMEs

In the SPOCK program all SOMEs between singlet and triplet states are initially computed with the $\hat{S}_{+1}$ operator. In this paper, the Cartesian $x$- and $y$-components of SOMEs between the $M_s = 1$ sublevel of a triplet state and a singlet state ($\langle T, M_s = 1 | \hat{H}_{SO \ x/y} | S \rangle$) are presented. The $x$-components could be obtained from the initially calculated mixed-representation matrix element ($\langle T, M_s = 1 | \hat{L}_x \hat{S}_{+1} | S \rangle$) by multiplication with $-1/\sqrt{2}$ which arises from the relationship between the Cartesian and tensor forms of the spin operator, $\hat{S}_x = (\hat{S}_- - \hat{S}_+ + 1)/\sqrt{2}$. The corresponding relationship for the $\hat{S}_y$ operator, $\hat{S}_y = i(\hat{S}_- + \hat{S}_+)/\sqrt{2}$ leads to the same factor of $-1/\sqrt{2}$ for the $y$-component of SOMEs. One should note that this choice of the imaginary phase in the $\hat{S}_y$ operator is the reason for the real values of the $\hat{H}_{SO y}$ matrix elements. The $x$ and $z$-components are imaginary since the angular momentum operator is a purely imaginary operator. [1] The chosen $z$-component of the Hamiltonian couples a singlet state with the $M_s = 0$ sublevel of a triplet ($\langle T, M_s = 0 | \hat{H}_{SO \ z} | S \rangle$). To arrive at $\langle T, M_s = 0 | \hat{L}_z \hat{S}_{+1} | S \rangle$, one first needs to obtain the reduced matrix element (RME) by dividing the initially calculated matrix element by a 3-j symbol (only for the spin part, $\langle T, M_s = 1 | \hat{S}_{+1} | S \rangle$), and then multiplying the RME with the new, appropriate 3-j symbol (corresponding to the $\langle T, M_s = 0 | \hat{S}_0 | S \rangle$). The values of these 3-j symbols happen to be the same, $1/\sqrt{3}$, and since $\hat{S}_z = \hat{S}_0$, the conversion factor between the calculated “wrong” SOMEs and the appropriate ones is 1. The presented matrix elements between two triplet states are always of the form: $\langle T, M_s = 1 | \hat{H}_{SO \ x/y} | T, M_s = 0 \rangle$ and $\langle T, M_s = 1 | \hat{H}_{SO \ z} | T, M_s = 1 \rangle$ and could be obtained from the computed matrix elements by multiplying them with $1/\sqrt{2}$ in the case of $x$ and $y$-components while the $z$-component does not need to be modified. In the tables, the imaginary unit ($i$) is omitted from the complex-valued matrix elements of the $\hat{H}_{SO \ x}$ and $\hat{H}_{SO \ z}$ operators and absolute values are presented instead.
S2. Statistical data and correlation plots

Table S1 shows the statistical data with regard the excitation energies employing the valence basis obtained at the DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BHLYP) levels of theory with respect to DFT/MRCI. Table S2 contains the corresponding statistical data for the SOMEs of each molecule individually and for the complete set of selected SOMEs, 278 in total. As the sign of an individual SOME depends on the (arbitrary) phases of the molecular orbitals (MOs) and of the wave functions, absolute values have been employed when computing the maximum positive and negative deviations of the SOMEs. Normalized RMSD (NRMSD), expressed as percentage, are given as the RMSD normalized by the range, i.e. the maximum value minus the minimum absolute value of the evaluated data.
Table S1. Deviations in energies of polyatomic molecules calculated with DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) with respect to DFT/MRCI. The values are given in eV and the normalized RMSD (NRMSD) is expressed as percentage.

| Molecule          | DFT/MRCI-R | MR-MP2(HF) | MR-MP2(BH-LYP) |
|-------------------|------------|------------|----------------|
|                   | RMSD      | NRMSD     | Max. (+) | Max. (-) | RMSD      | NRMSD     | Max. (+) | Max. (-) | RMSD      | NRMSD     | Max. (+) | Max. (-) |
| o-benzyne         | 0.73      | 15         | 2.26     | 0.16     | 0.73      | 15         | 2.19     | 0.53     | 0.75      | 15         | 2.20     | 0.64     |
| Formaldehyde      | 0.12      | 2          | 0.16     | 0.17     | 0.17      | 3          | 0.36     | 0.02     | 0.23      | 4          | 0.44     |
| Thioformaldehyde  | 0.59      | 10         | 0.53     | 1.82     | 0.33      | 6          | 0.37     | 0.71     | 0.34      | 6          | 0.36     | 0.73     |
| Furan             | 0.04      | 1          | 0.06     | 0.09     | 0.25      | 6          | 0.40     | 0.31     | 0.30      | 7          | 0.42     | 0.44     |
| Thiophene         | 0.04      | 1          | 0.07     | 0.06     | 0.16      | 5          | 0.17     | 0.32     | 0.20      | 6          | 0.10     | 0.46     |
| Quinoxaline       | 0.10      | 5          | 0.18     | 0.12     | 0.30      | 16         | 0.32     | 0.58     | 0.39      | 21         | 0.21     | 0.77     |
| Quinazoline       | 0.09      | 4          | 0.14     | 0.06     | 0.31      | 18         | 0.14     | 0.46     | 0.50      | 30         | 0.76     |
| Pyranthione       | 0.08      | 2          | 0.06     | 0.19     | 0.12      | 4          | 0.19     | 0.16     | 0.15      | 5          | 0.11     | 0.22     |
| Dithiin           | 0.07      | 2          | 0.11     | 0.11     | 0.34      | 14         | 0.53     | 0.46     | 0.46      | 19         | 0.76     |
| Bithiophene       | 0.05      | 2          | 0.09     | 0.06     | 0.19      | 7          | 0.26     | 0.37     | 0.52      | 21         | 0.77     |
| Nitromethane      | 0.39      | 7          | 0.16     | 1.26     | 0.42      | 8          | 1.15     | 0.37     | 0.47      | 9          | 1.34     | 0.41     |
| Nitrobenzene      | 0.09      | 5          | 0.17     | 0.01     | 0.85      | 20         | 2.56     | 0.11     | 0.78      | 20         | 2.37     | 0.15     |
| Dithiosuccinimide | 0.58      | 23         | 0.13     | 1.32     | 0.65      | 15         | 1.99     | 0.56     | 0.69      | 17         | 1.87     | 0.81     |
| Methionine        | 0.26      | 19         | 0.33     | 0.04     | 0.37      | 27         | 0.68     | 0.19     | 0.34      | 22         | 0.69     | 0.39     |
| Isoalloxazine     | 0.09      | 5          | 0.15     | 0.04     | 0.37      | 27         | 0.68     | 0.19     | 0.34      | 22         | 0.69     | 0.39     |
| All (161 exc states) | 0.33    | 5          | 2.26     | 1.82     | 0.47      | 6          | 2.56     | 0.71     | 0.49      | 6          | 2.37     | 0.81     |
Table S2. Deviations in SOMEs of polyatomic molecules calculated with DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) with respect to DFT/MRCI. The values are given in cm$^{-1}$ and the normalized RMSD (NRMSD) is expressed as percentage.

| Molecule         | DFT/MRCI-R | MR-MP2(HF) | MR-MP2(BH-LYP) |
|------------------|------------|------------|----------------|
|                  | RMSD | NRMSD | Max. (+) | Max. (-) | RMSD | NRMSD | Max. (+) | Max. (-) | RMSD | NRMSD | Max. (+) | Max. (-) |
| o-benzyne        | 0.1  | 2     | 0.1      | 0.2      | 0.4  | 6     | 1.1      | 0.4      | 0.3  | 4     | 0.8      | 0.3      |
| Formaldehyde     | 5.2  | 9     | 0.6      | 20.5     | 2.7  | 4     | 2.9      | 8.7      | 3.1  | 5     | 3.4      | 9.9      |
| Thioformaldehyde | 30.2 | 18   | 79.8     | 100.9    | 10.4 | 7     | 5.5      | 25.0     | 7.5  | 5     | 4.7      | 16.6     |
| Furan            | 0.2  | 2     | 0.3      | 0.8      | 8    | 0.4   | 0.4      | 1.6      | 0.6  | 7     | 0.6      | 1.1      |
| Thiophene        | 1.1  | 1     | 2.0      | 9.6      | 9    | 5.1   | 18.6     | 7.4      | 7    | 7.2   | 14.6     |          |
| Quinoxaline      | 0.7  | 2     | 0.9      | 0.9      | 2    | 0.4   | 0.4      | 2.3      | 0.5  | 1     | 0.4      | 1.0      |
| Quinazoline      | 0.4  | 2     | 0.2      | 0.9      | 5    | 1.7   | 2.0      | 0.8      | 5    | 1.8   | 1.8      |          |
| Pyrantonione     | 2.2  | 1     | 4.3      | 8.8      | 6    | 5.1   | 17.3     | 4.8      | 3    | 6.0   | 10.0     |          |
| Dithiin          | 1.7  | 1     | 2.7      | 14.1     | 10   | 42.7  | 57.4     | 15.2     | 10   | 46.6  | 51.2     |          |
| Bithiophene      | 1.4  | 4     | 0.8      | 8.3      | 27   | 15.8  | 22.9     | 6.5      | 23   | 12.7  | 15.7     |          |
| Nitromethane     | 0.8  | 2     | 0.5      | 2.6      | 6    | 6.3   | 5.5      | 1.6      | 4    | 3.0   | 1.6      |          |
| Nitrobenzene     | 2.4  | 4     | 6.2      | 2.4      | 4    | 5.7   | 5.0      | 2.5      | 4    | 5.3   | 5.1      |          |
| Dithiosuccinimide| 1.5  | 1     | 4.2      | 6.1      | 5    | 0.1   | 14.7     | 3.8      | 3    | 4.0   | 6.8      |          |
| Methionine       | 0.7  | 0     | 0.3      | 5.5      | 7    | 1.4   | 16.5     | 4.2      | 5    | 1.0   | 12.7     |          |
| Isoalloxazine    | 1.0  | 5     | 1.2      | 3.7      | 14   | 5.4   | 8.7      | 3.7      | 14   | 5.7   | 10.3     |          |
| All (278 SOMEs)  | 8.3  | 5     | 79.8     | 100.9    | 8.1  | 5     | 42.7     | 57.4     | 7.7  | 5     | 46.6     | 51.2     |
Figure S1. Correlation plots of SOMEs for individual polyatomic molecules calculated with DFT-MRCI-R method vs SOMEs calculated with DFT/MRCI.
Figure S2. Correlation plots of SOMEs for individual polyatomic molecules calculated with MR-MP2(HF) method vs SOMEs calculated with DFT/MRCI.
Figure S3. Correlation plots of SOMEs for individual polyatomic molecules calculated with MR-MP2(BH-LYP) method vs SOMEs calculated with DFT/MRCI.
S3. Molecular orbitals

Figure S4. Molecular orbitals of thiophene, calculated employing the valence basis. a) HF orbitals, b) BH-LYP orbitals.

Figure S5. BH-LYP molecular orbitals of dithiin involved in the discussed states.

Figure S6. BH-LYP molecular orbitals of nitrobenzene involved in the discussed states.
S4. Individual molecules

S4.1. o-benzyne

Table S3. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of o-benzyne. The oscillator strengths are given in the parentheses.

| State | Dominant character | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) | Experiment |
|-------|--------------------|----------|------------|------------|-----------------|------------|
| $1^1A_2$ | $\pi \rightarrow \pi^*$ | 3.89 (0) | 3.83 (0) | 4.22 (0) | 4.20 (0) |
| $1^1B_2$ | $\pi \rightarrow \pi^*$ | 3.97 (0.002) | 3.92 (0.002) | 4.27 (0.002) | 4.21 (0.002) |
| $2^1A_1$ | $\pi \rightarrow \pi^*, \pi \rightarrow \pi^*$ | 4.24 (0) | 6.50 (0.003) | 6.43 (0) | 6.44 (0) |
| $1^1B_1$ | $\pi \rightarrow \pi^*$ | 5.09 (0.037) | 4.94 (0.046) | 5.12 (0.024) | 5.01 (0.030) | 5.08$^a$ |
| $3^1A_1$ | $\pi \rightarrow \pi^*$ | 5.28 (0.013) | 5.19 (0.018) | 4.75 (0.006) | 4.64 (0.002) | 4.64 (0.002) |
| $2^1B_2$ | $\pi \rightarrow \pi^*$ | 5.38 (0.005) | 5.38 (0.005) | 5.54 (0.004) | 5.47 (0.005) |
| $2^1B_1$ | $\pi \rightarrow \pi^*, \pi \rightarrow \pi^*$ | 5.74 (0) | 7.25 (0.019) | 7.22 (0.001) | 7.22 (0.001) |
| ... | ... | ... | ... | ... | ... | ... |
| $3^1B_1$ | $\pi \rightarrow \pi^*$ | 6.38 (0.183) | 6.23 (0.178) | 6.34 (0.106) | 6.08 (0.089) | 6.25$^a$ |
| $1^3B_1$ | $\pi \rightarrow \pi^*$ | 2.43 | 2.30 | 2.25 | 2.25 |
| $1^3A_2$ | $\pi \rightarrow \pi^*$ | 3.49 | 3.44 | 3.68 | 3.64 |
| $1^3B_2$ | $\pi \rightarrow \pi^*$ | 3.88 | 3.80 | 4.12 | 4.10 |
| $2^3B_1$ | $\pi \rightarrow \pi^*$ | 4.18 | 4.03 | 3.93 | 3.82 |
| $2^3A_1$ | $\pi \rightarrow \pi^*$ | 4.83 | 4.67 | 4.58 | 4.46 |
| $2^3B_2$ | $\pi \rightarrow \pi^*$ | 5.30 | 5.26 | 5.38 | 5.43 |
| ... | ... | ... | ... | ... | ... | ... |
| $2^3A_1$ | $\pi \rightarrow \pi^*, \pi \rightarrow \pi^*$ | 5.69 | 6.37$^5$ | 6.27$^5$ | 6.26$^5$ |

DFT/MRCI-R: $^13^1A_1, ^22^1A_1, ^33^1B_1, ^42^1B_1, ^53^3A_1$
MR-MP2(HF): $^13^1A_1, ^22^1A_1, ^33^1B_1, ^42^1B_1, ^53^3A_1$
MR-MP2(BH-LYP): $^13^1A_1, ^22^1A_1, ^33^1B_1, ^42^1B_1, ^53^3A_1$

$^a$ (Absorption maximum (Ar matrix)) [2]
Table S4: Calculated percentage of electron configurations in the excited states wave functions of \textit{o-benzene} obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | \text{DFT/MRCI} | \text{MRMP2} (BH-LYP) | \text{MRMP2} (HF) | \text{MRMP2} (BH-LYP) |
|-------|------------------|-----------------------|------------------|-----------------------|
|       | % from | to | % from | to | % from | to | % from | to |
| $1^1A_2$ | 89 $\pi_{H-1}$ | $\pi^*$ | 65 $\pi_{H-1}$ | $\pi^*$ | 65 $\pi_{H-1}$ | $\pi^*$ |
| | 3 $\pi_{H-3}$ | $\pi^*$ | 4 $\pi_{H-3}$ | $\pi^*$ | 3 $\pi_{H-3}$ | $\pi^*$ |
| | 2 $\pi_{H-1,\pi L-1}$ | $\pi^*$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi^*$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi^*$ |
| $1^1B_2$ | 88 $\pi^*$ | 65 $\pi^*$ | 64 $\pi^*$ |
| | 4 $\pi_{H-1,\pi L-1}$ | $\pi^*$ | 3 $\pi_{H-1,\pi L-1}$ | $\pi^*$ | 4 $\pi_{H-1,\pi L-1}$ | $\pi^*$ |
| | 2 $\pi_{H-3,\pi L-1}$ | $\pi^*$ | 2 $\pi_{H-3,\pi L-1}$ | $\pi^*$ | 2 $\pi_{H-3,\pi L-1}$ | $\pi^*$ |
| $2^1A_1$ | 88 $\pi_{H-1}$ | $\pi_{L-2}$ | 59 $\pi_{H-1}$ | $\pi_{L-2}$ | 61 $\pi_{H-1}$ | $\pi_{L-2}$ |
| | 11 $\pi_{H-3}$ | $\pi_{L-2}$ | 14 $\pi_{H-3}$ | $\pi_{L-2}$ | 12 $\pi_{H-3}$ | $\pi_{L-2}$ |
| | 2 $\pi_{H-1,\pi L-2}$ | $\pi_{L-2}$ | 2 $\pi_{H-1,\pi L-2}$ | $\pi_{L-2}$ | 2 $\pi_{H-1,\pi L-2}$ | $\pi_{L-2}$ |
| $1^1B_1$ | 79 $\pi_{\pi}$ | 53 $\pi_{\pi}$ | 54 $\pi_{\pi}$ |
| | 11 $\pi_{H-1}$ | $\pi_{L-2}$ | 14 $\pi_{H-1}$ | $\pi_{L-2}$ | 12 $\pi_{H-1}$ | $\pi_{L-2}$ |
| | 2 $\pi_{H-3}$ | $\pi_{L-2}$ | 2 $\pi_{H-3}$ | $\pi_{L-2}$ | 2 $\pi_{H-3}$ | $\pi_{L-2}$ |
| $1^3B_1$ | 62 $\pi_{H-1}$ | $\pi_{L-1}$ | 42 $\pi_{H-1}$ | $\pi_{L-1}$ | 42 $\pi_{H-1}$ | $\pi_{L-1}$ |
| | 27 $\pi_{H-3}$ | $\pi_{L-1}$ | 21 $\pi_{H-3}$ | $\pi_{L-1}$ | 21 $\pi_{H-3}$ | $\pi_{L-1}$ |
| $1^3B_2$ | 91 $\pi_{\pi}$ | 69 $\pi_{\pi}$ | 69 $\pi_{\pi}$ |
| | 6 $\pi_{H-3}$ | $\pi_{\pi}$ | 6 $\pi_{H-3}$ | $\pi_{\pi}$ |
| $1^3B_2$ | 91 $\pi_{\pi}$ | 65 $\pi_{\pi}$ | 64 $\pi_{\pi}$ |
| | 3 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 4 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 4 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ |
| | 2 $\pi_{H-3,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-3,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-3,\pi L-1}$ | $\pi_{\pi}$ |
| $1^3B_1$ | 87 $\pi_{\pi}$ | 62 $\pi_{\pi}$ | 62 $\pi_{\pi}$ |
| | 5 $\pi_{H-1}$ | $\pi_{\pi}$ | 6 $\pi_{H-1}$ | $\pi_{\pi}$ |
| | 12 $\pi_{H-3}$ | $\pi_{\pi}$ | 18 $\pi_{H-3}$ | $\pi_{\pi}$ |
| | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ |
| $2^1B_1$ | 79 $\pi_{\pi}$ | 50 $\pi_{\pi}$ | 47 $\pi_{\pi}$ |
| | 12 $\pi_{H-3}$ | $\pi_{\pi}$ | 16 $\pi_{H-3}$ | $\pi_{\pi}$ | 18 $\pi_{H-3}$ | $\pi_{\pi}$ |
| | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ |
| $2^1B_2$ | 92 $\pi_{\pi}$ | 68 $\pi_{\pi}$ | 67 $\pi_{\pi}$ |
| | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 2 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ |
| $2^1A_2$ | 87 $\pi_{\pi}$ | 61 $\pi_{\pi}$ | 61 $\pi_{\pi}$ |
| | 3 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 3 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ | 3 $\pi_{H-1,\pi L-1}$ | $\pi_{\pi}$ |
Table S5.: Calculated percentage of electron configurations in the excited states wave functions of o-benzyne obtained at the DFT/MRCI and DFT/MRCI-R levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | State | % from | to |
|-------|--------|----|-------|--------|----|
| $^1A_2$ | 89     | $\pi_{H-1}$ | 90     | $\pi_{H-1}^*$ | $\pi_{L+2}$ |
|        | 3      | $\pi_{H-3}$ | 3      | $\pi_{H-3}$ | $\pi_{L+2}^*$ |
|        | 2      | $\pi_{H-1}\pi_{H}$ | 1      | $\pi_{H-1}\pi_{H}$ | $\pi_{L+1}^*\pi_{L+3}$ |
| $^1B_2$ | 88     | $\pi_{H}$ | 89     | $\pi_{H}$ | $\pi_{L+2}^*$ |
|        | 4      | $\pi_{H-1}\pi_{H}$ | 2      | $\pi_{H-1}\pi_{H}$ | $\pi_{L+1}^*\pi_{L+2}$ |
|        | 2      | $\pi_{H-3}\pi_{H}$ | 2      | $\pi_{H-3}\pi_{H}$ | $\pi_{L+2}^*\pi_{L+2}$ |
| $^2A_1$ | 90     | $\pi_{L+2}$ | 85     | $\pi_{L+2}^*$ | $\pi_{L+1}^*\pi_{L+2}$ |
|        | 2      | $\pi_{L+1}^*$ | 3      | $\pi_{L+1}^*\pi_{H}$ | $\pi_{L+1}^*\pi_{L+2}$ |
| $^1B_1$ | 79     | $\pi_{L+1}$ | 81     | $\pi_{L+1}$ | $\pi_{L+2}^*$ |
|        | 11     | $\pi_{H-1}$ | 11     | $\pi_{H-1}$ | $\pi_{L+2}^*$ |
|        | 2      | $\pi_{H-3}$ | 1      | $\pi_{H-3}$ | $\pi_{L+2}^*$ |
| $^2B_2$ | 90     | $\pi_{L+2}^*$ | 92     | $\pi_{L+2}^*$ | $\pi_{L+1}^*\pi_{L+2}$ |
| $^2B_1$ | 62     | $\pi_{L+2}^*$ | 71     | $\pi_{L+2}^*$ | $\pi_{L+1}^*\pi_{L+2}$ |
|        | 27     | $\pi_{H-1}\pi_{H}$ | 15     | $\pi_{H-1}\pi_{H}$ | $\pi_{L+2}^*\pi_{L+1}$ |
| $^3B_1$ | 94     | $\pi_{L+2}^*$ | 95     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
| $^3A_2$ | 88     | $\pi_{L+2}^*$ | 88     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
|        | 6      | $\pi_{H-3}$ | 5      | $\pi_{H-3}$ | $\pi_{L+2}^*$ |
| $^3B_2$ | 91     | $\pi_{L+2}^*$ | 90     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
|        | 3      | $\pi_{H-1}\pi_{H}$ | 2      | $\pi_{H-1}\pi_{H}$ | $\pi_{L+1}^*\pi_{L+2}$ |
| $^2B_1$ | 87     | $\pi_{L+2}^*$ | 89     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
|        | 5      | $\pi_{L+2}^*$ | 4      | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
| $^3A_1$ | 79     | $\pi_{L+2}^*$ | 80     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
|        | 12     | $\pi_{L+2}^*$ | 12     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
| $^2B_2$ | 92     | $\pi_{L+2}^*$ | 92     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
|        | 2      | $\pi_{H-5}\pi_{H}$ | 3      | $\pi_{H-5}\pi_{H}$ | $\pi_{L+2}^*$ |
| $^3A_1$ | 87     | $\pi_{L+2}^*$ | 86     | $\pi_{L+2}^*$ | $\pi_{L+2}^*$ |
### S4.2. Formaldehyde

Table S6. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of formaldehyde using the valence basis. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | Experiment |
|-------|--------------------|-------------|------------|
|       |                    | DFT/MRCI    | DFT/MRCI-R | MR-MP2(HF)| MR-MP2(BH-LYP) |
| $1^1A_2$ | $n \rightarrow \pi^*$ | 3.86 (0) | 3.94 (0) | 3.97 (0) | 4.07 (0) | 3.79$^a$, 3.94$^b$ |
| $1^1B_2$ | $n \rightarrow \text{Ryd}$ | 8.31 (0.121) | 8.14 (0.119) | 8.29 (0.099) | 8.35 (0.117) |
| $1^1B_1$ | $\sigma \rightarrow \pi^*$ | 9.00 (0.004) | 9.03 (0.005) | 9.17 (0.002) | 9.26 (0.002) | 9.0$^c$ |
| $2^1A_1$ | $\pi \rightarrow \pi^*$ | 9.42 (0.079) | 9.26 (0.077) | 9.43 (0.063) | 9.50 (0.031) |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 3.43 | 3.59 | 3.57 | 3.66 | 3.50$^a$, 3.50$^b$ |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 5.77 | 5.76 | 6.13 | 6.21 | 5.82$^a$, 5.86$^b$ |
| $1^3B_2$ | $n \rightarrow \text{Ryd}$ | 7.77 | 7.69 | 7.75 | 7.80 |
| $1^3B_1$ | $\sigma \rightarrow \pi^*$ | 8.23 | 8.36 | 8.40 | 8.45 |

$^a$ Energy-loss maximum (vapor) [3]
$^b$ Energy-loss maximum (vapor) [4]
$^c$ Energy-loss band origin (vapor) [5]
Table S7.: Calculated percentage of electron configurations in the excited states wave functions of formaldehyde obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | % from | to | % from | to |
|-------|--------|----|--------|----|--------|----|
| $1^1A_2$ | 93 | $n_H$ | $\pi^*_L$ | 78 | $n_H$ | $\pi^*_L$ |
| 3 | $\pi_{H-1}n_H$ | $\pi^*_L,\pi^*_L$ | 4 | $n_H$ | $\pi^*_L,\pi^*_L$ |
| 2 | $n_H$ | 3 | $\pi_{H-3}$ | $\pi^*_L,\pi^*_L$ | 2 | $\pi_{H-3}$ |
| $1^1B_2$ | 94 | $n_H$ | $\pi_{H-1}n_H$ | 78 | $n_H$ | $\pi_{H-1}n_H$ |
| 3 | $\pi_{H-1}n_H$ | $\pi^*_L,\pi^*_L,\pi^*_L$ | 3 | $n_H$ | $\pi^*_L,\pi^*_L,\pi^*_L$ |
| $1^1B_1$ | 93 | $\sigma_{H-2}$ | $\pi^*_L$ | 78 | $\sigma_{H-2}$ | $\pi^*_L$ |
| 3 | $\sigma_{H-2}^2\pi_{H-1}$ | $\pi^*_L,\pi^*_L$ | 4 | $\sigma_{H-2}^2\pi_{H-1}$ | $\pi^*_L,\pi^*_L$ |
| 2 | $\sigma_{H-2}^2\pi_{H-1}$ | 3 | $\sigma_{H-2}^2\pi_{H-1}$ | $\pi^*_L,\pi^*_L$ | 5 | $\sigma_{H-2}^2\pi_{H-1}$ |
| $2^1A_1$ | 67 | $\pi_{H-1}$ | $\pi^*_L$ | 59 | $\pi_{H-1}$ | $\pi^*_L$ |
| 2 | $\pi_{H-1}$ | 13 | $\sigma^*$ | $\pi^*_L$ | 17 | $\pi_{H-1}$ |
| 4 | $\pi_{H-1},\pi_{H-1}$ | 4 | $\pi_{H-1},\pi_{H-1}$ | $\pi^*_L,\pi^*_L,\pi^*_L$ | 5 | $\pi_{H-1},\pi_{H-1}$ |
| $1^3A_2$ | 95 | $n_H$ | $\pi^*_L$ | 79 | $n_H$ | $\pi^*_L$ |
| 2 | $n_H$ | 3 | $\pi_{H-3}$ | $\pi^*_L$ | 2 | $\pi_{H-3}$ |
| $1^3A_1$ | 97 | $\pi_{H-1}$ | $\pi^*_L$ | 84 | $\pi_{H-1}$ | $\pi^*_L$ |
| 2 | $\pi_{H-1}$ | 6 | $\pi_{H-1}$ | $\pi^*_L$ | 2 | $\pi_{H-1}$ |
| 4 | $\pi_{H-1},\pi_{H-1}$ | 2 | $\pi_{H-1},\pi_{H-1}$ | $\pi^*_L,\pi^*_L,\pi^*_L$ | 2 | $\pi_{H-1},\pi_{H-1}$ |
| $1^3B_2$ | 95 | $n_H$ | $\pi_{H-1}^2\pi_{H-1}$ | 80 | $n_H$ | $\pi_{H-1}^2\pi_{H-1}$ |
| 2 | $n_H$ | 3 | $n_H$ | $\pi_{H-1}^2\pi_{H-1}$ | $\pi^*_L,\pi^*_L$ | 2 | $\pi_{H-1}^2\pi_{H-1}$ |
| $1^3B_1$ | 95 | $\sigma_{H-2}$ | $\pi^*_L$ | 78 | $\sigma_{H-2}$ | $\pi^*_L$ |
| 2 | $\sigma_{H-2}$ | 6 | $\sigma_{H-2}$ | $\pi^*_L$ | 3 | $\sigma_{H-2}$ |

Table S8.: Calculated percentage of electron configurations in the $2^1A_1$ state wave function of formaldehyde obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | % from | to |
|-------|--------|----|--------|----|
| $2^1A_1$ | 67 | $\pi_{H-1}$ | $\pi^*_L$ | 56 | $\pi_{H-1}$ | $\pi^*_L$ |
| 22 | $n_H$ | $\pi^*_L$ | 19 | $n_H$ | $\pi^*_L$ |
| 4 | $\pi_{H-1},\pi_{H-1}$ | $\pi^*_L,\pi^*_L$ | 17 | $n_H, n_H$ | $\pi^*_L,\pi^*_L$ |
| 2 | $n_H, n_H$ | 2 | $\pi_{H-1},\pi_{H-1}$ | $\pi^*_L,\pi^*_L$ | 2 | $\pi_{H-1},\pi_{H-1}$ |
Table S9. Selected matrix elements (cm\(^{-1}\)) for formaldehyde calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

| \(\langle 1^3A_2 | \hat{H}_{SO} z | 1^1A_1 \rangle\) | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |
|---|---|---|---|---|
| \(\langle 1^3A_2 | \hat{H}_{SO} x | 1^1A_1 \rangle\) | 62.0 | 59.8 | 64.1 | 64.6 |
| \(\langle 1^3A_2 | \hat{H}_{SO} y | 1^1A_1 \rangle\) | 41.5 | 21.0 | 32.8 | 31.6 |
| \(\langle 1^3B_1 | \hat{H}_{SO} y | 1^1A_1 \rangle\) | 43.1 | 41.9 | 44.7 | 45.1 |
| \(\langle 1^3B_1 | \hat{H}_{SO} x | 1^1A_1 \rangle\) | 19.6 | 17.4 | 18.6 | 18.0 |
| \(\langle 1^3A_1 | \hat{H}_{SO} x | 1^1A_2 \rangle\) | 53.6 | 52.5 | 55.8 | 56.1 |
| \(\langle 1^3B_1 | \hat{H}_{SO} y | 1^1B_1 \rangle\) | 36.3 | 36.3 | 38.2 | 38.3 |
| \(\langle 1^3A_2 | \hat{H}_{SO} y | 1^1B_1 \rangle\) | 30.7 | 30.6 | 31.9 | 32.3 |
| \(\langle 1^3B_2 | \hat{H}_{SO} x | 1^1A_1 \rangle\) | 7.5 | 7.4 | 7.5 | 7.5 |
| \(\langle 1^3B_2 | \hat{H}_{SO} x | 1^1A_2 \rangle\) | 1.9 | 1.4 | 1.1 | 1.6 |
| \(\langle 1^3B_2 | \hat{H}_{SO} y | 1^1A_2 \rangle\) | 6.5 | 6.3 | 6.3 | 6.4 |
| \(\langle 1^3B_2 | \hat{H}_{SO} x | 1^1B_1 \rangle\) | 2.3 | 2.0 | 3.2 | 3.9 |
| \(\langle 1^3A_1 | \hat{H}_{SO} x | 1^1B_2 \rangle\) | 0.3 | 0.3 | 0.5 | 0.4 |
| \(\langle 1^3A_2 | \hat{H}_{SO} z | 1^3A_1 \rangle\) | 50.8 | 51.2 | 53.7 | 54.2 |
| \(\langle 1^3B_1 | \hat{H}_{SO} y | 1^3A_1 \rangle\) | 29.0 | 29.6 | 31.3 | 31.3 |
| \(\langle 1^3B_1 | \hat{H}_{SO} x | 1^3A_2 \rangle\) | 36.0 | 36.0 | 37.9 | 38.1 |
Table S10. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 vertical excitation energies of formaldehyde using the augmented basis. The CASPT2 (8,11) active space consists of following occupied/unoccupied orbitals: 1/3 $a_1$, 1/2 $b_1$ and 2/2 $b_2$. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | Experiment |
|-------|-------------------|-------------|------------|
|       |                   | DFT/MRCI | DFT/MRCI-R | MR-MP2(HF) | MR-MP2(BH-LYP) | CASPT2 (8,9) | CASPT2 (8,11) |          |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 3.67 (0) | 3.81 (0) | 3.88 (0) | 3.93 (0) | 3.90 | 3.99 (0) | 3.79$^c$, 3.94$^b$ |
| $1^3B_2$ | $n \rightarrow 3s$ | 7.02 (0.032) | 6.93 (0.034) | 6.99 (0.010) | 6.99 (0.023) | 6.77 | 6.87 (0.035) | 7.09$^c$ |
| $2^1B_2$ | $n \rightarrow 3p_x$ | 7.86 (0.039) | 7.84 (0.032) | 7.92 (0.026) | 8.17 (0.034) | 7.68 | 7.76 (0.027) | 8.13$^c$ |
| $2^1A_1$ | $n \rightarrow 3p_y$ | 7.96 (0.054) | 7.88 (0.052) | 7.99 (0.035) | 8.04 (0.042) | 7.78 | 7.84 (0.058) | 7.98$^c$ |
| $2^1A_2$ | $n \rightarrow 3p_x$ | 8.40 (0) | 8.26 (0) | 8.14 (0) | 8.24 (0) | 7.95 | 8.00 (0) | 8.37$^d$ |
| $1^1B_1$ | $\sigma \rightarrow \pi^*$ | 8.81 (0.004) | 8.90 (0.005) | 9.12 (0.006) | 9.20 (0.002) | 9.21 | 9.43 (0.014) | 9.0$^e$ |
|          |                   |           |            |            |            |    |         |          |
| $3^1A_1$ | $\pi \rightarrow \pi^*$ | 9.51 (0.193) | 9.50 (0.197)$^\dagger$ | 9.64 (0.129) | 9.64 (0.126) | 9.33 | 10.41 (0.129)$^n$ |
|          |                   |           |            |            |            |    |         |          |
| $5^1A_1$ | $n^2 \rightarrow \pi^2$ | 11.06 (0.008) | 9.20 (0.022)$^\ddagger$ | 10.67 (0.007) | 10.75 (0.016) | 10.29$^m$ | 10.87 (0.030)$^p$ |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 3.23 | 3.46 | 3.42 | 3.46 | 3.45 | 3.56 | 3.56$^c$, 3.50$^b$ |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 5.58 | 5.71 | 6.13 | 6.18 | 6.04 | 6.04 | 5.82$^d$, 5.86$^b$ |
| $1^3B_2$ | $n \rightarrow 3s$ | 6.78 | 6.75 | 6.79 | 6.79 | 6.65 | 6.75 | 6.75 |
| $2^3B_2$ | $n \rightarrow 3p_x$ | 7.67 | 7.71 | 7.82 | 7.86 | 7.57 | 7.65 | 7.65 |
| $2^3A_1$ | $n \rightarrow 3p_y$ | 7.76 | 7.72 | 7.90 | 8.11 | 7.67 | 7.73 | 7.73 |
| $1^3B_1$ | $\sigma \rightarrow \pi^*$ | 8.01 | 8.23 | 8.33 | 8.42 | 8.36 | 8.56 | 8.56 |
| $2^3A_2$ | $n \rightarrow 3p_x$ | 8.32 | 8.20 | 8.20 | 8.23 | 7.97 | 8.03 | 8.03 |

$^\dagger$ Mixed with $\pi - 3p_x$, positive linear combination at 11.07

$^\ddagger$ Mixed of $\pi - \pi^* (51\%), \pi - 3p_x (32\%),$ and $n^2 - \pi^2 (6\%)$

$^m$ Mixture of $n^2 - \pi^2 (43\%), \pi - 3p_x (39\%),$ and $\pi - \pi^* (4\%).$ There is another, almost degenerate state at 10.81 eV with oscillator strengths of 0.104, comprised of $n^2 - \pi^2 (31\%), \pi - \pi^* (25\%)$ and $\pi - 3p_x (21\%)$ excitations

$^a$ Energy-loss maximum (vapor) [3]

$^b$ Energy-loss maximum (vapor) [4]

$^c$ Absorption band origin (vapor) [6]

$^d$ Energy-loss band origin (vapor) [4]

$^e$ Energy-loss band origin (vapor) [5]
Table S11.: Calculated percentage of electron configurations in the excited states wave functions of formaldehyde obtained at the DFT/MRCI, MRMP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | DFT/MRCI | MRMP2 (HF) | MRMP2 (BH-LYP) |
|-------|----------|------------|----------------|
|       | Excitation | Excitation | Excitation     |
|       | % from to | % from to | % from to      |
| $1^1A_2$ | 81 $n_H$ $\pi^*_L$ | 67 $n_H$ $\pi^*_L$ | 74 $n_H$ $\pi^*_L$ |
|        | 10 $n_H$ 3$s(c)$ | 11 $n_H$ 3$p_x(c)$ | 5 $n_H$ 3$p_x(c)$ |
| $1^1B_2$ | 85 $n_H$ 3$s(c)$ | 58 $n_H$ 3$s(c)$ | 75 $n_H$ 3$s(c)$ |
|        | 7 $n_H$ 3$p_x(c)$ | 12 $n_H$ 3$s(o)$ | 5 $n_H$ 3$p_x(c)$ |
| $1^1B_1$ | 82 $\sigma_{H-2}$ $\pi^*_L$ | 71 $\sigma_{H-2}$ $\pi^*_L$ | 74 $\sigma_{H-2}$ $\pi^*_L$ |
|        | 11 $\sigma_{H-2}$ 3$p_x(c)$ | 9 $\sigma_{H-2}$ 3$p_x(c)$ | 7 $\sigma_{H-2}$ 3$p_x(c)$ |
| $4^1A_1$ | 53 $\pi_{H-1}$ $\pi^*_L$ | 43 $\pi_{H-1}$ $\pi^*_L$ | 61 $\pi_{H-1}$ $\pi^*_L$ |
|        | 25 $n_H$ 3$p_y(o)$ | 19 $n_H$ 3$p_y(c)$ | 6 $n_H$ 3$p_y(o)$ |
|        | 5 $\pi_{H-1}$ 3$p_x(c)$ | 7 $n_H$ 3$p_y(o)$ | 6 $\pi_{H,L}, \pi_{H}^*$ |
|        |               |               | 5 $n_H$ 3$p_y(o)$ | $\pi_{L}^*, \pi_{L}^*$ |
| $5^1A_1$ | 72 $n_H^2$ $\pi_{H}^*$ | 54 $n_H^2$ $\pi_{H}^*$ | 64 $n_H^2$ $\pi_{H}^*$ |
|        | 13 $n_H^2$ 3$p_x$ | 17 $n_H^2$ 3$p_x$ | 6 $n_H^2$ 3$p_x$ |
| $1^3A_2$ | 83 $n_H$ 3$p_x(c)$ | 70 $n_H$ 3$p_x(c)$ | 75 $n_H$ 3$p_x(c)$ |
|        | 10 $n_H$ 3$p_x(c)$ | 11 $n_H$ 3$p_x(c)$ | 6 $n_H$ 3$p_x(c)$ |
| $1^3A_1$ | 84 $\pi_{H-1}$ $\pi_{H-1}$ | 75 $\pi_{H-1}$ $\pi_{H-1}$ | 78 $\pi_{H-1}$ $\pi_{H-1}$ |
|        | 11 $\pi_{H-1}$ 3$p_x(c)$ | 10 $\pi_{H-1}$ 3$p_x(c)$ | 9 $\pi_{H-1}$ 3$p_x(c)$ |
| $1^3B_2$ | 84 $n_H$ 3$s(c)$ | 58 $n_H$ 3$s(c)$ | 75 $n_H$ 3$s(c)$ |
|        | 7 $n_H$ $\sigma_{L}^*+10$ | 10 $n_H$ 3$p_y(c)$ | 75 $n_H$ 3$s(c)$ |
|        |               |               | 3$s(o)$ | 3$s(o)$ |
| $1^3B_1$ | 82 $\sigma_{H-2}$ $\pi_{H}^*$ | 72 $\sigma_{H-2}$ $\pi_{H}^*$ | 75 $\sigma_{H-2}$ $\pi_{H}^*$ |
|        | 11 $\sigma_{H-2}$ 3$p_x(c)$ | 9 $\sigma_{H-2}$ 3$p_x(c)$ | 7 $\sigma_{H-2}$ 3$p_x(c)$ |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different: The $\pi_{H,2}^*$ BH-LYP orbital corresponds to the $\pi_{L,z}^*$ HF orbital.
Table S12.: Calculated percentage of electron configurations in the excited states wave functions of formaldehyde obtained at the DFT/MRCI-R and CASPT2 (8,11) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | DFT/MRCI-R | CASPT2 (8,11) |
|-------|-------------|---------------|
|       | Excitation  | Excitation    |               |
|       | % from to   | % from to     |               |
| 1^1A_2 | 83 n_H     | 95 n_H  |               |
| 1^1B_2 | 87 n_H 3s(c) | 94 n_H 3s(c) |               |
| 1^1B_1 | 82 σ_H-2 π_* | 96 σ_H-2 π_* |               |
| 4^1A_1 | 53 π_H-1 | 51 π_H-1 |               |
|        | 13 n_H^2 | 32 n_H^2 |               |
|        | 12 n_H | 6 n_H^2 |               |
| 5^1A_1 | 52 n_H^2 | 43 n_H^2 |               |
|        | 17 n_H | 39 n_H |               |
|        | 12 n_H^2 | 39 n_H^2 |               |
|        | 5 π_H-1 | 6 n_H |               |
|        | 10 π_H-1 | 10 π_H-1 |               |
| 1^3A_2 | 84 n_H 3π (c) | 94 n_H π_* |               |
| 1^3A_1 | 86 π_H-1 3π (c) | 97 π_H-1 π_* |               |
| 1^3B_2 | 85 n_H 3s(c) | 94 n_H 3s(c) |               |
| 1^3B_1 | 83 σ_H-2 π_* | 96 σ_H-2 π_* |               |
### S4.3. Thioformaldehyde

Table S13. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of thioformaldehyde using the valence basis. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) | Experiment |
|-------|-------------------|-------------|----------|------------|-------------|----------------|------------|
|       |                   |             |          |            |             |                |            |
| $1^1A_2$ | $n \rightarrow \pi^*$ | 2.18 (0) 2.22 (0) 2.11 (0) 2.10 (0) |
| $2^1A_1$ | $\pi \rightarrow \pi^*$ | 6.49 (0.213) 6.50 (0.177)† 6.40 (0.162) 6.32 (0.151) 6.2a |
| $1^1B_1$ | $n \rightarrow \sigma^*$ | 6.88 (0.001) 6.87 (0.001) 7.17 (0) 7.06 (0.001) |
| $1^1B_2$ | $\sigma \rightarrow \pi^*$ | 6.91 (0.019) 6.90 (0.021) 6.75 (0.010) 6.71 (0.008) |
| $2^1A_2$ | $\pi, n \rightarrow \pi^*$ | 7.18 (0) 7.71 (0) 7.55 (0) 7.54 (0) |
| $3^1A_1$ | $n^2 \rightarrow \pi^*$ | 7.89 (0.011) 6.07 (0.074)‡ 7.29 (0.015) 7.25 (0.015) |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 1.86 1.93 1.81 1.81 |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 3.31 3.24 3.34 3.32 |
| $1^3B_2$ | $\sigma \rightarrow \pi^*$ | 6.06 6.13 5.84 5.80 |
| $1^3B_1$ | $n \rightarrow \sigma^*$ | 6.36 6.41 6.53 6.43 |
|       |                   |             |          |            |             |                |            |
| $2^2A_2$ | $\pi, n \rightarrow \pi^*$ | 7.79 7.31 7.08 7.06 |

‡ Peak maximum [7]

† $3^1A_1$

‡ $2^1A_1$
Table S14: Calculated percentage of electron configurations in the excited states wave functions of thioformaldehyde obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | % from to | State | % from to | State | % from to |
|-------|-----------|-------|-----------|-------|-----------|
|      |           |       | DFT/MRCI  | MRMP2  | MRMP2     |
|       |           |       | (BH-LYP)  | (HF)    | (BH-LYP)  |
|       |           |       | Excitation| Excitation| Excitation|
| $1^1A_2$ | 92 n$_H$ | $\pi^*_L$ | 79 n$_H$ | $\pi^*_L$ | 80 n$_H$ | $\pi^*_L$ |
|        | 7 $\pi_{H-1}$ | n$_H$ | 6 $\pi_{H-1}$ | n$_H$ | 7 n$_H$ | n$_H$ |
|        | $\pi_{L,\sigma}^*$ | $\pi_L^*$ | $\pi_L^*$ | $\pi_L^*$ | $\pi_L^*$ | $\pi_L^*$ |
| $2^1A_1$ | 89 $\pi_{H-1}$ | 72 $\pi_{L}^*$ | 72 $\pi_{H-1}$ | $\pi_L^*$ | 4 n$_H$ | $\pi_L^*$ |
|        | 2 n$_H$ | n$_H$ | 5 n$_H$ | n$_H$ | 3 n$_H$ | n$_H$ |
|        | $\pi_{L,\sigma}^*$ | $\pi_L^*$ | $\pi_L^*$ | $\pi_L^*$ |
| $1^1B_1$ | 88 n$_H$ | 73 n$_H$ | 76 n$_H$ | $\sigma_{L+1}$ | 3 n$_H$ | $\sigma_{L+1}$ |
|        | 4 n$_H$ | 6 n$_H$ | 3 n$_H$ | $\sigma_{L+4}$ | 3 n$_H$ | $\sigma_{L+4}$ |
|        | 3 $\pi_{H-1}$ | n$_H$ | 3 $\pi_{H-1}$ | n$_H$ | 3 n$_H$ | n$_H$ |
| $1^1B_2$ | 94 $\sigma_{H-2}$ | 78 $\sigma_{H-2}$ | 79 $\sigma_{H-2}$ | $\pi_L^*$ | 3 $\pi_2$, 3 | $\pi_L^*$ |
|        | 2 $\sigma_{H-2}$ | $\pi_{H-1}$ | $\pi_L^*$ | $\pi_L^*$ | 3 $\sigma_{H-1}$ | $\pi_L^*$ |
|        | $\sigma_{L+1}$ | $\sigma_{L+1}$ | $\sigma_{L+1}$ |
| $2^1A_2$ | 72 $\pi_{H-1}$ | 41 $\pi_{H-1}$ | 43 $\pi_{H-1}$ | $\pi_L^*$ | 5 $\pi_{H-1}$ | $\pi_L^*$ |
|        | 18 $\pi_{H-3}$ | 33 $\sigma_{H-3}$ | 32 $\sigma_{H-3}$ | $\pi_L^*$ | 5 $\pi_{H-3}$ | $\pi_L^*$ |
|        | 3 $\pi_{H-1}$ | 4 n$_H$ | 4 n$_H$ | $\pi_L^*$ | 4 n$_H$ | $\pi_L^*$ |
| $3^1A_1$ | 86 n$_H$ | 70 n$_H$ | 70 n$_H$ | n$_H$ | 4 n$_H$ | n$_H$ |
|        | 8 n$_H$ | 7 n$_H$ | 9 n$_H$ | n$_H$ | 4 n$_H$ | n$_H$ |
|        | $\sigma_{H-3}$ | $\sigma_{H-3}$ | $\sigma_{H-3}$ | $\pi_L^*$ | $\pi_L^*$ |
| $1^3A_2$ | 96 n$_H$ | 82 n$_H$ | 83 n$_H$ | $\pi_L^*$ | 83 n$_H$ | $\pi_L^*$ |
| $1^3A_1$ | 99 $\pi_{H-1}$ | 86 $\pi_{H-1}$ | 88 $\pi_{H-1}$ | $\pi_L^*$ | 88 $\pi_{H-1}$ | $\pi_L^*$ |
| $1^3B_2$ | 97 $\sigma_{H-2}$ | 82 $\sigma_{H-2}$ | 82 $\sigma_{H-2}$ | $\pi_L^*$ | 82 $\sigma_{H-2}$ | $\pi_L^*$ |
| $1^3B_1$ | 78 n$_H$ | 56 n$_H$ | 64 n$_H$ | $\sigma_{H-1}$ | 10 n$_H$ | $\sigma_{H-1}$ |
|        | 9 n$_H$ | 16 n$_H$ | 10 n$_H$ | $\sigma_{H-4}$ | 5 n$_H$ | $\sigma_{H-4}$ |
|        | 7 n$_H$ | 6 n$_H$ | 5 n$_H$ | $\sigma_{H-3}$ |
| $2^3A_2$ | 51 $\pi_{H-1}$ | 63 $\pi_{H-1}$ | 64 $\pi_{H-1}$ | $\pi_L^*$ | 14 $\sigma_{H-3}$ | $\pi_L^*$ |
|        | 44 $\pi_{H-1}$ | 14 $\sigma_{H-3}$ | 14 $\sigma_{H-3}$ | $\pi_L^*$ | 14 $\sigma_{H-3}$ | $\pi_L^*$ |

20
Table S15.: Calculated percentage of electron configurations in the discussed wave functions of thioformaldehyde obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | % from | to       | % from | to       |
|-------|--------|----------|--------|----------|
| 2\textsuperscript{1}A\textsubscript{1} | 89     | \(\pi_{H-1}\) | 2      | \(n_{H}\, n_{H}\) |
|       | 65     | \(\pi^*_{L}\) | 28     | \(n_{H}, n_{H}\) |
| 2\textsuperscript{1}A\textsubscript{2} | 72     | \(\pi_{H-1}, n_{H}\) | 18     | \(\sigma_{H-3}\) |
|       | 63     | \(\pi_{L}^*\) | 29     | \(\sigma_{H-3}\) |
|       | 5      | \(n_{H}\) | 3      | \(n_{H}\) |
| 3\textsuperscript{1}A\textsubscript{1} | 86     | \(n_{H}, n_{H}\) | 8      | \(n_{H}, \sigma_{H-3}\) |
|       | 66     | \(\pi_{L}^*\) | 28     | \(\pi_{H-1}\) |
|       | 2      | \(\pi_{H-3}\) | 2      | \(n_{H}, \sigma_{H-3}\) |
| 2\textsuperscript{3}A\textsubscript{2} | 51     | \(\sigma_{H-3}\) | 44     | \(\pi_{H-1}, n_{H}\) |
|       | 79     | \(\pi_{L}^*\) | 14     | \(\sigma_{H-3}\) |
Table S16. Selected matrix elements (cm\(^{-1}\)) for thioformaldehyde calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

| SOMEs(cm\(^{-1}\)) | DFT/MRCI | DFT/MRCI-R | MR-MP2(HF) | MR-MP2(BH-LYP) |
|-----------------------|-----------|-------------|-------------|-----------------|
| \(1^3A_2 \mid \hat{H}_{SO} \times \mid 1^1A_1 \) | 180.3 | 178.2 | 163.6 | 168.8 |
| \(1^3A_2 \mid \hat{H}_{SO} \times \mid 2^1A_1 \) | 99.4 | 179.2 | 74.4 | 83.0 |
| \(1^3A_2 \mid \hat{H}_{SO} \times \mid 3^1A_1 \) | 156.8 | 55.8 | 148.5 | 147.8 |
| \(1^3B_1 \mid \hat{H}_{SO} \gamma \mid 1^1A_1 \) | 66.3 | 63.8 | 57.7 | 58.9 |
| \(1^3B_1 \mid \hat{H}_{SO} \gamma \mid 2^1A_1 \) | 16.5 | 15.9 | 18.3 | 17.4 |
| \(1^3B_1 \mid \hat{H}_{SO} \gamma \mid 3^1A_1 \) | 6.9 | 6.7 | 8.3 | 5.6 |
| \(1^3B_2 \mid \hat{H}_{SO} \times \mid 1^1A_1 \) | 105.6 | 105.2 | 98.2 | 101.6 |
| \(1^3B_2 \mid \hat{H}_{SO} \times \mid 2^1A_1 \) | 76.0 | 60.9 | 67.2 | 70.1 |
| \(1^3B_2 \mid \hat{H}_{SO} \times \mid 3^1A_1 \) | 6.3 | 44.3 | 11.8 | 11.0 |
| \(1^3A_1 \mid \hat{H}_{SO} \times \mid 1^1A_2 \) | 168.2 | 163.2 | 155.5 | 160.9 |
| \(1^3A_1 \mid \hat{H}_{SO} \times \mid 2^1A_2 \) | 89.6 | 95.8 | 70.1 | 73.0 |
| \(1^3B_1 \mid \hat{H}_{SO} \times \mid 1^1A_2 \) | 32.4 | 31.3 | 27.6 | 28.3 |
| \(1^3B_2 \mid \hat{H}_{SO} \gamma \mid 1^1A_2 \) | 105.8 | 106.3 | 99.7 | 103.2 |
| \(1^3A_2 \mid \hat{H}_{SO} \times \mid 1^1B_1 \) | 23.4 | 22.6 | 16.2 | 17.1 |
| \(1^3A_1 \mid \hat{H}_{SO} \times \mid 1^1B_2 \) | 88.0 | 85.8 | 81.0 | 81.6 |
| \(1^3A_2 \mid \hat{H}_{SO} \gamma \mid 1^1B_2 \) | 104.7 | 104.9 | 96.5 | 99.6 |
| \(1^3A_2 \mid \hat{H}_{SO} \times \mid 1^3A_1 \) | 157.2 | 158.4 | 148.4 | 154.4 |
| \(1^3B_1 \mid \hat{H}_{SO} \times \mid 1^3A_2 \) | 28.9 | 27.5 | 23.1 | 22.9 |
| \(1^3B_2 \mid \hat{H}_{SO} \times \mid 1^3A_1 \) | 82.0 | 82.5 | 78.6 | 81.8 |
| \(1^3B_2 \mid \hat{H}_{SO} \gamma \mid 1^3A_2 \) | 106.9 | 106.6 | 100.4 | 103.6 |
Table S17. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 vertical excitation energies of thioformaldehyde using the augmented basis. The CASPT2 (8,11) active space consists of following occupied/unoccupied orbitals: 1/3 \(a_1\), 1/2 \(b_2\) and 2/2 \(b_1\). The oscillator strengths are given in the parentheses.

| State       | Character | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) | CASPT2 (8,11) | Experiment    |
|-------------|-----------|----------|------------|------------|----------------|----------------|---------------|
| \(1^1A_2\)  | \(n \rightarrow \pi^*\) | 2.16 (0) | 2.20 (0)   | 2.10 (0)   | 2.16 (0)       | 2.11 (0)       | \(2.03^a\)    |
| \(1^1B_1\)  | \(n \rightarrow 4s\) | 5.67 (0.009) | 5.67 (0.009) | 6.07 (0.015) | 5.99 (0.016) | 5.84 (0.027) | \(5.84^b\)    |
| \(2^2B_1\)  | \(n \rightarrow 4p_z\) | 6.35 (0.039) | 6.35 (0.039) | 6.83 (0.030) | 6.73 (0.033) | 6.57 (0.024) | \(6.59^b\)    |
| \(2^1A_1\)  | \(\pi \rightarrow \pi^*\) | 6.46 (0.243) | 6.48 (0.216) \(^1\) | 6.30 (0.178) | 6.50 (0.146) \(^1\) | 6.29 (0.126) \(^m\) | \(6.2^c\)    |
| \(3^3A_1\)  | \(n \rightarrow 4p_z\) | 6.53 (0.014) | 6.53 (0) \(^2\) | 7.04 (0.003) | 6.45 (0.046) \(^2\) | 6.78 (0.019) | \(6.84^b\)    |
| \(2^1A_2\)  | \(n \rightarrow 4p_y\) | 6.67 (0) | 6.65 (0)   | 7.19 (0)   | 7.08 (0)       | 6.94 (0)       | \(6.94\)      |
| \(1^1B_2\)  | \(\sigma \rightarrow \pi^*\) | 6.89 (0.016) | 6.89 (0.018) | 6.72 (0.008) | 6.78 (0.002) | 7.15 (0.058) | \(6.84^b\)    |
| \(3^3A_2\)  | \(\pi, n \rightarrow \pi^*\) | 7.19 (0) | 7.70 (0) \(^3\) | 7.61 (0)   | 7.58 (0)       | 7.66 (0)       | \(7.66\)      |
|              | \(\ldots\) |           |            |            |                |                |               |
| \(5^3A_1\)  | \(n^2 \rightarrow \pi^*\) | 7.84 (0.006) | 6.06 (0.076) \(^4\) | 7.27 (0.010) \(^1\) | 7.26 (0.019) \(^3\) | 7.11 (0.086) \(^n\) | \(1.80^a\)    |
| \(1^3A_2\)  | \(n \rightarrow \pi^*\) | 1.84       | 1.92       | 1.81       | 1.89           | 1.84           | \(1.84\)      |
| \(1^3A_1\)  | \(\pi \rightarrow \pi^*\) | 3.29       | 3.23       | 3.33       | 3.37           | 3.34           | \(3.34\)      |
| \(1^3B_1\)  | \(n \rightarrow 4s\) | 5.54       | 5.54       | 5.93       | 5.85           | 5.75           | \(5.75\)      |
| \(1^3B_2\)  | \(\sigma \rightarrow \pi^*\) | 6.04       | 6.12       | 5.81       | 5.85           | 6.24           | \(6.24\)      |
|              | \(\ldots\) |           |            |            |                |                |               |
| \(4^3A_2\)  | \(\pi, n \rightarrow \pi^*\) | 7.77       | 7.28 \(^5\) | 7.11 \(^2\) | 7.24           | 7.19           | \(7.19\)      |

DFT/MRCI-R: \(^1\) 3\(^1A_1\), \(^2\) 4\(^1A_1\), \(^3\) 4\(^1A_2\), \(^4\) 2\(^1A_1\), \(^5\) 3\(^1A_2\)
MR-MP2(HF): \(^1\) 4\(^1A_1\), \(^2\) 2\(^3A_2\)
MR-MP2(BH-LYP): \(^1\) 3\(^1A_1\), \(^2\) 2\(^1A_1\), \(^3\) 4\(^1A_1\)
\(^m\) Mixture of \(\pi - \pi^*\) (50%) and \(n^2 - \pi^*\) (37%)
\(^n\) Mixture of \(n^2 - \pi^*\) (51%) and \(\pi - \pi^*\) (36%)
\(^a\) Vertical transition (absorption) \([8]\)
\(^b\) Absorption band origin \([9]\)
\(^c\) Absorption peak maximum (vapor) \([7]\)
| State | % from | to | % from | to | % from | to |
|-------|--------|----|--------|----|--------|----|
| \(1^1A_2\) | 91 | \(n_H\) | \(\pi^*_L\) | 6 | \(\pi^*_L\) | \(\sigma_{L+10}\) | 51 | \(n_H\) | \(\pi^*_L\) | 28 | \(\pi^*_L\) | \(\sigma_{L+4}\) | 78 | \(n_H\) | \(\pi^*_L\) | \(\sigma_{L+4}\) |
| \(2^1A_1\) | 87 | \(\pi_{H-1}\) | \(\pi^*_L\) | 50 | \(\pi_{H-1}\) | \(\pi^*_L\) | 36 | \(\pi_{H-1}\) | \(\sigma_{L-10}\) | 36 | \(\pi_{H-1}\) | \(4p_{xz}\) |
| \(1^1B_1\) | 86 | \(n_H\) | \(4s(c)\) | 52 | \(n_H\) | \(4s(c)\) | 73 | \(n_H\) | \(4s(c)\) |
| \(1^1B_2\) | 92 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 49 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 73 | \(\sigma_{H-2}\) | \(\pi^*_L\) | \(3d_{xy}\) |
| \(3^1A_2\) | 66 | \(\pi_{H-1,n_H}\) | \(\pi^*_L,\pi^*_L\) | 27 | \(\sigma_{H-3}\) | \(\pi^*_L\) | 38 | \(\pi_{H-1,n_H}\) | \(\pi^*_L,\pi^*_L\) | 34 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L\) | 5 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L\) |
| \(5^1A_1\) | 85 | \(n_H^2\) | \(\pi^*_L,\pi^*_L\) | 28 | \(n_H^2\) | \(\pi^*_L,\pi^*_L\) | 68 | \(n_H^2\) | \(\pi^*_L,\pi^*_L\) | 9 | \(n_H^2\) | \(\pi^*_L,\pi^*_L\) | 6 | \(n_H^2\) | \(\pi^*_L,\pi^*_L\) |
| \(1^3A_2\) | 95 | \(n_H\) | \(\pi^*_L\) | 52 | \(n_H\) | \(\pi^*_L\) | 82 | \(n_H\) | \(\pi^*_L\) |
| \(1^3A_1\) | 98 | \(\pi_{H-1}\) | \(\pi^*_L\) | 52 | \(\pi_{H-1}\) | \(\pi^*_L\) | 88 | \(\pi_{H-1}\) | \(\pi^*_L\) |
| \(1^3B_1\) | 81 | \(n_H\) | \(4s(c)\) | 48 | \(n_H\) | \(4s(c)\) | 71 | \(n_H\) | \(4s(c)\) | 5 | \(n_H\) | \(p_x\) |
| \(1^3B_2\) | 96 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 50 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 82 | \(\sigma_{H-2}\) | \(\pi^*_L\) |
| \(4^1A_2\) | 50 | \(\pi_{H-3}\) | \(\pi^*_L\) | 19 | \(\pi_{H-1,n_H}\) | \(\pi^*_L,\pi^*_L\) | 42 | \(n_H\) | \(3d_{yz}\) | 17 | \(\pi_{H-1,n_H}\) | \(\pi^*_L,\pi^*_L\) | 28 | \(\pi_{H-1,n_H}\) | \(\pi^*_L,\pi^*_L\) | 5 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L\) | 13 | \(\pi_{H-3}\) | \(\pi^*_L,\pi^*_L\) | 5 | \(n_H\) | \(\pi^*_L,\pi^*_L\) | 5 | \(n_H\) | \(\pi^*_L,\pi^*_L\) |

† HF orbital which valence part is the same as \(\pi^*_L\) (BH-LYP), but with the opposite phase.

The \(\sigma^*\) and \(d_{yz}\) orbitals are mixed at the HF level.

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

The \(\pi^*_L\) bh-lyp orbital corresponds to the \(\pi^*_L+1\) hf orbital.
Table S19.: Calculated percentage of electron configurations in the discussed wave functions of thioformaldehyde obtained at the DFT/MRCI-R, and CASPT2 (8,11) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | % from | to | % from | to |
|-------|--------|----|--------|----|
| 1^1A_2 | 93 | \(n_H\) | \(\sigma_{L+10}\) | 92 | \(n_H\) | \(\pi^*_L\) |
| 2^1A_1 | 54 | \(n^{2+}_H\) | \(\pi^*_L\) | 50 | \(n^{2+}_H\) | \(\pi^*_L\) |
| | 22 | \(n^{2+}_H\) | \(\pi^*_L\) | 37 | \(n^{2+}_H\) | \(\pi^*_L\) |
| | 16 | \(n_H\) | | 4p_x | |
| 1^1B_1 | 87 | \(n_H\) | 4s(c) | 92 | \(n_H\) | 4s(c) |
| | 5 | \(n_H\) | | \(\sigma_{L+10}\) | |
| 1^1B_2 | 94 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 94 | \(\sigma_{H-2}\) | \(\pi^*_L\) |
| 3^1A_2 | 59 | \(n^{2+}_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | 60 | \(n^{2+}_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) |
| | 28 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | 25 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) |
| | \(n_H\) | \(\pi^*_L\) | | | |
| 5^1A_1 | 65 | \(n^{2+}_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | 51 | \(n^{2+}_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) |
| | 28 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | 36 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) |
| | 2 | \(n_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | | | |
| 1^3A_2 | 95 | \(n_H\) | \(\pi^*_L\) | 95 | \(n_H\) | \(\pi^*_L\) |
| 1^3A_1 | 98 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 97 | \(\sigma_{H-2}\) | \(\pi^*_L\) |
| 1^3B_1 | 83 | \(n_H\) | 4s(c) | 93 | \(n_H\) | 4s(c) |
| | 9 | \(n_H\) | | \(\sigma_{L+10}\) | |
| 1^3B_2 | 96 | \(\sigma_{H-2}\) | \(\pi^*_L\) | 94 | \(\sigma_{H-2}\) | \(\pi^*_L\) |
| 4^1A_2 | 65 | \(n^{2+}_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | 75 | \(n^{2+}_H\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) |
| | 12 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) | 12 | \(\sigma_{H-3}\) | \(\pi^*_L,\pi^*_L,\pi^*_L\) |
| | 11 | \(n_H\) | 3d_{x^2} | | | |
### S4.4. Furan

Table S20. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of furan using the valence basis. The oscillator strengths are given in the parentheses.

| State   | Dominant character | DFT/MRCI     | DFT/MRCI-R   | MRMP2 (HF) | MRMP2 (BH-LYP) | Experiment       |
|---------|--------------------|--------------|--------------|------------|----------------|------------------|
| $2^1A_1$ | $\pi \rightarrow \pi^*$ | 6.40 (0)     | 6.43 (0)     | 6.20 (0.001) | 6.12 (0.002)   |                  |
| $1^1B_1$ | $\pi \rightarrow \pi^*$ | 6.43 (0.235) | 6.34 (0.253) | 6.42 (0.165) | 6.30 (0.163)   | **6.04$^{a,b}$, 6.06$^c$** |
| $1^1A_2$ | $\pi \rightarrow Ryd$   | 7.46 (0)     | 7.48 (0)     | 7.75 (0)    | 7.81 (0)       |                  |
| $2^1A_2$ | $\pi \rightarrow Ryd$   | 8.03 (0)     | 8.06 (0)     | 8.24 (0)    | 8.44 (0)       |                  |
| $1^1B_2$ | $\pi \rightarrow Ryd$   | 8.13 (0.014) | 8.14 (0.014) | 8.50 (0.020) | 8.50 (0.022)   |                  |
| $3^1A_1$ | $\pi \rightarrow \pi^*$ | 8.28 (0.698) | 8.23 (0.772) | 7.97 (0.415) | 7.84 (0.390)   | **7.82$^d$, 7.80$^e$** |
| $1^3B_1$ | $\pi \rightarrow \pi^*$ | 4.00         | 4.01         | 4.08        | 4.08           |                  |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 5.19         | 5.20         | 5.23        | 5.20           | **4.00$^{d}$, 3.99$^e$** |
| $2^3A_1$ | $\pi \rightarrow \pi^*$ | 6.67         | 6.63         | 6.45        | 6.37           |                  |
| $2^3B_1$ | $\pi \rightarrow \pi^*$ | 7.25         | 7.20         | 7.09        | 7.05           |                  |
| $1^3A_2$ | $\pi \rightarrow Ryd$   | 7.33         | 7.37         | 7.66        | 7.66           |                  |
| $2^3A_2$ | $\pi \rightarrow Ryd$   | 7.69         | 7.75         | 7.91        | 7.84           |                  |
| $1^3B_2$ | $\pi \rightarrow Ryd$   | 7.97         | 8.02         | 8.37$^d$   | 8.39$^d$       |                  |

MRMP2 (HF)$^12^3B_2$
MRMP2 (BH-LYP)$^12^3B_2$

$^a$ VUV maximum (gas) [10]

$^b$ Electron energy-loss maximum (gas) [11]

$^c$ Electron energy-loss maximum (gas) [12]

$^d$ Electron impact maximum (gas) [13]
Table S21: Calculated percentage of electron configurations in the excited states wave functions of furan obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | Excitation | Excitation | Excitation |
|-------|------------|------------|------------|
|       | DFT/MRCI   | MRMP2      | MRMP2      |
|       | (BH-LYP)   | (HF)       | (BH-LYP)   |
|       | % from     | % from     | % from     |
|       | to         | to         | to         |
|       | % from     | % from     | % from     |
|       | to         | to         | to         |
| $2^1A_1$ | 45 | $\pi_{H-1}$ | $\pi_{L}^*$ | 31 | $\pi_{H-1}$ | $\pi_{L}^*$ | 31 | $\pi_{H-1}$ | $\pi_{L}^*$ |
|        | 37 | $\pi_{H}$ | $\pi_{L+2}^*$ | 26 | $\pi_{H}$ | $\pi_{L+2}^*$ | 27 | $\pi_{H}$ | $\pi_{L+2}^*$ |
|        | 5  | $\pi_{H-1}\pi_{H}$ | $\pi_{L}^*$ | 6  | $\pi_{H-1}\pi_{H}$ | $\pi_{L}^*$ | 6 | $\pi_{H-1}\pi_{H}$ | $\pi_{L}^*$ |
|        | 4  | $\pi_{H}\pi_{H}$ | $\pi_{L+2}^*$ | 6 | $\pi_{H-1}\pi_{H}$ | $\pi_{L+2}^*$ | 5 | $\pi_{H-1}\pi_{H}$ | $\pi_{L+2}^*$ |
|        | 2  | $\pi_{H}\pi_{H}$ | $\pi_{L+2}^*$ | 2 | $\pi_{H}\pi_{H}$ | $\pi_{L+2}^*$ | 2 | $\pi_{H}\pi_{H}$ | $\pi_{L+2}^*$ |
| $1^1B_1$ | 95 | $\pi_{H}$ | $\pi_{L}^*$ | 74 | $\pi_{H}$ | $\pi_{L}^*$ | 72 | $\pi_{H}$ | $\pi_{L}^*$ |
| $1^1A_2$ | 89 | $\pi_{H}$ | Ry$_{L+1}$ | 68 | $\pi_{H}$ | Ry$_{L+1}$ | 71 | $\pi_{H}$ | Ry$_{L+1}$ |
|        | 4  | $\pi_{H}$ | Ry$_{L+1}$ | 4 | $\pi_{H}$ | Ry$_{L+1}$ | 10 | $\pi_{H}$ | Ry$_{L+1}$ |
| $1^1B_2$ | 9 | $\pi_{H}$ | Ry$_{L+1}$ | 56 | $\pi_{H}$ | Ry$_{L+1}$ | 61 | $\pi_{H}$ | Ry$_{L+1}$ |
|        | 10 | $\pi_{H}$ | Ry$_{L+1}$ | 10 | $\pi_{H}$ | Ry$_{L+1}$ | 4 | $\pi_{H}$ | Ry$_{L+1}$ |
| $1^3B_1$ | 92 | $\pi_{H}$ | $\pi_{L}^*$ | 69 | $\pi_{H}$ | $\pi_{L}^*$ | 70 | $\pi_{H}$ | $\pi_{L}^*$ |
|        | 4  | $\pi_{H-1}$ | $\pi_{L}^*$ | 4 | $\pi_{H-1}$ | $\pi_{L}^*$ | 5 | $\pi_{H-1}$ | $\pi_{L}^*$ |
| $1^3A_1$ | 51 | $\pi_{H}$ | $\pi_{L+2}^*$ | 36 | $\pi_{H}$ | $\pi_{L+2}^*$ | 37 | $\pi_{H}$ | $\pi_{L+2}^*$ |
|        | 44 | $\pi_{H}$ | $\pi_{L+2}^*$ | 35 | $\pi_{H}$ | $\pi_{L+2}^*$ | 35 | $\pi_{H}$ | $\pi_{L+2}^*$ |
|        | 2  | $\pi_{H-1}\pi_{H}$ | $\pi_{L}^*$ | 2 | $\pi_{H-1}\pi_{H}$ | $\pi_{L}^*$ | 3 | $\pi_{H-1}\pi_{H}$ | $\pi_{L}^*$ |
| $1^3A_2$ | 89 | $\pi_{H}$ | Ry$_{L+1}$ | 68 | $\pi_{H}$ | Ry$_{L+1}$ | 69 | $\pi_{H}$ | Ry$_{L+1}$ |
|        | 4  | $\pi_{H}$ | Ry$_{L+1}$ | 3 | $\pi_{H}$ | Ry$_{L+1}$ | 3 | $\pi_{H}$ | Ry$_{L+1}$ |
|        | 2  | $\pi_{H-1}$ | Ry$_{L+1}$ | 2 | $\pi_{H-1}$ | Ry$_{L+1}$ | 2 | $\pi_{H-1}$ | Ry$_{L+1}$ |
| $1^3B_2$ | 84 | $\pi_{H}$ | Ry$_{L+1}$ | 55 | $\pi_{H}$ | Ry$_{L+1}$ | 62 | $\pi_{H}$ | Ry$_{L+1}$ |
|        | 11 | $\pi_{H}$ | Ry$_{L+1}$ | 11 | $\pi_{H}$ | Ry$_{L+1}$ | 12 | $\pi_{H}$ | Ry$_{L+1}$ |
|        | 8  | $\pi_{H}$ | Ry$_{L+1}$ | 8 | $\pi_{H}$ | Ry$_{L+1}$ | 8 | $\pi_{H}$ | Ry$_{L+1}$ |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:
The $\pi_{L+2}^*$ bh-lyp orbital corresponds to the $\pi_{L+2}^*$ hf orbital;
The Ry$_{L+2}^*$ bh-lyp orbital corresponds to the Ry$_{L+2}^*$ hf orbital;
The Ry$_{L+2}^*$ bh-lyp orbital corresponds to the Ry$_{L+2}^*$ hf orbital.
Table S22. Selected matrix elements (cm$^{-1}$) for furan calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

|                  | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |
|------------------|----------|------------|------------|----------------|
| $\langle 1^3A_2 | H_{SO} \hat{z} | 1^1A_1 \rangle$ | 9.6      | 9.3        | 9.1          | 9.1            |
| $\langle 1^3A_2 | H_{SO} \hat{z} | 2^1A_1 \rangle$ | 1.1      | 1.0        | 1.0          | 1.2            |
| $\langle 1^3B_1 | H_{SO} \hat{x} | 1^1A_2 \rangle$ | 5.2      | 5.0        | 4.4          | 4.7            |
| $\langle 1^3A_2 | H_{SO} \hat{x} | 1^1B_1 \rangle$ | 4.6      | 4.4        | 3.4          | 3.5            |
| $\langle 1^3A_1 | H_{SO} \hat{x} | 1^1B_2 \rangle$ | 3.8      | 3.7        | 4.1          | 4.3            |
| $\langle 1^3A_2 | H_{SO} \hat{y} | 1^1B_2 \rangle$ | 0.3      | 0.2        | 0.1          | 0.1            |
| $\langle 1^3B_1 | H_{SO} \hat{x} | 1^1B_2 \rangle$ | 9.4      | 9.3        | 7.8          | 8.2            |
| $\langle 1^3A_2 | H_{SO} \hat{x} | 1^3A_1 \rangle$ | 1.1      | 0.9        | 1.4          | 1.1            |
| $\langle 1^3B_1 | H_{SO} \hat{x} | 1^3A_2 \rangle$ | 5.1      | 5.0        | 4.4          | 4.7            |
| $\langle 1^3B_2 | H_{SO} \hat{x} | 1^3A_1 \rangle$ | 3.9      | 3.7        | 4.2          | 4.2            |
Table S23. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 (6,9) vertical excitation energies of furan using the augmented basis. The CASPT2 active space consists of following occupied/unoccupied orbitals: 0/1 $a_1$, 0/1 $b_1$, 2/2 $b_2$ and 1/1 $a_2$. The oscillator strengths are given in the parentheses.

| State | Dominant character | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) | CASPT2 (6,9) | Experiment |
|-------|--------------------|----------|------------|------------|----------------|--------------|------------|
| $^1A_2$ | $\pi \rightarrow 3s$ | 5.91 (0) | 5.90 (0) | 6.10 (0) | 6.00 (0) | 5.98 (0) | 5.91$^c$ |
| $^1B_1$ | $\pi \rightarrow \pi^*$ | 6.05 (0.238) | 6.04 (0.253) | 6.47 (0.106) | 6.48 (0.092) | 6.11 (0.144) | 6.04$^{a,b}$, 6.06$^c$ |
| $^2A_1$ | $\pi \rightarrow \pi^*$ | 6.29 (0.006) | 6.30 (0.004) | 6.11 (0.001) | 5.93 (0.001) | 6.22 (0.003) | 6.03 |
| $^1B_2$ | $\pi \rightarrow 3p_x$ | 6.38 (0.047) | 6.36 (0.047) | 6.59 (0.050) | 6.48 (0.056) | 6.51 (0.047) | 6.47$^c$ |
| $^2A_2$ | $\pi \rightarrow 3p_z$ | 6.55 (0) | 6.54 (0) | 6.89 (0) | 6.74 (0) | 6.70 (0) | 6.61$^c$ |
| $^2B_1$ | $\pi \rightarrow 3p_y$ | 6.80 (0) | 6.77 (0) | 6.92 (0.015) | 6.92 (0.011) | 6.63 (0.029) | 6.75$^c$ |
| | $\ldots$ | $\ldots$ | $\ldots$ | $\ldots$ | $\ldots$ | $\ldots$ | $\ldots$ |
| $^4A_1$ | $\pi \rightarrow \pi^*$ | 8.13 (0.506) | 8.09 (0.549) | 8.31 (0.307)$^l$ | 8.12 (0.366)$^l$ | 7.87 (0.446) | 7.82$^c$, 7.80$^a$ |
| $^1B_1$ | $\pi \rightarrow \pi^*$ | 3.74 | 3.90 | 4.03 | 3.97 | 4.13 | 4.00$^d$, 3.99$^e$ |
| $^1A_1$ | $\pi \rightarrow \pi^*$ | 5.03 | 5.15 | 5.15 | 5.10 | 5.25 | 5.20$^d$, 5.22$^e$ |
| $^1A_2$ | $\pi \rightarrow 3s$ | 5.80 | 5.83 | 6.00 | 5.90 | 5.93 | 5.8$^l$ |
| $^1B_2$ | $\pi \rightarrow 3p_x$ | 6.27 | 6.30 | 6.51 | 6.44 | 6.46 | 6.28 |
| $^2A_2$ | $\pi \rightarrow 3p_y$ | 6.48 | 6.50 | 6.84 | 6.72 | 6.69 | 6.66 |

MRMP2 (HF)$^a$,$^6^1A_1$
MRMP2 (BH-LYP)$^b$,$^6^1A_1$

$^a$ VUV maximum (gas) [10]
$^b$ Electron energy-loss maximum (gas) [11]
$^c$ Electron energy-loss maximum (gas) [12]
$^d$ Electron impact maximum (gas) [13]
$^e$ Resonantly enhanced multiphoton ionization [14]
$^f$ Electron energy-loss maximum (gas) [10]
Table S24: Calculated percentage of electron configurations in the excited states wave functions of furan obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | Excitation | DFT/MRCI (BH-LYP) | MRMP2 (HF) | MRMP2 (BH-LYP) |
|-------|-------------|-------------------|------------|----------------|
|       | % from to | % from to | % from to | % from to |
| 2^1A_1 | 32 π_H | 30 π_H | 26 π_H | 26 π_H |
|       | 28 π_H-1 | 26 π_H | 19 π_H | 14 π_H |
|       | 23 π_H | 6 π_H | 14 π_H | 14 π_H |
| 1^1B_1 | 71 π_H | 59 π_H | 50 π_H | 50 π_H |
|       | 24 π_H | 14 π_H | 26 π_H | 26 π_H |
| 1^1A_2 | 90 π_H | 57 π_H | 68 π_H | 68 π_H |
|       | 13 π_H | 3p_z | 3p_z | 3p_z |
| 1^1B_2 | 91 π_H | 66 π_H | 71 π_H | 71 π_H |
|       | 3p_x | 7 π_H | 3p_x | 3p_x |
| 1^3A_1 | 46 π_H | 67 π_H | 36 π_H | 36 π_H |
|       | 39 π_H | 5 π_H | 36 π_H | 36 π_H |
| 1^3A_2 | 36 π_H | 39 π_H | 38 π_H | 38 π_H |
|       | 32 π_H | 5 π_H | 18 π_H | 18 π_H |
| 1^3B_2 | 89 π_H | 54 π_H | 67 π_H | 67 π_H |
|       | 17 π_H | 3p_z | 3p_z | 3p_z |
| 1^3B_1 | 89 π_H | 65 π_H | 69 π_H | 69 π_H |
|       | 3p_x | 6 π_H | 5 π_H | 5 π_H |

π^-L+9/π_y and π^+L+9/π_y BH-LYP orbitals arise from combination of π^-L+9 and π_y orbitals. In HF and CASSCF calculations this orbitals do not mix.
Table S25.: Calculated percentage of electron configurations in the discussed wave functions of furan obtained at the DFT/MRCI-R, and CASPT2 (6,9) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State  | Excitation | DFT/MRCI-R  |  | CASPT2 (6,9)  |
|--------|------------|-------------|---|---------------|
|        | % from to  | % from to   |   | % from to     |
| \(2^1A_1\) | \(\pi_H\) | \(\pi_{L+10}^*\) | 33 | \(\pi_{H-1}\) | \(\pi_{L+9}^*\) |
|        | \(\pi_{H-1}\) | \(\pi_{L+3}/p_y\) | 28 | \(\pi_H\) | \(\pi_{L+10}^*\) |
|        | \(\pi_{H-1}\) | \(\pi_{L+9}/p_y\) | 22 | \(\pi_2\) | \(\pi_{L+9}^*\) |
|        | \(\pi_H, \pi_{H-1}\) | \(\pi_{L+9}, \pi_{L+10}^*\) | 7 |  |  |
| \(1^1B_1\) | \(\pi_H\) | \(\pi_{L+3}/p_y\) | 73 | \(\pi_H\) | \(\pi_{L+9}\) |
|        | \(\pi_H\) | \(\pi_{L+9}/p_y\) | 23 | \(\pi_H\) | \(p_y\) |
| \(1^1A_2\) | \(\pi_H\) | 3s | 91 | \(\pi_H\) | 3s |
| \(1^1B_2\) | \(\pi_H\) | 3\(p_x\) | 92 | \(\pi_H\) | 3\(p_x\) |
| \(1^3B_1\) | \(\pi_H\) | \(\pi_{L+3}/p_y\) | 47 | \(\pi_H\) | \(\pi_{L+9}^*\) |
|        | \(\pi_H\) | \(\pi_{L+9}/p_y\) | 46 | \(\pi_{H-1}\) | \(\pi_{L+10}^*\) |
| \(1^3A_1\) | \(\pi_H\) | \(\pi_{L+10}\) | 39 | \(\pi_H\) | \(\pi_{L+10}^*\) |
|        | \(\pi_{H-1}\) | \(\pi_{L+3}/p_y\) | 29 | \(\pi_{H-1}\) | \(\pi_{L+9}^*\) |
|        | \(\pi_{H-1}\) | \(\pi_{L+9}/p_y\) | 26 |  |  |
| \(1^3A_2\) | \(\pi_H\) | 3s | 90 | \(\pi_H\) | 3s |
| \(1^3B_2\) | \(\pi_H\) | 3\(p_x\) | 90 | \(\pi_H\) | 3\(p_x\) |
|        | \(\pi_{H-1}\) | 3s | 5 |  |  |

\(\pi_{L+3}/p_y\) and \(\pi_{L+9}/p_y\) BH-LYP orbitals arise from combination of \(\pi_{L+9}^*\) and \(p_y\) orbitals. In HF and CASSCF calculations these orbitals do not mix.
S4.5. Thiophene

Table S26. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of thiophene using the valence basis. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies (eV) | Energies (eV) | Energies (eV) | Energies (eV) | Experiment |
|-------|--------------------|---------------|---------------|---------------|---------------|------------|
|       |                    | DFT/MRCI      | DFT/MRCI-R    | MR-MP2(HF)    | MR-MP2(BH-LYP)|            |
| $2^1A_1$ | $\pi \rightarrow \pi^*$ | 5.55 (0.095) | 5.54 (0.109) | 5.27 (0.030) | 5.23 (0.057) | 5.43<sup>a</sup> |
| $1^3B_1$ | $\pi \rightarrow \pi^*$ | 5.81 (0.109) | 5.75 (0.120) | 5.75 (0.074) | 5.74 (0.078) | 5.61<sup>a</sup> |
| $1^3B_2$ | $\pi \rightarrow \sigma^*$ | 6.06 (0) | 6.13 (0) | 6.23 (0.001) | 6.16 (0.001) |            |
| $1^1A_2$ | $\pi \rightarrow \sigma^*$ | 6.28 (0) | 6.31 (0) | 6.27 (0) | 6.17 (0) |            |
| $3^1A_1$ | $\pi \rightarrow \pi^*$ | 7.29 (0.321) | 7.35 (0.400) | 6.97 (0.173) | 6.83 (0.223) | 7.05<sup>b</sup> |
| $1^3B_1$ | $\pi \rightarrow \pi^*$ | 3.78 | 3.78 | 3.71 | 3.74 | 3.75<sup>c</sup>, 3.80<sup>d</sup> |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 4.58 | 4.56 | 4.48 | 4.46 | 4.62<sup>c</sup>, 4.70<sup>d</sup> |
| $1^3B_2$ | $\pi \rightarrow \sigma^*$ | 5.86 | 5.91 | 6.00 | 5.92 |            |
| $2^3A_1$ | $\pi \rightarrow \pi^*$ | 5.92 | 5.94 | 5.77 | 5.72 |            |
| $1^3A_2$ | $\pi \rightarrow \sigma^*$ | 5.95 | 6.01 | 5.95 | 5.90 |            |

<sup>a</sup> Electron energy-loss maximum (gas) [11]
<sup>b</sup> VUV absorption maximum (gas) [15]
<sup>c</sup> Electron impact maximum (gas) [12]
<sup>d</sup> Electron energy-loss maximum (gas) [15]
Table S27. Calculated percentage of electron configurations in the excited states wave functions of thiophene obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | % from | to | % from | to |
|-------|--------|----|--------|----|--------|----|
| 2A1   | 74     | \(\pi_{H-1}\) | 47 | \(\pi_{L}^*\) | 16 | \(\pi_{H-1}\) | 3 | \(\pi_{L}^*\) |
|       | 15     | \(\pi_{H}\) | 3 | \(\pi_{L}^*\) | 3 | \(\pi_{H-1}\) | 3 | \(\pi_{L}^*\) |
|       | 3      | \(\pi_{H-1,\pi_H}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-\pi_H}^{-}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
| 1B1   | 89     | \(\pi_{H}\) | 66 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-1,\pi_H}\) | 2 | \(\pi_{L}^*\) | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-\pi_H}^{-}\) | 2 | \(\pi_{L}^*\) | \(\pi_{L}^*\) |
| 1B2   | 85     | \(\pi_{H}\) | 54 | \(\pi_{L}^*\) | 8 | \(\pi_{H-1}\) | 6 | \(\pi_{L}^*\) |
|       | 5      | \(\pi_{H-1,\pi_H}\) | 6 | \(\pi_{L}^*\) | 5 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H}\) | 14 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-\pi_H}^{-}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
| 1B2   | 87     | \(\pi_{H-1}\) | 57 | \(\pi_{L}^*\) | 9 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
|       | 3      | \(\pi_{H-1}\) | 9 | \(\pi_{L}^*\) | 5 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) | 5 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
| 3A1   | 46     | \(\pi_{H}\) | 18 | \(\pi_{L}^*\) | 16 | \(\pi_{H-1}\) | 17 | \(\pi_{L}^*\) |
|       | 15     | \(\pi_{H-3}\) | 15 | \(\pi_{L}^*\) | 15 | \(\pi_{H-1}\) | 15 | \(\pi_{L}^*\) |
|       | 13     | \(\pi_{H-1}\) | 14 | \(\pi_{L}^*\) | 14 | \(\pi_{H-1}\) | 14 | \(\pi_{L}^*\) |
|       | 12     | \(\pi_{H-\pi_H}^{-}\) | 3 | \(\pi_{L}^*\) | 3 | \(\pi_{H-1}\) | 3 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-\pi_H}^{-}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-\pi_H}^{-}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
| 1B1   | 93     | \(\pi_{H}\) | 70 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
| 1A2   | 87     | \(\pi_{H-1}\) | 54 | \(\pi_{L}^*\) | 17 | \(\pi_{H-1}\) | 54 | \(\pi_{L}^*\) |
|       | 9      | \(\pi_{H}\) | 17 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 16 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |
| 3B2   | 88     | \(\pi_{H}\) | 53 | \(\pi_{L}^*\) | 9 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
|       | 4      | \(\pi_{H-1,\pi_H}\) | 9 | \(\pi_{L}^*\) | 5 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H}\) | 5 | \(\pi_{L}^*\) | 5 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
|       | 2      | \(\pi_{H}\) | 5 | \(\pi_{L}^*\) | 5 | \(\pi_{H-1}\) | 5 | \(\pi_{L}^*\) |
| 2A1   | 74     | \(\pi_{H}\) | 42 | \(\pi_{L}^*\) | 11 | \(\pi_{H-1}\) | 45 | \(\pi_{L}^*\) |
|       | 11     | \(\pi_{H-3}\) | 21 | \(\pi_{L}^*\) | 20 | \(\pi_{H-1}\) | 11 | \(\pi_{L}^*\) |
|       | 10     | \(\pi_{H-1}\) | 9 | \(\pi_{L}^*\) | 9 | \(\pi_{H-1}\) | 9 | \(\pi_{L}^*\) |
| 3A2   | 86     | \(\pi_{H-1}\) | 53 | \(\pi_{L}^*\) | 3 | \(\pi_{H-1}\) | 3 | \(\pi_{L}^*\) |
|       | 3      | \(\pi_{H-1}\) | 11 | \(\pi_{L}^*\) | 3 | \(\pi_{H-1}\) | 3 | \(\pi_{L}^*\) |
|       | 3      | \(\pi_{H-1}\) | 6 | \(\pi_{L}^*\) | 6 | \(\pi_{H-1}\) | 6 | \(\pi_{L}^*\) |
|       | 3      | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) | 2 | \(\pi_{H-1}\) | 2 | \(\pi_{L}^*\) |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:
The \(\sigma_{L+1}^\dagger\) bh-lyp orbital corresponds to the \(\sigma_{L+2}^\dagger\) hf orbital;
Table S28. Selected matrix elements (cm$^{-1}$) for thiophene calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

| SOMEs (cm$^{-1}$) | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |
|-------------------|-----------|------------|-------------|-----------------|
| \langle 1^3A_2| \hat{H}_{SO \, z} | 1^1A_1 \rangle | 127.7 | 125.7 | 109.1 | 113.5 |
| \langle 1^3A_2| \hat{H}_{SO \, z} | 2^1A_1 \rangle | 55.6 | 56.0 | 39.9 | 41.0 |
| \langle 1^3A_2| \hat{H}_{SO \, z} | 3^1A_1 \rangle | 29.6 | 28.0 | 29.3 | 36.7 |
| \langle 1^3B_1| \hat{H}_{SO \, y} | 1^1A_1 \rangle | 0.1 | 0.3 | 0.6 | 0.4 |
| \langle 1^3B_2| \hat{H}_{SO \, x} | 1^1A_1 \rangle | 6.9 | 6.4 | 6.1 | 6.5 |
| \langle 1^3B_2| \hat{H}_{SO \, x} | 2^1A_1 \rangle | 1.8 | 2.2 | 3.3 | 3.9 |
| \langle 1^3A_2| \hat{H}_{SO \, z} | 1^1A_2 \rangle | 47.1 | 45.9 | 32.5 | 36.1 |
| \langle 1^3A_1| \hat{H}_{SO \, y} | 1^1B_1 \rangle | 0.5 | 0.4 | 0.4 | 0.4 |
| \langle 1^3A_2| \hat{H}_{SO \, x} | 1^1B_1 \rangle | 17.6 | 17.2 | 15.5 | 15.7 |
| \langle 1^3B_1| \hat{H}_{SO \, z} | 1^1B_2 \rangle | 65.0 | 64.0 | 49.5 | 57.5 |
| \langle 1^3A_2| \hat{H}_{SO \, z} | 2^1A_1 \rangle | 41.2 | 41.0 | 27.9 | 29.4 |
| \langle 1^3A_2| \hat{H}_{SO \, z} | 2^1A_1 \rangle | 13.2 | 11.5 | 18.3 | 17.3 |
| \langle 1^3B_1| \hat{H}_{SO \, y} | 1^3A_1 \rangle | 0.2 | 0.2 | 0.1 | 0.0 |
| \langle 1^3B_1| \hat{H}_{SO \, x} | 1^3A_2 \rangle | 3.0 | 2.5 | 3.2 | 3.7 |
| \langle 1^3B_2| \hat{H}_{SO \, z} | 1^3B_1 \rangle | 64.7 | 66.6 | 53.9 | 60.1 |
Table S29. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) and CASPT2 (6,10) vertical excitation energies of thiophene using the augmented basis. The CASPT2 active space consists of following occupied/unoccupied orbitals: 0/2 ɑ_1, 0/2 ɑ_2, 2/2 ɑ_2 and 1/1 ɑ_2. The oscillator strengths are given in the parentheses.

| State   | Dominant character | Energies (eV) |
|---------|--------------------|---------------|
|         |                    | DFT/MRCI   | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) | CASPT2 (6,10) | Experiment |
| 2^1A_1  | ɑ_1 → ɑ^*          | 5.43 (0.114) | 5.43 (0.124) | 5.23 (0.270) | 5.18 (0.063) | 5.47 (0.080) | 5.43^a      |
| 1^1B_1  | ɑ_1 → ɑ^*          | 5.65 (0.102) | 5.62 (0.115) | 6.10 (0.096) | 5.62 (0.042) | 5.47 (0.124) | 5.61^a      |
| 1^1B_2  | ɑ_2 → σ^*/4p_π     | 5.83 (0.004) | 5.88 (0.005) | 6.19 (0.016) | 6.21 (0.014) | 6.28 (0.015) |            |
| 1^1A_2  | ɑ_1 → 4s           | 5.85 (0)    | 5.84 (0)    | 5.91 (0)    | 6.16 (0)    | 6.03 (0)    | 5.93^c      |
| 2^1A_2  | ɑ_2 → σ^*/4p_π     | 6.06 (0)    | 6.10 (0)    | 6.28 (0)    | 6.21 (0)    | 6.33 (0)    |            |
| 3^1A_1  | ɑ_1 → ɑ^*          | 7.08 (0.167) | 7.02 (0.114) | 7.04 (0.150) | 6.89 (0.158) | 6.99 (0.332) | 7.05^b      |
| 1^3B_1  | ɑ_1 → ɑ^*          | 3.62        | 3.67        | 3.78        | 3.75        | 3.75        | 3.75,c 3.80^d |
| 1^3A_1  | ɑ_1 → ɑ^*          | 4.45        | 4.50        | 4.53        | 4.47        | 4.59        | 4.62,c 4.70^d |
| 1^3B_2  | ɑ_2 → σ^*/4p_π     | 5.64        | 5.71        | 6.06        | 6.04        | 6.11        |            |
| 1^3A_2  | ɑ_1 → 4s           | 5.77        | 5.77        | 6.09^1      | 6.09^1      | 6.00        |            |
| 2^3A_2  | ɑ_2 → σ^*/4p_π     | 5.79        | 5.86        | 5.95^2      | 5.88^2      | 5.99        |            |
| 2^3A_1  | ɑ_1 → ɑ^*          | 5.88        | 5.92        | 5.78        | 5.70        | 5.68        |            |

MR-MP2(HF): 1^3A_2, 2^3A_2
MR-MP2(BH-LYP): 1^3A_2, 2^3A_2

^a Electron energy-loss maximum (gas) [11]
^b VUV absorption maximum (gas) [15]
^c Electron impact maximum (gas) [12]
^d Electron energy-loss maximum (gas) [15]
Table S30. Calculated percentage of electron configurations in the excited states wave functions of thiophene obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | % from to | % from to | % from to |
|-------|-----------|-----------|-----------|
| $^2A_1$ | $\pi_{H^{-1}}$ $\pi_L^{+4}$ | $\pi_{H^{-1}}$ $\pi_L^{+4}$ | $\pi_{H^{-1}}$ $\pi_L^{+4}$ |
| | $3\pi_y$ | $4\pi_y$ | $3\pi_y$ |
| | $\pi_{L^{-1}+11}$ | $\pi_{L^{-1}+11}$ | $\pi_{L^{-1}+11}$ |
| $^2B_1$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ |
| | $2\pi_y$ | $4\pi_y$ | $2\pi_y$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| $^2A_2$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ |
| | $2\pi_y$ | $4\pi_x$ | $2\pi_y$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| $^2B_2$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ | $\pi_{L^{-1}}$ $\pi_L^{+4}$ |
| | $2\pi_y$ | $4\pi_x$ | $2\pi_y$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |
| | $3\pi_{L^{-1}+10}$ | $4\pi_x$ | $3\pi_{L^{-1}+10}$ |
| | $4\pi_{L^{-1}+10}$ | $4\pi_x$ | $4\pi_{L^{-1}+10}$ |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The $\pi_{L^{-1}+4}$ bh-lyp orbital corresponds to the $\pi_{L^{-1}+9}$ hf orbital;
Table S31.: Calculated percentage of electron configurations in the discussed wave functions of thiophene obtained at the DFT/MRCI-R, and CASPT2 (6,10) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | Excitation | % from | to   | % from | to   |
|-------|------------|--------|------|--------|------|
| $2^1A_1$ | $\pi_{H-1}$ | 56     | $\pi_{L+4}^*$ | 46     | $\pi_{H-1}$ | $\pi_{L+4}^*$ |
|       | $\pi_{H-1}$ | 20     | $4p_y$ | 19     | $\pi_{H}$ | $\pi_{L+11}^*$ |
|       | $\pi_{H}$   | 13     | $\pi_{L+11}^*$ | 10     | $\pi_{H-1}$ | $4p_y$ |
| $1^3B_1$ | $\pi_H$     | 69     | $\pi_{L+4}^*$ | 82     | $\pi_H$     | $\pi_{L+4}^*$ |
|       | $\pi_H$     | 22     | $4p_y$ | 7      | $\pi_{H-1}$ | $\pi_{L+11}^*$ |
| $1^3B_2$ | $\pi_H$     | 44     | $\sigma_{L+10}^*$ | 78     | $\pi_H$     | $\pi_{L+11}^*$ |
|       | $\pi_H$     | 40     | $4p_x$ | 5      | $\pi_H$     | $4p_x$ |
|       | $\pi_H$     | 7      | $3d_{ex}$ | 7      | $\pi_{H-1}$ | $\sigma^*/p_x$ |
| $2^1A_2$ | $\pi_{H-1}$ | 53     | $\sigma_{L+10}^*$ | 85     | $\pi_{H-1}$ | $\sigma^*/p_x$ |
|       | $\pi_{H-1}$ | 30     | $4p_x$ | 5      | $\pi_{H-1}$ | $3d_{ex}$ |
|       | $\pi_{H-1}$ | 11     | $3d_{ex}$ | 7      | $\pi_{H-1}$ | $\sigma^*/p_x$ |
| $3^1A_1$ | $\pi_{H-1}$ | 66     | $4p_y$ | 25     | $\pi_{H-1}$ | $\pi_{L+4}^*$ |
|       | $\pi_H$     | 11     | $\pi_{L+11}^*$ | 25     | $\pi_H$     | $\pi_{L+11}^*$ |
|       | $\pi_{H-1}$ | 9      | $\pi_{L+4}^*$ | 21     | $\pi_{H-1}$ | $\pi_{L+4}^*$ |
|       | $\pi_{H-1}$ | 9      | $\pi_{H-1}$ | 7      | $\pi_{H-1}$ | $\pi_{L+11}^*$ |
| $1^3B_1$ | $\pi_H$     | 74     | $\pi_{L+4}^*$ | 87     | $\pi_H$     | $\pi_{L+4}^*$ |
|       | $\pi_H$     | 20     | $4p_y$ | 7      | $\pi_{H-1}$ | $\pi_{L+11}^*$ |
| $1^3A_1$ | $\pi_{H-1}$ | 71     | $\pi_{L+4}^*$ | 60     | $\pi_{H-1}$ | $\pi_{L+4}^*$ |
|       | $\pi_{H-1}$ | 17     | $4p_y$ | 25     | $\pi_{H-1}$ | $\pi_{L+11}^*$ |
|       | $\pi_H$     | 7      | $\pi_{L+11}^*$ | 7      | $\pi_{H-1}$ | $\sigma^*/p_x$ |
| $1^3B_2$ | $\pi_H$     | 51     | $\sigma_{L+10}^*$ | 79     | $\pi_H$     | $\sigma^*/p_x$ |
|       | $\pi_H$     | 32     | $4p_x$ | 7      | $\pi_{H-1}$ | $4s$ |
|       | $\pi_H$     | 9      | $3d_{ex}$ | 7      | $\pi_{H-1}$ | $\sigma^*/p_x$ |
| $2^1A_2$ | $\pi_{H-1}$ | 59     | $\sigma_{L+10}^*$ | 77     | $\pi_{H-1}$ | $\sigma^*/p_x$ |
|       | $\pi_{H-1}$ | 23     | $4p_x$ | 7      | $\pi_{H-1}$ | $\sigma^*/p_x$ |
|       | $\pi_{H-1}$ | 10     | $3d_{ex}$ | 7      | $\pi_{H-1}$ | $\sigma^*/p_x$ |
| $2^1A_1$ | $\pi_H$     | 75     | $\pi_{L+11}^*$ | 43     | $\pi_H$     | $\pi_{L+11}^*$ |
|       | $\pi_{H-1}$ | 8      | $\pi_{L+4}^*$ | 35     | $\pi_{H-1}$ | $\pi_{L+11}^*$ |
|       | $\pi_{H-1}$ | 6      | $\pi_{L+11}^*$ | 18     | $\pi_{H-1}$ | $\pi_{L+11}^*$ |

The $\sigma^*/p_x$ and $\sigma^*/p_x$ CASSCF orbitals are, respectively, positive and negative linear combinations of $\sigma^*$ and $p_x$ orbitals. In HF and DFT calculations these orbitals do not mix.
### S4.6. Quinoxaline

Table S32. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of quinoxaline. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies (eV)          | Experiment |
|-------|--------------------|------------------------|------------|
|       |                    | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |
| $1^1B_1$ | $n \rightarrow \pi^*$ | 3.54 (0.007) | 3.63 (0.008) | 3.24 (0.004) | 3.24 (0.005) | **3.96**a |
| $2^1A_1$ | $\pi \rightarrow \pi^*$ | 4.14 (0.080) | 4.13 (0.094) | 3.75 (0.060) | 3.61 (0.064) |
| $1^1B_2$ | $\pi \rightarrow \pi^*$ | 4.36 (0.052) | 4.33 (0.059) | 4.68 (0.033) | 4.57 (0.025) |
| $1^1A_2$ | $n \rightarrow \pi^*$ | 4.75 (0) | 4.93 (0) | 4.68 (0)$^1$ | 4.56 (0)$^1$ |
| $2^1A_2$ | $n \rightarrow \pi^*$ | 5.05 (0) | 5.14 (0) | 4.47 (0)$^2$ | 4.28 (0)$^2$ |
| $1^3B_2$ | $\pi \rightarrow \pi^*$ | 3.06 | 3.02 | 3.00 | 2.88 |
| $1^3B_1$ | $n \rightarrow \pi^*$ | 3.16 | 3.25 | 2.83 | 2.74 |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 3.70 | 3.63 | 3.72 | 3.59 |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 4.42 | 4.57 | 4.32 | 4.17$^3$ |
| $2^3B_2$ | $\pi \rightarrow \pi^*$ | 4.53 | 4.41 | 4.22 | 4.10 |

MRMP2(HF): $^12^1A_2$, $^21^1A_2$

MRMP2(BH-LYP): $^12^1A_2$, $^21^1A_2$, $^32^3A_2$
a  Vapor absorption maximum [16]
Table S33.: Calculated percentage of electron configurations in the excited states wave functions of quinoxaline obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State   | % from to | % from to | % from to |
|---------|-----------|-----------|-----------|
| $1^1\text{B}_1$ | 83 $\pi_{n-H-2}$ $\pi^*_L$ | 53 $n_{H-2}$ $\pi^*_L$ | 53 $n_{H-2}$ $\pi^*_L$ |
| 5       | 5 $\pi^*_{L+2}$ | 5 $n_{H-2}$ $\pi^*_L$ | 4 $n_{H-2}$ $\pi^*_L$ |
| 2       | 2 $\pi^*_{L+3-H}$ | 2 $n_{H-3} \pi^*_{H-4}$ | 2 $n_{H-3} \pi^*_{H-4}$ |
| $2^1\text{A}_1$ | 63 $\pi^*_{H-1}$ | 41 $\pi^*_{L+1}$ | 40 $n_{H-1}$ $\pi^*_L$ |
| 24      | 16 $\pi^*_{L+1}$ | 15 $\pi^*_{L+1}$ | 15 $\pi^*_{L+1}$ |
| $1^1\text{B}_2$ | 83 $\pi^*_{H}$ | 53 $\pi^*_{H}$ | 51 $\pi^*_{H}$ |
| 2       | 2 $\pi^*_{H-1, \pi^*_{H}}$ | 3 $\pi^*_{H-1, \pi^*_{H}}$ | 3 $\pi^*_{H-1, \pi^*_{H}}$ |
| 2       | 2 $\pi^*_{H}$ | 4 $\pi^*_{L+2}$ | 4 $\pi^*_{L+2}$ |
| $1^1\text{A}_2$ | 61 $\pi^*_{H}$ | 43 $\pi^*_{L+3}$ | 39 $\pi^*_{L+3}$ |
| 11      | 4 $\pi^*_{L+2}$ | 6 $n_{H-2} \pi^*_{H-2}$ | 5 $n_{H-2} \pi^*_{H-2}$ |
| 8       | 8 $n_{H-2} \pi^*_{H-2}$ | 4 $\pi^*_{L+1}$ | 3 $\pi^*_{H-3}$ |
| 6       | 6 $\pi^*_{L+1}$ | 2 $\pi^*_{H-4} \pi^*_{H-2}$ | 2 $\pi^*_{H-4} \pi^*_{H-2}$ |
| 3       | 3 $\pi^*_{H-2}$ | 2 $\pi^*_{H-4} \pi^*_{H-2}$ | 2 $\pi^*_{H-4} \pi^*_{H-2}$ |
| $2^1\text{A}_2$ | 73 $\pi^*_{L+1}$ | 51 $\pi^*_{L+1}$ | 47 $\pi^*_{L+5}$ |
| 8       | 8 $\pi^*_{L+3}$ | 3 $\pi^*_{L+3}$ | 3 $\pi^*_{L+3}$ |
| 6       | 6 $\pi^*_{L+3}$ | 2 $\pi^*_{H-2} \pi^*_{H-2}$ | 2 $\pi^*_{H-2} \pi^*_{H-2}$ |
| 3       | 3 $\pi^*_{H-2} \pi^*_{H-2}$ | 2 $\pi^*_{H-2} \pi^*_{H-2}$ | 2 $\pi^*_{H-2} \pi^*_{H-2}$ |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:

- The $n_{H-3} \pi_{L-H}$ orbital corresponds to the $n_{H-3} \pi_{HF}$ orbital;
- The $\pi_{H-4} \pi_{HF}$ orbital corresponds to the $\pi_{H-3} \pi_{HF}$ orbital;
- The $\pi^*_{L+1}$ orbital corresponds to the $\pi^*_{L+1} \pi_{HF}$ orbital.

39
S4.7. Quinazoline

Table S34. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP) vertical excitation energies of quinazoline. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies (eV) | Experiment |
|-------|-------------------|---------------|------------|
|       |                   | DFT/MRCI      | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |
| $1^1\text{A}''$ | $n \rightarrow \pi^*$ | 3.80 (0.007) | 3.92 (0.008) | 3.49 (0.004) | 3.39 (0.004) | 4.07$^a$ |
| $2^1\text{A}'$ | $\pi \rightarrow \pi^*$ | 4.27 (0.032) | 4.26 (0.040) | 3.90 (0.019) | 3.55 (0.018) | 4.66$^a$ |
| $3^1\text{A}'$ | $\pi \rightarrow \pi^*$ | 4.72 (0.063) | 4.68 (0.067) | 4.86 (0.049) | 4.62 (0.034) |         |
| $2^1\text{A}''$ | $n \rightarrow \pi^*$ | 4.76 (0) | 4.89 (0) | 4.35 (0) | 4.13 (0) |         |
| $3^1\text{A}''$ | $n \rightarrow \pi^*$ | 5.18 (0.001) | 5.29 (0.001) | 4.72 (0) | 4.42 (0) |         |
| $1^3\text{A}'$ | $\pi \rightarrow \pi^*$ | 3.16 | 3.13 | 3.13 | 2.96 |         |
| $1^3\text{A}''$ | $n \rightarrow \pi^*$ | 3.54 | 3.66 | 3.16 | 3.10 |         |
| $2^3\text{A}'$ | $\pi \rightarrow \pi^*$ | 4.06 | 4.00 | 3.91 | 3.72 |         |
| $3^3\text{A}'$ | $\pi \rightarrow \pi^*$ | 4.38 | 4.33 | 4.50$^b$ | 4.27$^b$ |         |
| $2^3\text{A}''$ | $n \rightarrow \pi^*$ | 4.44 | 4.58 | 4.03 | 3.75 |         |

MRMP2(HF):$^14^3\text{A}'$
MRMP2(BH-LYP):$^14^3\text{A}'$

$^a$ Absorption maximum in cyclohexane and ethylether [17]
Table S35: Calculated percentage of electron configurations in the excited states wave functions of quinazoline obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | Excitation | DFT/MRCI (BH-LYP) | | MRMP2 (HF) | | MRMP2 (BH-LYP) |
|-------|------------|------------------|---|---------------|---|------------------|
| \(1^1\Delta''\) | \(n_{H-2}^1\pi_L^*\) | 81 | \(n_{H-2}^1\pi_L^*\) | 53 | \(n_{H-2}^1\pi_L^*\) | 52 |
| \(1^1\Delta''\) | \(n_{H-2}^1\pi_L^{+2}\) | 6 | \(n_{H-2}^1\pi_L^{+2}\) | 5 | \(n_{H-2}^1\pi_L^{+2}\) | 4 |
| \(3^1\Delta'\) | \(\pi_H^*\) | 52 | \(\pi_H^*\) | 32 | \(\pi_H^*\) | 38 |
| \(3^1\Delta'\) | \(\pi_H^{+1}\) | 23 | \(\pi_H^{+1}\) | 17 | \(\pi_H^{+1}\) | 5 |
| \(3^1\Delta'\) | \(\pi_H^{+1}\) | 12 | \(\pi_H^{+1}\) | 9 | \(\pi_H^{+1}\) | 5 |
| \(2^1\Delta''\) | \(n_{H-3}^1\pi_L^{+1}\) | 68 | \(n_{H-3}^1\pi_L^{+1}\) | 45 | \(n_{H-3}^1\pi_L^{+1}\) | 42 |
| \(2^1\Delta''\) | \(n_{H-3}^1\pi_L^{+5}\) | 13 | \(n_{H-3}^1\pi_L^{+5}\) | 9 | \(n_{H-3}^1\pi_L^{+5}\) | 10 |
| \(3^1\Delta''\) | \(n_{H-3}^1\pi_L^{+1}\) | 64 | \(n_{H-3}^1\pi_L^{+1}\) | 42 | \(n_{H-3}^1\pi_L^{+1}\) | 39 |
| \(3^1\Delta''\) | \(n_{H-3}^1\pi_L^{+5}\) | 15 | \(n_{H-3}^1\pi_L^{+5}\) | 11 | \(n_{H-3}^1\pi_L^{+5}\) | 12 |
| \(3^1\Delta''\) | \(n_{H-3}^1\pi_L^{+2}\) | 4 | \(n_{H-3}^1\pi_L^{+2}\) | 3 | \(n_{H-3}^1\pi_L^{+2}\) | 3 |
| \(3^1\Delta''\) | \(n_{H-3}^1\pi_L^{+2}\) | 2 | \(n_{H-3}^1\pi_L^{+2}\) | 2 | \(n_{H-3}^1\pi_L^{+2}\) | 2 |
| \(1^3\Delta'\) | \(\pi_H^*\) | 81 | \(\pi_H^*\) | 52 | \(\pi_H^*\) | 53 |
| \(1^3\Delta'\) | \(\pi_H^{+1}\) | 3 | \(\pi_H^{+1}\) | 4 | \(\pi_H^{+1}\) | 2 |
| \(1^3\Delta'\) | \(\pi_H^{+1}\) | 3 | \(\pi_H^{+1}\) | 2 | \(\pi_H^{+1}\) | 2 |
| \(1^3\Delta'\) | \(\pi_H^{+1}\) | 2 | \(\pi_H^{+1}\) | 2 | \(\pi_H^{+1}\) | 2 |
| \(1^3\Delta'\) | \(\pi_H^{+1}\) | 2 | \(\pi_H^{+1}\) | 2 | \(\pi_H^{+1}\) | 2 |
| \(2^3\Delta''\) | \(n_{H-2}^1\pi_L^{+1}\) | 80 | \(n_{H-2}^1\pi_L^{+1}\) | 51 | \(n_{H-2}^1\pi_L^{+1}\) | 51 |
| \(2^3\Delta''\) | \(n_{H-2}^1\pi_L^{+5}\) | 8 | \(n_{H-2}^1\pi_L^{+5}\) | 6 | \(n_{H-2}^1\pi_L^{+5}\) | 5 |
| \(2^3\Delta''\) | \(n_{H-2}^1\pi_L^{+5}\) | 2 | \(n_{H-2}^1\pi_L^{+5}\) | 3 | \(n_{H-2}^1\pi_L^{+5}\) | 3 |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:
The \(n_{H-3}^1\) bh-lyp orbital corresponds to the \(n_{H-3}^1\) hf orbital;
The \(\pi_H^{+1}\) bh-lyp orbital corresponds to the \(\pi_H^{+1}\) hf orbital;
The \(\pi_L^{+2}\) bh-lyp orbital corresponds to the \(\pi_L^{+2}\) hf orbital;
Table S36. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of pyranthione. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) |  |
|-------|-------------------|--------------|---|
|       |                   | DFT/MRCI     | DFT/MRCI-R | MRMP2(KHF) | MRMP2(BH-LYP) | Experiment |
| $1^1A_2$ | n → π*         | 2.16 (0)     | 2.22 (0)   | 2.26 (0)   | 2.25 (0)      | 2.25$^a$   |
| $1^1B_2$ | n → π*         | 3.76 (0)     | 3.66 (0)   | 3.95 (0.001) | 3.85 (0)     |            |
| $2^1A_1$ | π → π*         | 3.92 (0.497) | 3.90 (0.544) | 3.76 (0.495) | 3.71 (0.482) | 3.78$^a$   |
| $1^1B_1$ | π → π*         | 4.32 (0.003) | 4.35 (0.002) | 4.39 (0.001) | 4.30 (0.002) |            |
| $2^1B_1$ | π → π*         | 5.59 (0.107) | 5.63 (0.121) | 5.54 (0.082) | 5.37 (0.067) |            |
| $1^3A_2$ | n → π*         | 2.05         | 2.08       | 2.15       | 2.16         |            |
| $1^3A_1$ | π → π*         | 2.28         | 2.19       | 2.22       | 2.19         |            |
| $1^3B_1$ | π → π*         | 3.70         | 3.71       | 3.57       | 3.49         |            |
| $1^3B_2$ | n → π*         | 3.80         | 3.61       | 3.94       | 3.83         |            |
| $2^3A_1$ | π → π*         | 4.85         | 4.82       | 4.74       | 4.66         |            |

$^a$ Absorption maximum in 3-methylpentane [18]
Table S37.: Calculated percentage of electron configurations in the excited states wave functions of pyranthione obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | % from to | DFT/MRCI | % from to | MRMP2 (BH-LYP) | % from to | MRMP2 (HF) | % from to | MRMP2 (BH-LYP) |
|-------|-----------|----------|-----------|----------------|-----------|-----------|-----------|----------------|
| 1^1A_2 | 87 | n_H | π^* | 62 | n_H | π^* | 60 | n_H | π^* |
| | 6 | π_H-1,n_H | π_L^* | 6 | π_H-1,n_H | π_L^* | 7 | π_H-1,n_H | π_L^* |
| | 2 | π_H-2,n_H | π_L^* | 1 | π_H-2,n_H | π_L^* | 5 | π_H-2,n_H | π_L^* |
| 1^1B_2 | 76 | n_H | π_L | 50 | n_H | π_L | 48 | n_H | π_L |
| | 12 | π_H-1,n_H | π_L^* | 13 | π_H-1,n_H | π_L^* | 13 | π_H-1,n_H | π_L^* |
| | 5 | π_H-2,n_H | π_L^* | 4 | π_H-2,n_H | π_L^* | 5 | π_H-2,n_H | π_L^* |
| 2^1A_1 | 81 | π_H-1 | π_L | 55 | π_H-1 | π_L | 53 | π_H-1 | π_L |
| | 6 | π_H-1,n_H-1 | π_L^* | 6 | π_H-1,n_H-1 | π_L^* | 6 | π_H-1,n_H-1 | π_L^* |
| | 4 | π_H-2,n_H-1 | π_L^* | 2 | π_H-2,n_H-1 | π_L^* | 2 | π_H-2,n_H-1 | π_L^* |
| 1^1B_1 | 77 | π_H-1 | π_L | 51 | π_H-1 | π_L | 48 | π_H-1 | π_L |
| | 10 | π_H-1,n_H-1 | π_L^* | 9 | π_H-1,n_H-1 | π_L^* | 11 | π_H-1,n_H-1 | π_L^* |
| | 3 | π_H-2,n_H-1 | π_L^* | 3 | π_H-2,n_H-1 | π_L^* | 3 | π_H-2,n_H-1 | π_L^* |
| | 2 | π_H-3,n_H-1 | π_L^* | 2 | π_H-3,n_H-1 | π_L^* | 3 | π_H-3,n_H-1 | π_L^* |
| 1^3A_2 | 91 | n_H | π_L | 63 | n_H | π_L | 61 | n_H | π_L |
| | 3 | π_H-1,n_H | π_L^* | 5 | π_H-1,n_H | π_L^* | 5 | π_H-1,n_H | π_L^* |
| 1^3A_1 | 94 | π_H-1 | π_L | 66 | π_H-1 | π_L | 65 | π_H-1 | π_L |
| | 2 | π_H-2 | π_L^* | 2 | π_H-2 | π_L^* | 2 | π_H-2 | π_L^* |
| 1^3B_1 | 71 | π_H-1 | π_L^* | 40 | π_H-1 | π_L^* | 42 | π_H-1 | π_L^* |
| | 16 | π_H-2 | π_L | 20 | π_H-2 | π_L | 16 | π_H-2 | π_L |
| | 2 | π_H-3 | π_L^* | 4 | π_H-3 | π_L^* | 3 | π_H-3 | π_L^* |
| | 2 | π_H-4 | π_L^* | 3 | π_H-4 | π_L^* | 3 | π_H-4 | π_L^* |
| 1^3B_2 | 81 | n_H | π_L | 51 | n_H | π_L | 49 | n_H | π_L |
| | 10 | π_H-1,n_H | π_L^* | 13 | π_H-1,n_H | π_L^* | 13 | π_H-1,n_H | π_L^* |
| | 3 | π_H-2,n_H | π_L^* | 4 | π_H-2,n_H | π_L^* | 5 | π_H-2,n_H | π_L^* |
| 2^3A_1 | 63 | π_H-2 | π_L^* | 43 | π_H-2 | π_L^* | 42 | π_H-2 | π_L^* |
| | 18 | π_H-3 | π_L | 15 | π_H-3 | π_L | 15 | π_H-3 | π_L |
| | 11 | π_H-4 | π_L^* | 7 | π_H-4 | π_L^* | 7 | π_H-4 | π_L^* |
| | 2 | π_H-5 | π_L^* | 2 | π_H-5 | π_L^* | 2 | π_H-5 | π_L^* |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:
The n_H reference orbital corresponds to the n_H-1 reference orbital;
The π_H-1 reference orbital corresponds to the π_H+1 reference orbital;
The π_H+1 reference orbital corresponds to the π_H-1 reference orbital.

The π_L reference orbital corresponds to the π_L+1 reference orbital.
### S4.9. Dithiin

Table S38. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of dithiin. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | Experiment |
|-------|--------------------|--------------|------------|
|       |                    | DFT/MRCI     | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |          |
| $1^1B$ | $\pi \rightarrow \pi^*$ | 2.60 (0.001) | 2.58 (0.001) | 2.38 (0.001) | 2.33 (0.001) | 2.74<sup>a</sup> |
| $2^1A$ | $\pi \rightarrow \pi^*$ | 4.36 (0.035) | 4.36 (0.038) | 4.17 (0.015) | 4.01 (0.010) | 4.44<sup>a</sup> |
| $2^1B$ | $\pi \rightarrow \pi^*/\sigma^*$ | 4.54 (0.018) | 4.52 (0.019) | 4.26 (0.014)<sup>1</sup> | 4.14 (0.009)<sup>1</sup> | 5.00<sup>a</sup> |
| $3^1B$ | $\pi \rightarrow \pi^*/\sigma^*$ | 4.73 (0.005) | 4.69 (0.006) | 4.20 (0.006)<sup>2</sup> | 3.97 (0.005)<sup>2</sup> |
| $3^1A$ | $\pi^2 \rightarrow \pi^*$ | 4.80 (0) | 4.69 (0) | 4.39 (0) | 4.23 (0) |
| $1^3B$ | $\pi \rightarrow \pi^*$ | 2.00 | 2.06 | 1.86 | 1.84 |
| $2^3B$ | $\pi \rightarrow \pi^*/\sigma^*$ | 3.31 | 3.40 | 2.88 | 2.85 |
| $1^3A$ | $\pi \rightarrow \pi^*$ | 3.75 | 3.82 | 3.74 | 3.68 |
| $3^3B$ | $\pi \rightarrow \pi^*/\sigma^*$ | 4.36 | 4.36 | 3.91 | 3.81 |
| $2^3A$ | $\pi \rightarrow \pi^*$ | 4.77 | 4.88 | 4.37 | 4.24 |

MR-MP2(HF): $1^3B, 2^3B$
MR-MP2(BH-LYP): $1^3B, 2^3B$
<sup>a</sup> UV-vis absorption maximum in CH₂Cl₂ [19]
Table S39. Calculated percentage of electron configurations in the excited states wave functions of \textit{dithiin} obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | % from | to | % from | to |
|-------|--------|----|--------|----|--------|----|
| 1^B   | 89 π_H | π_L^* | 62 π_H | π_L^* | 64 π_H | π_L^* |
|       | 3 π_H  | σ_L^+1 | 2 π_H | σ_L^+1 | 2 π_H | σ_L^+1 |
|       | 2 π_H−2 | π_L | 2 π_H−2 | π_L | 2 π_H−2 | π_L |
| 2^A   | 83 π_H−1 | π_L^* | 54 π_H−1 | π_L^* | 55 π_H−1 | π_L^* |
|       | 4 π_H−1 | σ_L^+1 | 4 π_H−1 | σ_L^+1 | 3 π_H−1 | σ_L^+1 |
|       | 5 π_H  | π_L | 5 π_H | π_L | 2 π_H | π_L |
| 2^B   | 44 π_H | σ_L^+1 | 28 π_H−2 | σ_L^+1 | 30 π_H−2 | σ_L^+1 |
|       | 36 π_H−2 | π_L | 27 π_H−2 | π_L | 29 π_H−2 | π_L |
|       | 7 π_H−2 | σ_L^+1 | 6 π_H−2 | σ_L^+1 | 4 π_H−2 | σ_L^+1 |
|       | 5 π_H  | π_L | 5 π_H | π_L | 2 π_H | π_L |
| 3^B   | 48 π_H−2 | π_L^* | 31 π_H−2 | π_L^* | 31 π_H−2 | π_L^* |
|       | 40 π_H  | σ_L^+1 | 31 π_H−2 | σ_L^+1 | 29 π_H−2 | σ_L^+1 |
| 3^A   | 81 π_H−1, π_H | π_L^*, σ_L^* | 49 π_H−1, π_H | π_L^*, σ_L^* | 49 π_H−1, π_H | π_L^*, σ_L^* |
|       | 3 π_H−2, π_H | π_L^*, σ_L^+1 | 3 π_H−2, π_H | π_L^*, σ_L^+1 | 3 π_H−2, π_H | π_L^*, σ_L^+1 |
|       | 2 π_H−1, π_H−1 | π_L^*, σ_L^L | 2 π_H−1, π_H−1 | π_L^*, σ_L^L | 2 π_H−1, π_H−1 | π_L^*, σ_L^L |
|       | 2 π_H−2, π_H−2 | σ_L^L | 2 π_H−2, π_H−2 | σ_L^L | 2 π_H−2, π_H−2 | σ_L^L |
| 1^B   | 92 π_H | π_L^* | 64 π_H−2 | π_L^* | 61 π_H | π_L^* |
|       | 2 π_H−2 | σ_L^+1 | 2 π_H−2 | σ_L^+1 | 3 π_H−2 | σ_L^+1 |
|       | 3 π_H  | σ_L^+1 | 3 π_H | σ_L^+1 | 3 π_H | σ_L^+1 |
| 2^B   | 52 π_H−2 | π_L^* | 33 π_H−2 | π_L^* | 32 π_H−2 | π_L^* |
|       | 40 π_H  | σ_L^+1 | 30 π_H−2 | σ_L^+1 | 31 π_H−2 | σ_L^+1 |
|       | 3 π_H  | σ_L^+1 | 3 π_H | σ_L^+1 | 3 π_H | σ_L^+1 |
| 1^A   | 84 π_H−1 | π_L^* | 43 π_H−1 | π_L^* | 42 π_H−1 | π_L^* |
|       | 4 π_H  | π_L^L+4 | 12 π_H−1 | π_L^L+4 | 10 π_H−1 | π_L^L+4 |
|       | 3 π_H  | π_L^L−3 | 3 π_H−3 | π_L^L−3 | 5 π_H−3 | π_L^L−3 |
|       | 2 π_H−3 | π_L^L+4 | 2 π_H−3 | π_L^L+4 | 4 π_H−3 | π_L^L+4 |
| 3^B   | 49 π_H | σ_L^+1 | 29 π_H−2 | σ_L^+1 | 28 π_H−2 | σ_L^+1 |
|       | 39 π_H−2 | π_L^* | 28 π_H−2 | σ_L^+1 | 28 π_H−2 | σ_L^+1 |
|       | 4 π_H−4 | π_L^* | 5 π_H−4 | π_L^* | 5 π_H−4 | π_L^* |
|       | 2 π_H−4 | σ_L^+1 | 2 π_H−4 | σ_L^+1 | 2 π_H−4 | σ_L^+1 |
| 2^A   | 23 π_H | π_L^L+4 | 16 π_H−1 | σ_L^L+1 | 17 π_H−1 | σ_L^L+1 |
|       | 21 π_H | σ_L^L+2 | 12 π_H−1 | σ_L^L+2 | 16 π_H−1 | σ_L^L+2 |
|       | 18 π_H−1 | σ_L^L+1 | 10 π_H−1 | σ_L^L+1 | 9 π_H−1 | σ_L^L+1 |
|       | 17 π_H−3 | σ_L^L−3 | 8 π_H−3 | σ_L^L−3 | 9 π_H−3 | σ_L^L−3 |
|       | 6 π_H−6 | π_L^L+4 | 7 π_H−6 | σ_L^L+4 | 6 π_H−6 | σ_L^L+4 |
|       | 3 π_H−2 | π_L^L+4 | 6 π_H−6 | σ_L^L+4 | 5 π_H−6 | σ_L^L+4 |
|       | 2 π_H−2 | σ_L^L+2 | 2 π_H−2 | σ_L^L+2 | 3 π_H−2 | σ_L^L+2 |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

- The π_H−2 bh-lyp orbital corresponds to the π_H−1 hf orbital;
- The π_H−1 bh-lyp orbital corresponds to the π_H−2 hf orbital;
- The σ_L^L+2 bh-lyp orbital corresponds to the σ_L^L+3 hf orbital.
- The R^L+1,3 bh-lyp orbital corresponds to the R^L+1,3 hf orbital.
- The π^L+1,4 bh-lyp orbital corresponds to the π^L+1,5 hf orbital.
### S4.10. Bithiophene

Table S40. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of s-trans bithiophene. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies (eV) | Experiment |
|-------|--------------------|---------------|------------|
|       |                    | DFT/MRCI      | DFT/MRCI-R | MR-MP2     | MR-MP2     |            |
|       |                    |               | (HF)       | (BH-LYP)   |            |            |
|       |                    | 1\(^1\)B \(\pi \rightarrow \pi^*\) | \(4.17\) (0.446) | \(4.15\) (0.472) | \(4.02\) (0.437) | \(3.93\) (0.401) | \(3.86^a\), \(4.09\) (4.11)\(^b\) |
|       |                    | 2\(^1\)A \(\pi \rightarrow \pi^*\) | \(4.81\) (0.005) | \(4.87\) (0.006) | \(4.66\) (0.001) | \(4.39\) (0)\(^1\) |
|       |                    | 2\(^1\)B \(\pi \rightarrow \pi^*\) | \(4.95\) (0.112) | \(5.00\) (0.129) | \(4.58\) (0.092) | \(4.18\) (0.066) | \(5.02^b\) |
|       |                    | 3\(^1\)A \(\pi \rightarrow \pi^*\) | \(5.02\) (0.003) | \(5.11\) (0.004) | \(4.69\) (0.003) | \(4.28\) (0.002)\(^2\) |
|       |                    | 4\(^1\)A \(\pi \rightarrow \sigma^*\) | \(5.34\) (0.001) | \(5.39\) (0.002) | \(5.27\) (0.001)\(^1\) | \(4.81\) (0)\(^3\) |
|       |                    | 3\(^1\)B \(\pi \rightarrow \sigma^*\) | \(5.42\) (0.023) | \(5.46\) (0.029) | \(5.44\) (0.030) | \(4.92\) (0.028) |
| 1\(^4\)B | \(\pi \rightarrow \pi^*\) | 2.78          | 2.81       | 2.62       | 2.44       | 2.32\(^a\) |
| 1\(^2\)A | \(\pi \rightarrow \pi^*\) | 3.72          | 3.79       | 3.50       | 3.25       |           |
| 2\(^2\)A | \(\pi \rightarrow \pi^*\) | 4.17          | 4.22       | 4.02       | 3.72       |           |
| 2\(^2\)B | \(\pi \rightarrow \pi^*\) | 4.21          | 4.26       | 3.98       | 3.71       |           |
| 3\(^3\)B | \(\pi \rightarrow \sigma^*\) | 5.09          | 5.14       | 5.03       | 4.55       |           |
| 3\(^3\)A | \(\pi \rightarrow \sigma^*\) | 5.09          | 5.14       | 5.35       | 4.76       |           |
| 4\(^3\)B | \(\pi \rightarrow \pi^*\) | 5.43          | 5.49       | 5.46       | 4.76       |           |
| 4\(^3\)A | \(\pi \rightarrow \pi^*\) | 5.45          | 5.39       | 5.38       | 4.92       |           |

MRMP2(HF): 1\(^1\)A
MRMP2(BH-LYP): 1\(^3\)A, 2\(^1\)A, 3\(^5\)A
\(^a\) PD-PES in the gas phase [20]
\(^b\) Absorption maximum in dioxane. [21]
\(^b\) Value in parentheses is for the spectra in methylcyclohexane [21]
Table S41.: Calculated percentage of electron configurations in the excited states wave functions of s-trans bithiophene obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | Excitation | DFT/MRCl (BH-LYP) | MRMP2 (HF) | MRMP2 (BH-LYP) |
|-------|------------|--------------------|------------|----------------|
| 1B    |            | 58                 |            |                |
|       | π_H        | π_L+               | π_H        | π_L+           |
| 2^1  | π_H−1      |                   | 21         | π_H−1          |
|       |            | 21                 | π_H        | π_L+           |
|       | π_H        | π_L+               | π_H        | π_L+           |
|       | π_H−2      | 8                  | π_H−2      | π_L+           |
|       | π_H−3      | 3                  | π_H−3      | π_L+           |
|       | π_H−4      | 2                  | π_H−3      | π_L+           |
| 2    | π_H−5      | 5                  | π_H−5      | π_L+           |
|       | π_H−6      | 1                  | π_H−6      | π_L+           |
|       | π_H−7      | 3                  | π_H−7      | π_L+           |
|       | π_H−8      | 2                  | π_H−8      | π_L+           |
| 3    | π_H−9      | 1                  | π_H−9      | π_L+           |
|       | π_H−10     | 2                  | π_H−10     | π_L+           |

Continued on next page
The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The $\pi^*_{L+8}$ bh-lyp orbital corresponds to the $\pi^*_{L+7}$ hf orbital;

The $\pi_{L+10}$ bh-lyp orbital corresponds to the $\pi_{L+11}$ hf orbital;

The $\pi_{L+11}$ bh-lyp orbital corresponds to the $\pi_{L+10}$ hf orbital.
## S4.11. Nitromethane

Table S42. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of nitromethane using the valence basis. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | Experiment |
|-------|--------------------|--------------|------------|
|       |                    | DFT/MRCI     | DFT/MRCI-R | MR-MP2(HF) | MR-MP2(BH-LYP) |
| $1^1A''$ | $n \rightarrow \pi^*$ | 3.92 (0) | 4.00 (0) | 3.83 (0) | 3.77 (0) | 4.25<sup>a</sup> |
| $2^1A''$ | $n \rightarrow \pi^*$ | 4.34 (0) | 4.36 (0) | 4.04 (0) | 4.07 (0) | 4.50<sup>b</sup>, 4.45<sup>c</sup>, 4.51<sup>d</sup>, 4.59<sup>e</sup> |
| $2^1A'$ | $\pi \rightarrow \pi^*$ | 6.39 (0.260) | 6.44 (0.305) | 6.46 (0.209) | 6.47 (0.198) | 6.25<sup>b</sup>, 6.23<sup>a</sup>, 6.29<sup>d</sup>, 6.26<sup>e</sup> |
| $3^1A'$ | $\pi \rightarrow \pi^*$ | 8.86 (0.093) | 9.02 (0.045)† | 8.60 (0.196)<sup>1</sup> | 8.59 (0.260)<sup>1</sup> | 6.29<sup>d</sup>, 6.26<sup>e</sup> |
| $4^1A'$ | $\pi \rightarrow \text{Ryd}$ | 8.92 (0.007) | 8.88 (0.002) | 8.58 (0.019)<sup>2</sup> | 8.54 (0.003)<sup>2</sup> |
| $1^3A'$ | $\pi \rightarrow \pi^*$ | 3.43 | 3.31 | 3.54 | 3.55 |
| $1^3A''$ | $n \rightarrow \pi^*$ | 3.71 | 3.80 | 3.55 | 3.60 |
| $2^3A''$ | $n \rightarrow \pi^*$ | 4.10 | 4.13 | 3.85 | 3.92 |
| $2^3A'$ | $n, n \rightarrow \pi^*$<sup>2</sup> | 7.51 | 6.25 | 8.66<sup>3</sup> | 8.85<sup>3</sup> |
| $3^3A'$ | $\pi \rightarrow \pi^*$ | 7.98 | 8.13 | 8.27<sup>4</sup> | 8.26<sup>4</sup> |
| $4^3A'$ | $\pi \rightarrow \text{Ryd}$ | 8.81 | 8.75 | 8.44<sup>5</sup> | 8.40<sup>5</sup> |

<sup>a</sup> MRMP2(HF): $1^4A', 2^3A', 3^4A', 4^2A', 5^3A'$  
<sup>b</sup> MRMP2(BHLYP): $1^4A', 2^3A', 3^4A', 4^2A', 5^3A'$  
<sup>c</sup> Electron energy-loss maximum in gas [22]  
<sup>d</sup> Absorption maximum in gas [22]  
<sup>e</sup> Absorption maximum in gas [23]  
<sup>f</sup> Absorption maximum in gas [24]  
<sup>g</sup> Absorption maximum in gas [25]
Table S43.: Calculated percentage of electron configurations in the excited states wave functions of nitromethane obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the valence basis. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | Excitation | Excitation | Excitation |
|-------|--------|----|------------|------------|------------|
|       | n_{H-1} | π^\_L | 90 | 62 | 70 |
| 1^A'' | n_{H-1,\pi H} | π^\_L,π^\_L | 7 | n_{H-1} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 5 | n_{H-2} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 2 | R_{gy1+4} | π^\_L,π^\_L |
| 2^A'' | n_{H-2} | π^\_L | 89 | 62 | 71 |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 8 | n_{H-2} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 6 | n_{H-1} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 2 | R_{gy1+4} | π^\_L,π^\_L |
| 2^A' | π_H | π^\_L | 83 | 65 | 63 |
|       | π_{H-7,\pi H} | π^\_L,π^\_L | 6 | π_{H-7,\pi H} | π^\_L,π^\_L |
|       | π_{H-3,\pi H} | π^\_L,π^\_L | 3 | π_{H-3,\pi H} | π^\_L,π^\_L |
| 1^A' | π_H | π^\_L | 98 | 78 | 80 |
|       | π_H | π^\_L | 2 | R_{gy1+4} | π^\_L |
| 1^A'' | n_{H-1} | π^\_L | 93 | 64 | 71 |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 6 | n_{H-1} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 4 | n_{H-2} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 2 | R_{gy1+4} | π^\_L,π^\_L |
| 2^A'' | n_{H-2} | π^\_L | 94 | 65 | 72 |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 7 | n_{H-2} | π^\_L,π^\_L |
|       | n_{H-1,\pi H} | π^\_L,π^\_L | 5 | R_{gy1+4} | π^\_L,π^\_L |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.

In the following cases the ordering of the Hartree-Fock orbitals is different:
The π_{H-7} bh-lyp orbital corresponds to the π_{H-6} hf orbital;
The n_{H-1} bh-lyp orbital corresponds to the n_{H-2} hf orbital;
The n_{H-2} bh-lyp orbital corresponds to the n_{H-3} hf orbital.
Table S44. Selected matrix elements (cm\(^{-1}\)) for nitromethane calculated with DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) methods using the valence basis.

|                | DFT/MRCI | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |
|----------------|----------|------------|------------|----------------|
| \(\langle 1^3A'|\hat{\mathbf{H}}_{\text{SO}}|1^1A'\rangle\) | 0.3      | 0.3        | 0.2        | 0.0            |
| \(\langle 1^3A'|\hat{\mathbf{H}}_{\text{SO}}|1^1A''\rangle\) | 33.9     | 32.8       | 31.8       | 36.6           |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|2^1A'\rangle\) | 17.0     | 16.0       | 17.2       | 17.4           |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|2^1A''\rangle\) | 16.5     | 16.7       | 22.8       | 18.0           |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|1^1A''\rangle\) | 23.8     | 23.3       | 22.3       | 23.7           |
| \(\langle 1^3A'|\hat{\mathbf{H}}_{\text{SO}}|1^1A''\rangle\) | 9.5      | 9.4        | 10.6       | 7.9            |
| \(\langle 1^3A'|\hat{\mathbf{H}}_{\text{SO}}|2^1A''\rangle\) | 41.1     | 40.5       | 42.1       | 41.5           |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|2^1A''\rangle\) | 6.7      | 6.3        | 1.2        | 5.3            |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|2^1A''\rangle\) | 32.8     | 32.3       | 35.1       | 35.7           |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|1^3A'\rangle\) | 22.6     | 23.1       | 22.3       | 23.5           |
| \(\langle 1^3A''|\hat{\mathbf{H}}_{\text{SO}}|1^3A''\rangle\) | 39.0     | 40.0       | 41.2       | 40.7           |
| \(\langle 2^3A''|\hat{\mathbf{H}}_{\text{SO}}|1^3A''\rangle\) | 33.9     | 32.5       | 35.5       | 35.9           |
Table S45. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF), MR-MP2(BH-LYP), CASPT2 (8,7) and CASPT2 (8,6) vertical excitation energies of nitromethane using the augmented basis. The CASPT2 (8,7) active space consists of following occupied/unoccupied orbitals: 2/2 $a'$ and 2/1 $a''$. The (8,6) active space has one $a'$ orbital less. The oscillator strengths are given in the parentheses.

| State    | Dominant character | Energies (eV) | Energies (eV) | Energies (eV) | Energies (eV) | Energies (eV) | Energies (eV) | Energies (eV) | Experiment |
|----------|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|------------|
|          |                   | DFT/MRCI      | DFT/MRCI-R    | MRMP2(HF)     | MRMP2(BH-LYP) | CASPT2 (8,7)  | CASPT2 (8,6)  |              |            |
| $1^1A''$ | $n \rightarrow \pi^*$ | 3.83 (0)      | 3.92 (0)      | 3.64 (0)      | 3.71 (0)      | 3.92 (0)      | 3.88 (0)      | 4.25$^e$     |
| $2^1A''$ | $n \rightarrow \pi^*$ | 4.26 (0)      | 4.28 (0)      | 3.97 (0)      | 4.03 (0)      | 4.32 (0)      | 4.33 (0)      | 4.50$^b$, 4.45$^c$, 4.51$^d$, 4.59$^e$ | |
| $2^1A'$  | $\pi \rightarrow \pi^*$ | 6.30 (0.257)  | 6.34 (0.297)  | 6.18 (0.204)  | 6.31 (0.200)  | 6.38 (0.260)  | 5.63 (0.384)  | 6.25$^b$, 6.23$^{a,e}$, 6.29$^d$, 6.26$^e$ |
| $3^1A'$  | $n \rightarrow 3s$  | 7.74 (0.008)  | 7.66 (0.007)  | 7.55 (0.004)  | 7.49 (0.010)  | 7.07 (0.033)  | 7.42 (0.003)  |            |
| $4^1A'$  | $n \rightarrow 3s$  | 8.00 (0.041)  | 7.87 (0.042)  | 7.62 (0.022)  | 7.72 (0.033)  | 7.55 (0.078)  | 7.80 (0)      |            |
| $1^3A''$ | $\pi \rightarrow \pi^*$ | 3.36          | 3.30          | 3.54          | 3.57          | 3.65          | 3.70          |            |
| $1^3A''$ | $n \rightarrow \pi^*$ | 3.61          | 3.72          | 3.42          | 3.52          | 3.66          | 3.66          |            |
| $2^3A''$ | $n \rightarrow \pi^*$ | 4.01          | 4.06          | 3.80          | 3.93          | 4.15          | 4.16          |            |
| $2^3A'$  | $n, n \rightarrow \pi^*$ | 7.31          | 6.12          | 8.70$^1$      | 8.79$^2$      | 8.97          | 9.01          |            |
| $3^3A'$  | $n \rightarrow 3s$  | 7.65          | 7.56          | 7.50$^2$      | 7.46$^2$      | 7.43          | 7.48          |            |
| $4^3A'$  | $n \rightarrow 3s$  | 7.91          | 7.79          | 7.51$^3$      | 7.57$^3$      | 7.73          | 7.73          |            |

MRMP2(HF): 1 $1^3A'^1$, 2 $1^2A'^2$, 3 $1^3A'^3$
MRMP2(BH-LYP): 1 $8^3A'^1$, 2 $2^3A'^2$, 3 $3^3A'^3$

$^a$ Electron energy-loss maximum in gas [22]
$^b$ Absorption maximum in gas [22]
$^c$ Electron energy-loss maximum in gas [23]
$^d$ Absorption maximum in gas [24]
$^e$ Absorption maximum in gas [25]
Table S46.: Calculated percentage of electron configurations in the excited states wave functions of nitromethane obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | Excitation | DFT/MRCI  | MRMP2  | MRMP2 |
|-------|------------|-----------|---------|--------|
|       |            | BH-LYP    | HF      | BH-LYP |
| %     | from       | to        | from    | to     | from    | to     |
| 1^A'' |            |           |         |        |         |        |
| 86    | n_{H-1}   | π_{L}^*   | n_{H-1} | π_{L}^* | n_{H-1} | π_{L}^* |
| 6     | n_{H-2,π} | π_{L,π}^* | n_{H-1} | π^*/pz  | n_{H-2,π} | π_{L,π}^* |
| 52    | n_{H-1}   | π_{L}^*   | n_{H-1} | π^*/pz  | n_{H-1} | π_{L}^* |
| 10    | n_{H-1}   | π^*/pz    | n_{H-1} | π^*/pz  | n_{H-1} | π^*/pz |
| 5     | n_{H-2,π} | π_{L,π}^* | n_{H-1} | π^*/pz  | n_{H-1} | π_{L,π}^* |
| 6     | n_{H-2,π} | π_{L,π}^* | n_{H-1} | π^*/pz  | n_{H-1} | π_{L,π}^* |
| 52    | n_{H-1}   | π_{L}^*   | n_{H-1} | π^*/pz  | n_{H-1} | π_{L}^* |
| 10    | n_{H-1}   | π^*/pz    | n_{H-1} | π^*/pz  | n_{H-1} | π^*/pz |
| 5     | n_{H-2,π} | π_{L,π}^* | n_{H-1} | π^*/pz  | n_{H-1} | π_{L,π}^* |
| 6     | n_{H-2,π} | π_{L,π}^* | n_{H-1} | π^*/pz  | n_{H-1} | π_{L,π}^* |
| 2^A'' |            |           |         |        |         |        |
| 86    | n_{H-2}   | π_{L}^*   | n_{H-1} | π^*/pz  | n_{H-1} | π^*/pz |
| 7     | n_{H-1,π} | π_{L,π}^* | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 52    | n_{H-2}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 10    | n_{H-2}   | π^*/pz    | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 6     | n_{H-2}   | π^*/pz    | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 52    | n_{H-2}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 10    | n_{H-2}   | π^*/pz    | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 6     | n_{H-2}   | π^*/pz    | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 2^A' |            |           |         |        |         |        |
| 82    | π_{L}     | π_{L}^*   | π_{H}   | π^*/pz  | π_{H}   | π^*/pz |
| 6     | π_{H,π}   | π_{L,π}^* | π_{L}   | π^*/pz  | π_{H,π} | π_{L,π}^* |
| 39    | π_{H}     | π_{L}^*   | π_{H}   | π^*/pz  | π_{H}   | π^*/pz |
| 16    | π_{H}     | π_{L}^*   | π_{H}   | π^*/pz  | π_{H}   | π^*/pz |
| 11    | π_{H}     | π_{L}^*   | π_{H}   | π^*/pz  | π_{H}   | π^*/pz |
| 8     | π_{H,π}   | π_{L,π}^* | π_{H,π} | π_{L,π}^* | π_{H}   | π_{L}^* |
| 63    | π_{H}     | π_{L}^*   | π_{H}   | π^*/pz  | π_{H}   | π^*/pz |
| 5     | π_{H,π}   | π_{L,π}^* | π_{H,π} | π_{L,π}^* | π_{H}   | π_{L}^* |
| 77    | π_{H}     | π_{L}^*   | π_{H}   | π^*/pz  | π_{H}   | π_{L}^* |
| 13A' |            |           |         |        |         |        |
| 94    | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 6     | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 11    | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 7    | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 6     | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 5     | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 6     | π_{H}     | π_{L}^*   | π_{H}   | π_{L}   | π_{H}   | π_{L} |
| 58    | n_{H-1}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 9     | n_{H-1}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 54    | n_{H-1}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 10    | n_{H-2}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 6     | n_{H-2}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 53    | n_{H-1}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 10    | n_{H-2}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |
| 6     | n_{H-2}   | π_{L}^*   | n_{H-2} | π^*/pz  | n_{H-1} | π^*/pz |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory.
In the following cases the ordering of the Hartree-Fock orbitals is different:
The π_{L}^* bh-lyp orbital corresponds to the π_{L+3} hf orbital;
The n_{H-1} bh-lyp orbital corresponds to the n_{H-2} hf orbital;
The n_{H-2} bh-lyp orbital corresponds to the n_{H-1} hf orbital.
Table S47.: Calculated percentage of electron configurations in the discussed wave functions of nitromethane obtained at the DFT/MRCI-R, CASPT2 (8,7) and CASPT2 (8,6) levels of theory using the augmented basis. Only electron configurations with more than 5 percentage are presented.

| State | Excitation | DFT/MRCI-R | CASPT2 (8,7) | CASPT2 (8,6) |
|-------|------------|------------|--------------|--------------|
|       | % from to | % from to | % from to | % from to |
| \(1^1A''\) | 88 | \(n_{H-1}\) | \(\pi_L^*\) | 86 | \(n_{H-1}\) | \(\pi_L^*\) | 84 | \(n_{H-1}\) | \(\pi_L^*\) |
| \(\pi_{H-3}^\pi H\) | 5 | \(\pi_H\) | \(\pi_L^*\) | 11 | \(n_{H-2}\) | \(\pi_H\) | 16 | \(n_{H-2}\) | \(\pi_H\) |
| \(1^2A''\) | 87 | \(n_{H-2}\) | \(\pi_L^*\) | 82 | \(n_{H-2}\) | \(\pi_L^*\) | 81 | \(n_{H-2}\) | \(\pi_L^*\) |
| \(\pi_{H-1}^\pi H\) | 6 | \(\pi_{H-1}^\pi H\) | \(\pi_L^*\) | 16 | \(n_{H-1}^\pi H\) | \(\pi_L^*\) | 19 | \(n_{H-1}^\pi H\) | \(\pi_L^*\) |
| \(2^1A'\) | 85 | \(\pi_H\) | \(\pi_L^*\) | 57 | \(\pi_H\) | \(\pi_L^*\) | 81 | \(\pi_H\) | \(\pi_L^*\) |
| \(\pi_{H-7}^\pi H\) | 5 | \(\pi_{H-7}^\pi H\) | \(\pi_L^*\) | 12 | \(n_{H-1}\) | \(\pi_H\) | 15 | \(n_{H-1}^\pi H\) | \(\pi_L^*\) |
|       | 10 | \(n_{H-2}\) | \(\pi_H\) | 8 | \(n_{H-2}\) | \(\pi_H\) | |
| \(1^3A'\) | 95 | \(\pi_H\) | \(\pi_L^*\) | 97 | \(\pi_H\) | \(\pi_L^*\) | 98 | \(\pi_H\) | \(\pi_L^*\) |
| \(2^2A''\) | 89 | \(n_{H-1}\) | \(\pi_L^*\) | 88 | \(n_{H-1}\) | \(\pi_L^*\) | 86 | \(n_{H-1}\) | \(\pi_L^*\) |
| \(\pi_{H-2}^\pi H\) | 5 | \(\pi_{H-2}^\pi H\) | \(\pi_L^*\) | 9 | \(n_{H-2}^\pi H\) | \(\pi_L^*\) | 14 | \(n_{H-2}^\pi H\) | \(\pi_L^*\) |
| \(2^3A''\) | 89 | \(n_{H-2}\) | \(\pi_L^*\) | 84 | \(n_{H-2}\) | \(\pi_L^*\) | 83 | \(n_{H-2}\) | \(\pi_L^*\) |
| \(\pi_{H-1}^\pi H\) | 5 | \(\pi_{H-1}^\pi H\) | \(\pi_L^*\) | 13 | \(n_{H-1}^\pi H\) | \(\pi_L^*\) | 17 | \(n_{H-1}^\pi H\) | \(\pi_L^*\) |
### S4.12. Nitrobenzene

Table S48. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of nitrobenzene. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies (eV) | Experiment |
|-------|-------------------|--------------|------------|
|       |                   | DFT/MRCI     | DFT/MRCI-R | MRMP2 (HF) | MRMP2 (BH-LYP) |         |
| $1^1A_2$ | $n \rightarrow \pi^*$ | 3.29 (0) | 3.46 (0) | 3.25 (0) | 3.47 (0) | 3.65$^a$ |
| $1^1B_2$ | $n \rightarrow \pi^*$ | 3.88 (0) | 3.91 (0) | 3.82 (0) | 3.76 (0) |
| $1^1B_1$ | $\pi \rightarrow \pi^*$ | 4.29 (0.004) | 4.40 (0.021) | 4.28 (0.006) | 4.18 (0.004) |
| $2^1B_1$ | $\pi, \pi \rightarrow \pi^*, \pi^*$ | 4.63 (0.024) | 7.19 (0.170)$^1$ | 7.00 (0.198)$^1$ |
| $2^1A_1$ | $\pi \rightarrow \pi^*$ | 4.77 (0.249) | 4.81 (0.311) | 5.33 (0.246) | 5.08 (0.243) | 5.17$^b$ |
| $1^3B_1$ | $\pi \rightarrow \pi^*$ | 2.84 | 2.93 | 3.35 | 3.35 |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 3.11 | 3.26 | 3.00 | 3.09 |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 3.66 | 3.65 | 3.62 | 3.51 |
| $1^3B_2$ | $n \rightarrow \pi^*$ | 3.67 | 3.72 | 3.63 | 3.62 |
| $2^3B_1$ | $\pi \rightarrow \pi^*$ | 4.01 | 4.01 | 4.34 | 4.18 |

MR-MP2(HF): $^1$ $5^1B_1$
MR-MP2(HF): $^1$ $5^1B_1$

$^a$ Absorption maximum in n-hexane [26]
$^b$ Absorption maximum in gas phase [26]
Table S49. Calculated percentage of electron configurations in the excited states wave functions of nitrobenzene obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State  | DFT/MRCI      | MRMP2 (HF) | MRMP2 (BH-LYP) |
|--------|---------------|------------|----------------|
|        | Excitation    |            |                |
|        | % from to     | % from to  | % from to      |

- **1^1A_2**
  - 77 n_{H-3} \pi_{L}^* \pi_{L,1}^*<br>
  - 12 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2
  - 3 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*<br>
  - 45 n_{H-3} \pi_{L}^* \pi_{L,1}^*+2
  - 3 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*<br>
  - 2 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*+2
  - 75 π_{L,1}^* π_{L,1}^*+2

- **1^1B_2**
  - 76 n_{H-4} \pi_{L}^* \pi_{L,1}^*<br>
  - 11 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*+2
  - 4 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*<br>
  - 45 n_{H-4} \pi_{L}^* \pi_{L,1}^*+2
  - 3 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*<br>
  - 2 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2
  - 4 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2
  - 2 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2

- **1^1B_1**
  - 46 π_{L}^* \pi_{L,1}^*<br>
  - 26 π_{L}^* π_{L,1}^*+2
  - 5 π_{L}^* π_{L,1}^*+1
  - 9 π_{L}^* π_{L,1}^*+1<br>
  - 4 π_{L}^* π_{L,1}^*+2
  - 3 π_{L}^* π_{L,1}^*+2
  - 24 π_{L}^* π_{L,1}^*+1
  - 10 π_{L}^* π_{L,1}^*+2
  - 8 π_{L}^* π_{L,1}^*+1
  - 7 π_{L}^* π_{L,1}^*+1<br>
  - 3 π_{L}^* π_{L,1}^*+1<br>
  - 26 π_{L}^* π_{L,1}^*+1
  - 23 π_{L}^* π_{L,1}^*+1
  - 8 π_{L}^* π_{L,1}^*+1

- **2^1B_1**
  - 33 π_{L}^* π_{L,1}^*+1<br>
  - 25 π_{L}^* π_{L,1}^*+1
  - 12 π_{L}^* π_{L,1}^*+1
  - 5 π_{L}^* π_{L,1}^*+2<br>
  - 5 π_{L}^* π_{L,1}^*+2
  - 5 π_{L}^* π_{L,1}^*+2
  - 24 π_{L}^* π_{L,1}^*+1<br>
  - 10 π_{L}^* π_{L,1}^*+2<br>
  - 8 π_{L}^* π_{L,1}^*+1<br>
  - 7 π_{L}^* π_{L,1}^*+1<br>
  - 3 π_{L}^* π_{L,1}^*+1<br>
  - 24 π_{L}^* π_{L,1}^*+1<br>
  - 10 π_{L}^* π_{L,1}^*+2<br>

- **2^1A_1**
  - 75 π_{L}^* π_{L,1}^*<br>
  - 5 π_{L}^* π_{L,1}^*+1<br>
  - 3 π_{L}^* π_{L,1}^*<br>
  - 2 π_{L}^* π_{L,1}^*<br>
  - 2 π_{L}^* π_{L,1}^*<br>
  - 54 π_{L}^* π_{L,1}^*<br>
  - 7 π_{L}^* π_{L,1}^*<br>
  - 50 π_{L}^* π_{L,1}^*<br>
  - 6 π_{L}^* π_{L,1}^*<br>
  - 50 π_{L}^* π_{L,1}^*<br>
  - 6 π_{L}^* π_{L,1}^*<br>

- **3^1B_1**
  - 77 π_{L}^* π_{L,1}^*<br>
  - 15 π_{L}^* π_{L,1}^*+2<br>
  - 4 π_{L}^* π_{L,1}^*<br>
  - 49 π_{L}^* π_{L,1}^*<br>
  - 16 π_{L}^* π_{L,1}^*<br>
  - 10 π_{L}^* π_{L,1}^*<br>
  - 53 π_{L}^* π_{L,1}^*+2<br>
  - 10 π_{L}^* π_{L,1}^*+2<br>

- **3^1A_2**
  - 78 n_{H-3} \pi_{L}^* \pi_{L,1}^*<br>
  - 13 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2<br>
  - 2 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*<br>
  - 46 n_{H-3} \pi_{L}^* \pi_{L,1}^*+2<br>
  - 13 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2<br>
  - 2 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*+2<br>
  - 5 π_{L}^* π_{L,1}^*+2<br>
  - 7 π_{L}^* π_{L,1}^*+2<br>
  - 3 π_{L}^* π_{L,1}^*+2<br>

- **3^1A_1**
  - 77 π_{L}^* \pi_{L,1}^*<br>
  - 9 π_{L}^* \pi_{L,1}^*+2<br>
  - 8 π_{L}^* \pi_{L,1}^*<br>
  - 38 π_{L}^* π_{L,1}^*<br>
  - 15 π_{L}^* π_{L,1}^*+2<br>
  - 17 π_{L}^* π_{L,1}^*+2<br>
  - 13 π_{L}^* π_{L,1}^*+2<br>

- **3^1B_2**
  - 78 n_{H-4} \pi_{L}^* \pi_{L,1}^*<br>
  - 12 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*+2<br>
  - 2 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*<br>
  - 46 n_{H-4} \pi_{L}^* \pi_{L,1}^*+2<br>
  - 13 n_{H-4} \pi_{L,1}^* \pi_{L,1}^*+2<br>
  - 2 n_{H-3} \pi_{L,1}^* \pi_{L,1}^*+2<br>
  - 51 π_{L}^* π_{L,1}^*+2<br>
  - 7 π_{L}^* π_{L,1}^*+2<br>
  - 4 π_{L}^* π_{L,1}^*+2<br>

- **4^1B_1**
  - 55 π_{L}^* \pi_{L,1}^*+1<br>
  - 9 π_{L}^* \pi_{L,1}^*+1<br>
  - 7 π_{L}^* \pi_{L,1}^*+1<br>
  - 6 π_{L}^* \pi_{L,1}^*+1<br>

*The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

The π_{L,1}^*+2 bh-lyp corresponds to the π_{L,3}^* hf orbital;
Table S50.: Calculated percentage of electron configurations in the excited states wave functions of nitrobenzene obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | Excitation | DFT/MRCI | % from | to | % from | to | DFT/MRCI-R | % from | to |
|-------|------------|----------|--------|----|--------|----|------------|--------|----|
| 1^A_2 | n_H-3 77  | \pi_L^2 | 12  | n_H-3 78 | \pi_L^2 | 12  | n_H-4 4 | n_H-4 3 | \pi_L^2 |
| 1^A_2 | n_H-3 12  | \pi_L^2 | 78  | n_H-3 12  | \pi_L^2+2 | 4  | n_H-4 3 | n_H-4 4 | \pi_L^2+2 |
| 1^A_2 | n_H-3 3  | \pi_L^2,\pi_L^2 | 78  | n_H-3 12  | \pi_L^2,\pi_L^2+2 | 4  | n_H-4 3 | n_H-4 4 | \pi_L^2,\pi_L^2+2 |
| 1^B_2 | n_H-4 76  | \pi_H^3 | 75  | n_H-4 75  | \pi_H^3 | 14  | n_H-4 3 | n_H-4 4 | \pi_H^3,\pi_H^3 |
| 1^B_2 | n_H-4 11  | \pi_H^3 | 10  | n_H-4 10  | \pi_H^3 | 5  | n_H-4 3 | n_H-4 4 | \pi_H^3,\pi_H^3 |
| 1^B_2 | n_H-3 46  | \pi_H^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |
| 2^B_1 | \pi_H^2 26 | \pi_L^2,\pi_L^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |
| 2^B_1 | \pi_H 12  | \pi_L^2,\pi_L^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |
| 2^B_1 | \pi_H 5  | \pi_L^2,\pi_L^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |
| 2^B_1 | \pi_H 4  | \pi_L^2,\pi_L^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |
| 2^B_1 | \pi_H 3  | \pi_L^2,\pi_L^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |
| 2^B_1 | \pi_H 2  | \pi_L^2,\pi_L^2 | 73  | \pi_H^2 | 57  | \pi_H^2 | 73  | \pi_H^2 | 57  |

57
S4.13. *Dithiosuccinimide*

Table S51. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of *dithiosuccinimide*. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies (eV) | Experimental |
|-------|--------------------|---------------|--------------|
|       |                    | DFT/MRCI     | DFT/MRCI-R   | MRMP2 (HF) | MRMP2 (BH-LYP) | |
| $1^1B_1$ | $n \rightarrow \pi^*$ | 2.66 (0) | 2.73 (0) | 2.58 (0) | 2.45 (0) | **2.77**$^a$, **2.82**$^b$ |
| $1^1A_2$ | $n \rightarrow \pi^*$ | 2.85 (0) | 2.93 (0) | 2.80 (0) | 2.66 (0) | **3.04**$^a$, **3.08**$^b$ |
| $1^1B_2$ | $\pi \rightarrow \pi^*$ | 4.13 (0.722) | 4.09 (0.7222) | 3.85 (0.585) | 3.75 (0.544) | **3.96**$^a$, **3.87**$^b$ |
| $2^1A_2$ | $n \rightarrow \pi^*$ | 4.64 (0) | 4.64 (0) | 4.37 (0) | 4.00 (0) | |
| $2^1A_1$ | $n, n \rightarrow \pi^*, \pi^*$ | 4.71 (0) | 3.40 (0) | | | |
| $2^1B_1$ | $n \rightarrow \pi^*$ | 4.83 (0) | 4.80 (0) | 4.55 (0) | 4.20 (0) | |
| | |  | | | | |
| $5^1A_1$ | $n^2 \rightarrow \pi^*^2$ | 6.07 (0) | 5.08 (0)$^1$ | 5.51 (0)$^1$ | 5.26(0)$^1$ | **2.63**$^a$ |
| $1^3B_1$ | $n \rightarrow \pi^*$ | 2.44 | 2.57 | 2.42 | 2.42 | |
| $1^3A_2$ | $n \rightarrow \pi^*$ | 2.64 | 2.77 | 2.67 | 2.59 | |
| $1^3B_2$ | $\pi \rightarrow \pi^*$ | 2.77 | 2.84 | 2.67 | 2.55 | |
| $1^3A_1$ | $\pi \rightarrow \pi^*$ | 3.43 | 3.51 | 3.42 | 3.28 | |
| $2^3B_2$ | $n, n \rightarrow \pi^*^2$ | 4.60 | 3.87 | 5.70$^2$ | 5.29$^2$ | |
| $2^3A_1$ | $n, n \rightarrow \pi^*, \pi^*$ | 4.68 | 3.36$^2$ | 6.67$^3$ | 6.55$^3$ | |
| $2^3A_2$ | $n \rightarrow \pi^*$ | 4.70 | 4.60 | 4.38 | 4.03 | |
| $2^3B_1$ | $n \rightarrow \pi^*$ | 4.87 | 4.73 | 4.50 | 4.14 | |

DFT/MRCI-R: $^1$ $3^1A_1$, $^2$ $1^3A_1$
MRMP2(HF): $^1$ $4^1A_1$, $^2$ $3^3B_2$, $^3$ $4^3A_1$
MRMP2(BH-LYP): $^1$ $4^1A_1$, $^2$ $3^3B_2$, $^3$ $5^3A_1$

$^a$ Absorption maximum in cyclohexane [27]
$^b$ Absorption maximum in methanol [27]
Table S52.: Calculated percentage of electron configurations in the excited states wave functions of dithiosuccinimide obtained at the DFT/MRCI, MR-MP2(HF) and MR-MP2(BH-LYP) levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | % from | to | % from | to | % from | to |
|-------|--------|----|--------|----|--------|----|
| \(1^1B_1\) | | | | | | |
| 11 | \(n_H\) | \(\pi_L^*\) | 53 | \(n_H\) | \(\pi_L^*\) | 50 | \(n_H\) | \(\pi_L^*\) |
| 11 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 2 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 2 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) |
| \(1^1A_2\) | | | | | | |
| 16 | \(n_H\) | \(\pi_L^*\) | 49 | \(n_H\) | \(\pi_L^*\) | 45 | \(n_H\) | \(\pi_L^*\) |
| 3 | \(\pi_{H-2 n_H}\) | \(\pi_L^{\pi L+1}\) | 14 | \(\pi_{H-2 n_H}\) | \(\pi_L^{\pi L+1}\) | 17 | \(\pi_{H-2 n_H}\) | \(\pi_L^{\pi L+1}\) |
| \(1^1B_2\) | | | | | | |
| 4 | \(\pi_{H-3 n_H^2}\) | \(\pi_L^{\pi L+1}\) | 58 | \(\pi_{H-3 n_H^2}\) | \(\pi_L^{\pi L+1}\) | 56 | \(\pi_{H-2 n_H}\) | \(\pi_L^{\pi L+1}\) |
| 2 | \(\pi_{H-3 n_H^2}\) | \(\pi_L^{\pi L+1}\) | 2 | \(\pi_{H-3 n_H^2}\) | \(\pi_L^{\pi L+1}\) | 2 | \(\pi_{H-3 n_H^2}\) | \(\pi_L^{\pi L+1}\) |
| \(2^1A_2\) | | | | | | |
| 11 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 35 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 29 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) |
| 9 | \(\pi_{H-2 n_H-1}\) | \(\pi_L^{\pi L+1}\) | 7 | \(\pi_{H-2 n_H-1}\) | \(\pi_L^{\pi L+1}\) | 9 | \(\pi_{H-2 n_H-1}\) | \(\pi_L^{\pi L+1}\) |
| 8 | \(\pi_{H-2 n_H-1}\) | \(\pi_L^{\pi L+1}\) | 7 | \(\pi_{H-2 n_H-1}\) | \(\pi_L^{\pi L+1}\) | 8 | \(\pi_{H-2 n_H-1}\) | \(\pi_L^{\pi L+1}\) |
| \(2^1A_1\) | | | | | | |
| 11 | \(n_H\) | \(\pi_L^{\pi L+1}\) | 53 | \(n_H\) | \(\pi_L^{\pi L+1}\) | 51 | \(n_H\) | \(\pi_L^{\pi L+1}\) |
| 12 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 12 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 13 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) |
| \(5^1A_1\) | | | | | | |
| 18 | \(n_H\) | \(\pi_L^{\pi L+1}\) | 49 | \(n_H\) | \(\pi_L^{\pi L+1}\) | 46 | \(n_H\) | \(\pi_L^{\pi L+1}\) |
| 36 | \(\pi_{H-2}\) | \(\pi_L^{\pi L+1}\) | 59 | \(\pi_{H-2}\) | \(\pi_L^{\pi L+1}\) | 57 | \(\pi_{H-2}\) | \(\pi_L^{\pi L+1}\) |
| \(2^3B_2\) | | | | | | |
| 6 | \(n_{H-1 n_H}\) | \(\pi_L^{\pi L+1}\) | 58 | \(n_{H-1 n_H}\) | \(\pi_L^{\pi L+1}\) | 56 | \(n_{H-1 n_H}\) | \(\pi_L^{\pi L+1}\) |
| 8 | \(\pi_{H-2}\) | \(\pi_L^{\pi L+1}\) | 5 | \(\pi_{H-2}\) | \(\pi_L^{\pi L+1}\) | 7 | \(\pi_{H-2}\) | \(\pi_L^{\pi L+1}\) |
| \(2^3A_1\) | | | | | | |
| 15 | \(n_H\) | \(\pi_L^{\pi L+1}\) | 33 | \(n_H\) | \(\pi_L^{\pi L+1}\) | 30 | \(n_H\) | \(\pi_L^{\pi L+1}\) |
| \(2^3B_1\) | | | | | | |
| 11 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 35 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) | 32 | \(n_{H-1}\) | \(\pi_L^{\pi L+1}\) |

Continued on next page
| State | % from | to          | % from | to          | % from | to          |
|-------|--------|-------------|--------|-------------|--------|-------------|
| 9     | $n_H$  | $\pi^*_L$   | 9      | $\pi_{H-2:n_H}$ | 10     | $\pi_{H-2:n_H}$ |
| 8     | $\pi_{H-2:n_H}$ | $\pi_L^*, \pi_{L+1}^*$ | 7      | $n_H^*$ | 8      | $n_H^*$ |

The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:

- The $n_H$ bh-lyp orbital corresponds to the $n_{H-1}$ hf orbital;
- The $n_{H-1}$ bh-lyp orbital corresponds to the $n_{H-2}$ hf orbital;
- The $\pi_{H-2}$ bh-lyp orbital corresponds to the $\pi_H$ hf orbital.
Table S53.: Calculated percentage of electron configurations in the excited states wave functions of dithiosuccinimide obtained at the DFT/MRCI, and DFT/MRCI-R levels of theory. Only electron configurations with more than 2 percentage are presented.

| State | % from | % to | Excitation
|-------|-------|-----|----------------|
|       |       |     | DFT/MRCI       |
| 1^1B₁ | 81    | n₁₇ | π₁₇^*      |
|       | 11    | n₁₇₋₁| π₇₈^*      |
| 1^3A₂ | 75    | n₁₇₋₁| π₇₈      |
|       | 16    | n₁₇ | π₇₈^*      |
|       | 3     | π₁₇₋₂₋₃n₁₇| π₇₈^* |
| 1^1B₂ | 88    | π₁₇₋₁| π₇₈^*      |
|       | 4     | π₁₇₋₃π₇₋₂| π₇₈^* |
| 2^1A₁ | 86    | n₁₇₋₁n₁₇| π₇₈^* |
|       |       |       | π₇₈π₇₈^* |
| 2^3B₁ | 63    | n₁₇₋₁| π₇₈^*      |
|       | 11    | π₁₇₋₂₋₃n₁₇| π₇₈^* |
|       | 7     | π₁₇₋₂₋₃n₁₇| π₇₈π₇₈^* |
|       | 6     | n₁₇ | π₇₈π₇₈^* |
| 5^3A₁ | 49    | n₁₇₋₁n₁₇| π₇₈π₇₈^* |
|       | 37    | n₁₇₋₁n₁₇| π₇₈π₇₈^* |
| 1^3B₁ | 82    | n₁₇ | π₇₈π₇₈^* |
|       | 12    | n₁₇₋₁| π₇₈π₇₈^* |
| 1^3A₂ | 76    | n₁₇₋₁| π₇₈π₇₈^* |
|       | 18    | n₁₇ | π₇₈π₇₈^* |
| 1^3B₂ | 88    | π₁₇₋₂| π₇₈π₇₈^* |
|       | 8     | π₁₇₋₃| π₇₈π₇₈^* |
| 1^3A₁ | 58    | π₁₇₋₃| π₇₈π₇₈^* |
|       | 36    | π₁₇₋₂| π₇₈π₇₈^* |
| 2^3B₂ | 87    | n₁₇₋₁n₁₇| π₇₈π₇₈^* |
|       | 6     | n₁₇₋₁n₁₇| π₇₈π₇₈π₇₈^* |
| 2^3A₁ | 89    | n₁₇₋₁n₁₇| π₇₈π₇₈π₇₈^* |
| 2^3A₂ | 65    | n₁₇ | π₇₈π₇₈^* |
|       | 15    | n₁₇₋₁| π₇₈π₇₈^* |
| 2^3B₁ | 69    | n₁₇₋₁| π₇₈π₇₈^* |
|       | 9     | n₁₇ | π₇₈π₇₈^* |
|       | 8     | π₁₇₋₂₋₃n₁₇| π₇₈π₇₈π₇₈^* |

| State | % from | % to | Excitation
|-------|-------|-----|----------------|
| 1^1A₂ | 12    | π₈₊₁| π₇₈^*      |
| 2^1A₂ | 59    | n₁₇ | π₇₈π₇₈^* |
|       | 12    | π₈₊₁| π₇₈π₇₈^* |
| 2^1A₂ | 10    | n₁₇₋₁| π₇₈π₇₈^* |
| 2^1A₂ | 6     | π₈₊₁| π₇₈π₇₈^* |
| 1^3B₁ | 34    | n₁₇₋₁n₁₇| π₇₈π₇₈^* |
| 2^3B₁ | 36    | π₁₇₋₂| π₇₈π₇₈π₇₈^* |
| 2^3B₁ | 36    | π₁₇₋₂| π₇₈π₇₈π₇₈^* |
| 2^3B₁ | 85    | n₁₇₋₁n₁₇| π₇₈π₇₈π₇₈^* |
| 2^3B₁ | 6     | n₁₇₋₁n₁₇| π₇₈π₇₈π₇₈π₇₈^* |
| 2^3B₁ | 87    | n₁₇₋₁n₁₇| π₇₈π₇₈π₇₈π₇₈^* |
| 2^3A₁ | 60    | n₁₇ | π₇₈π₇₈π₇₈^* |
| 2^3A₂ | 59    | n₁₇ | π₇₈π₇₈π₇₈^* |
| 2^3B₁ | 60    | n₁₇ | π₇₈π₇₈π₇₈^* |
### S4.14. Methionine

Table S54. Computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of methionine. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | DFT/MRCI | DFT/MRCI-R | MR-MP2 (HF) | MR-MP2 (BH-LYP) |
|-------|--------------------|-------------|-----------|------------|-------------|----------------|
| \(2^1\text{A}\) | \(\pi \rightarrow \sigma^*/\text{Ry}\) | 5.12 (0) | 5.32 (0) | 5.99 (0) | 5.24 (0) |
| \(3^1\text{A}\) | \(n_O \rightarrow \pi^+\) | 5.48 (0.002) | 5.71 (0.003) | 5.97 (0.002) | 5.54 (0.002) |
| \(1^2\text{A}\) | \(\pi \rightarrow \sigma^*/\text{Ry}\) | 4.65 | 4.94 | 5.62 | 4.77 |
| \(2^2\text{A}\) | \(n_O \rightarrow \pi^+\) | 5.13 | 5.46 | 5.77 | 5.26 |
| \(3^3\text{A}\) | \(\pi \rightarrow \sigma^*/\text{Ry}\) | 5.74 | 6.00 | 6.74 | 5.74 |
| \(4^3\text{A}\) | \(\pi_{H-4} \rightarrow \pi^+\) | 6.06 | 6.31 | 7.01 | 6.24 |

MRMP2(HF): \(1^3\text{A}, 2^1\text{A}, 3^7\text{A}\)
MRMP2(BH-LYP): \(1^6\text{A}\)
Regarding the occupied orbitals, the BH-LYP orbitals are very different compared to the HF orbitals for Methionine, in the table are presented HF orbitals in original ordering, without correlation with BH-LYP orbitals. The BH-LYP virtual orbitals are very different compared to the HF orbitals for Methionine, in the table are presented HF orbitals in original ordering, without correlation with BH-LYP orbitals. The BH-LYP virtual orbitals correspond to the n(O)H−2 hf orbital.

| State | Excitation | DFT/MRCI (BH-LYP) | MRMP2 (HF) | MRMP2 (BH-LYP) |
|-------|------------|-------------------|------------|----------------|
|       | % from     | to                | % from     | to             | % from     | to             |
| 2^1A  | 44         | π_H              | 25         | π_H (σ*/Ry)_L+9 | 29         | π_H (σ*/Ry)_L+5 |
|       | 20         | π_H (σ*/Ry)_L+2  | 13         | π_H (σ*/Ry)_L+5 | 16         | π_H (σ*/Ry)_L+5 |
|       | 13         | π_H (σ*/Ry)_L+3  | 7          | π_H (σ*/Ry)_L+6 | 8          | π_H (σ*/Ry)_L+3 |
|       | 5          | π_H (σ*/Ry)_L+4  | 7          | π_H (σ*/Ry)_L+6 | 10         | π_H (σ*/Ry)_L+5 |
|       | 3^1A       | n(O)_H−2         | 28         | n(O)_H−3 (σ*/Ry)_L+1 | 48         | n(O)_H−2 π_L+ |
|       | 7          | n(O)_H−2 (σ*/Ry)_L+1 | 18        | n(O)_H−3 (σ*/Ry)_L+1 | 29         | n(O)_H−2 (σ*/Ry)_L+1 |
|       | 7          | n(S)_H−3 π_L     | 6          | n(S)_H−3 π_L | 8          | n(S)_H−3 π_L |
|       | 5          | n(N)_H−3 π_L     | 6          | n(N)_H−3 π_L | 10         | n(N)_H−3 π_L |
| 2^1A  | 63         | n(O)_H−2         | 29         | n(O)_H−3 (σ*/Ry)_L+1 | 50         | n(O)_H−2 π_L+ |
|       | 7          | n(O)_H−2 (σ*/Ry)_L+1 | 18        | n(O)_H−3 (σ*/Ry)_L+1 | 29         | n(O)_H−2 (σ*/Ry)_L+1 |
|       | 7          | n(S)_H−3 π_L     | 6          | n(S)_H−3 π_L | 8          | n(S)_H−3 π_L |
|       | 5          | n(N)_H−3 π_L     | 6          | n(N)_H−3 π_L | 10         | n(N)_H−3 π_L |
| 3^3A  | 33         | π_L (σ*/Ry)_L+7  | 15         | π_L (σ*/Ry)_L+8 | 29         | π_L (σ*/Ry)_L+7 |
|       | 26         | π_L (σ*/Ry)_L−7  | 13         | π_L (σ*/Ry)_L+8 | 11         | π_L (σ*/Ry)_L+5 |
|       | 12         | π_L (σ*/Ry)_L+5  | 10         | π_L (σ*/Ry)_L+9 | 8          | π_L (σ*/Ry)_L+5 |
|       | 10         | π_L (σ*/Ry)_L+2  | 8          | π_L (σ*/Ry)_L+7 | 7          | π_L (σ*/Ry)_L+2 |
| 4^3A  | 70         | π_H−4            | 26         | π_H−4 (σ*/Ry)_L+1 | 49         | π_H−4 π_L+ |
|       | 8          | π_H−4 (σ*/Ry)_L+1 | 18         | π_H−4 (σ*/Ry)_L+1 | 29         | π_H−4 (σ*/Ry)_L+1 |
|       |            |                   | 6          | π_H−4 (σ*/Ry)_L+1 | 8          | π_H−4 (σ*/Ry)_L+1 |
|       |            |                   | 5          | σ_H−5 π_L+      | 10         | σ_H−5 π_L+ |

† Since the BH-LYP virtual orbitals are very different compared to the HF orbitals for Methionine, in the table are presented HF orbitals in original ordering, without correlation with BH-LYP orbitals. Regarding the occupied orbitals, the n(O)_H−2 bh-lyp orbital corresponds to the n(O)_H−3 hf orbital.
S4.15. Isoalloxazine

Table S56. Experimental and computed DFT/MRCI, DFT/MRCI-R, MR-MP2(HF) and MR-MP2(BH-LYP) vertical excitation energies of *isoalloxazine*. The oscillator strengths are given in the parentheses.

| State | Dominant character | Energies(eV) | Experiment |
|-------|-------------------|--------------|------------|
|       |                   | DFT/MRCI     | DFT/MRCI-R | MR-MP2    | MR-MP2 (HF) | MR-MP2 (BH-LYP) |
| $^2\text{I}^A'$ | $\pi \rightarrow \pi^*$ | 3.03 (0.287) | 3.00 (0.311) | 2.84 (0.230) | 2.64 (0.253) | 2.85$^a$ |
| $^1\text{I}^A''$ | $n \rightarrow \pi^*$ | 3.16 (0.002) | 3.28 (0.002) | 3.52 (0)$^1$ | 3.85 (0)$^1$ |
| $^2\text{I}^A''$ | $n \rightarrow \pi^*$ | 3.34 (0.001) | 3.46 (0.001) | 3.45 (0.002)$^2$ | 3.11 (0.002)$^2$ |
| $^3\text{I}^A''$ | $n \rightarrow \pi^*$ | 3.90 (0) | 4.00 (0) | 3.87 (0) | 3.76 (0)$^3$ |
| $^3\text{I}^A'$ | $\pi \rightarrow \pi^*$ | 3.94 (0.194) | 3.94 (0.188) | 3.98 (0.097) | 3.71 (0.143)$^4$ | 3.76$^a$ |
| $^1\text{I}^A''$ | $\pi \rightarrow \pi^*$ | 2.31 | 2.27 | 2.60 | 2.29 |
| $^1\text{I}^A''$ | $n \rightarrow \pi^*$ | 2.86 | 3.01 | 3.53 | 2.98 |
| $^2\text{I}^A'$ | $\pi \rightarrow \pi^*$ | 3.12 | 3.13 | 3.31 | 2.84 |
| $^2\text{I}^A''$ | $n \rightarrow \pi^*$ | 3.19 | 3.28 | 3.87 | 3.61$^5$ |

MRMP2(HF): $^1\text{I}^A''$, $^2\text{I}^A''$
MRMP2(BHLYP): $^1\text{I}^A''$, $^2\text{I}^A''$, $^3\text{I}^A''$, $^4\text{I}^A'$, $^5\text{I}^A''$

$^a$ 8-methylisoalloxazine in ethanol [28]
The orbitals presented in the table are labeled according to the order obtained within the DFT theory. In the following cases the ordering of the Hartree-Fock orbitals is different:
The $n(O)_{H-2}$ bh-lyp orbital corresponds to the $n(O)_{H-2}$ hf orbital;
The $n(N)_{H-4}$ bh-lyp orbital corresponds to the $n(N)_{H-5}$ hf orbital;
The $n(O)_{H-3}$ bh-lyp orbital corresponds to the $n(O)_{H-6}$ hf orbital.
The $\pi^2_{L+4}$ bh-lyp orbital corresponds to the $\pi^2_{L+6}$ hf orbital.

| State | % from to | % from to | % from to |
|-------|-----------|-----------|-----------|
| $2^1A'$ | $\pi_H^*$, $\pi_L^*$ | $\pi_H^*$, $\pi_L^*$ | $\pi_H^*$, $\pi_L^*$ |
| $1^1A''$ | $n(O)_{H-2}$, $\pi_L^*$ | $n(O)_{H-2}$, $\pi_L^*$ | $n(O)_{H-2}$, $\pi_L^*$ |
| $2^1A''$ | $n(N)_{H-4}$, $\pi_L^*$ | $n(N)_{H-4}$, $\pi_L^*$ | $n(N)_{H-4}$, $\pi_L^*$ |
| $3^1A'$ | $\pi_H$, $\pi_L^*$ | $\pi_H$, $\pi_L^*$ | $\pi_H$, $\pi_L^*$ |
| $1^3A''$ | $n(N)_{H-4}$, $\pi_L^*$ | $n(N)_{H-4}$, $\pi_L^*$ | $n(N)_{H-4}$, $\pi_L^*$ |
| $2^3A''$ | $n(O)_{H-2}$, $\pi_L^*$ | $n(O)_{H-2}$, $\pi_L^*$ | $n(O)_{H-2}$, $\pi_L^*$ |
|                          | DFT/MRCI | MRMP2 (HF) | MRMP2 (BH-LYP) |
|--------------------------|----------|------------|----------------|
| $(1^3 A'' | HSO x | 1^1 A')    | 8.5       | 11.4          | 12.1           |
| $(1^3 A'' | HSO y | 2^1 A')    | 6.0       | 3.1           | 3.0            |
| $(1^3 A'' | HSO z | 3^1 A')    | 4.2       | 3.6           | 3.6            |
| $(2^3 A'' | HSO x | 1^1 A')    | 10.3      | 6.8           | 7.2            |
| $(1^3 A'' | HSO y | 1^1 A')    | 10.7      | 3.6           | 4.7            |
| $(1^3 A'' | HSO z | 2^1 A')    | 2.0       | 0.4           | 0.3            |
| $(1^3 A'' | HSO z | 3^1 A')    | 2.5       | 1.7           | 1.8            |
| $(2^3 A'' | HSO y | 1^1 A')    | 23.0      | 24.7          | 25.7           |
| $(1^3 A' | HSO x | 1^1 A')    | 11.1      | 2.4           | 0.9            |
| $(1^3 A' | HSO y | 2^1 A'')   | 2.4       | 7.4           | 7.8            |
| $(1^3 A' | HSO z | 1^1 A')    | 9.7       | 8.3           | 9.0            |
| $(1^3 A' | HSO z | 2^1 A')    | 7.3       | 2.3           | 3.1            |
| $(1^3 A'' | HSO x | 1^1 A'')   | 1.9       | 4.8           | 5.6            |
| $(1^3 A'' | HSO y | 2^1 A'')   | 3.2       | 0.5           | 0.8            |
| $(1^3 A'' | HSO z | 1^3 A')    | 9.7       | 6.9           | 7.1            |
| $(1^3 A'' | HSO y | 1^3 A')    | 4.4       | 1.8           | 2.1            |
| $(2^3 A'' | HSO x | 1^3 A')    | 2.3       | 1.6           | 1.7            |
| $(2^3 A'' | HSO y | 1^3 A')    | 10.3      | 8.1           | 8.3            |
| $(2^3 A'' | HSO z | 1^3 A')    | 4.2       | 5.9           | 5.9            |
S5. Optimized geometries of all polyatomic molecules in Turbomole format

o-benzyne

```plaintext
$coord
  1.17436585005558  0.00000000000000  -2.91783955856904  c
-1.17436585005558  0.00000000000000  -2.91783955856904  c
-2.75209598591275  0.00000000000000   0.84138302133177  c
-1.32564422167504  0.00000000000000  1.40629603021343  c
 1.32564422167504  0.00000000000000  1.40629603021343  c
 2.75209598591275  0.00000000000000   0.84138302133177  c
-4.79588042002593  0.00000000000000  -0.84670344838957  h
-2.31805929976997  0.00000000000000  3.1996299807835  h
 2.31805929976997  0.00000000000000  3.1996299807835  h
 4.79588042002593  0.00000000000000  -0.84670344838957  h
$user-defined bonds
$end
```

Formaldehyde

```plaintext
$coord
  0.00000000000000  0.00000000000000   1.3492173758470  c
  0.00000000000000  0.00000000000000   0.3487499210216  o
  0.00000000000000   1.7744219446536   1.3492173758470  c
  0.00000000000000  -1.7744219446536  -1.3492173758470  c
$user-defined bonds
$end
```

Thioformaldehyde

```plaintext
$coord
  0.00000000000000  0.00000000000000  -0.2127208063682  c
  0.00000000000000  0.00000000000000  2.83208049504587  s
-1.74201265716538  0.00000000000000  -1.30967984720453  h
 1.74201265716538  0.00000000000000  -1.30967984720453  h
$user-defined bonds
$end
```

67
Furan

$coord
  0.00000000000000  0.00000000000000  -2.60951767812713  o
-2.06944695013647  0.00000000000000  -1.07409817620120  c
-1.35446631345745  0.00000000000000   1.38655862649115  c
  2.06944695013647  0.00000000000000  -1.07409817620120  c
  1.35446631345745  0.00000000000000   1.38655862649115  c
-3.87275264412434  0.00000000000000  -2.01429504621195  h
-2.58841049419110  0.00000000000000   3.00661787535332  h
  2.58841049419110  0.00000000000000   3.00661787535332  h
  3.87275264412434  0.00000000000000  -2.01429504621195  h
$user-defined bonds
$end

########################################################################
Thiophene

$coord
  1.34566119550646  0.00000000000000  -2.48135783630059  c
-1.34566119550646  0.00000000000000  -2.48135783630059  c
-2.34140829359619  0.00000000000000  -0.10207603421092  c
  2.34140829359619  0.00000000000000  -0.10207603421092  c
  0.00000000000000  0.00000000000000   2.16998967240478  s
-4.30322604139690  0.00000000000000   0.44859441791091  h
-2.48480316694106  0.00000000000000  -4.17813269206495  h
  2.48480316694106  0.00000000000000  -4.17813269206495  h
  4.30322604139690  0.00000000000000   0.44859441791091  h
$user-defined bonds
$end

########################################################################
Quinoxaline

coord
0.00000000000000 1.34851448928290 -0.04308396822032 c
0.00000000000000 -1.34851448928290 -0.04308396822032 c
0.00000000000000 2.65971823554233 2.286734315383 c
0.00000000000000 1.33705869093915 4.51645111448426 c
0.00000000000000 -1.33705869093915 4.51645111448426 c
0.00000000000000 -2.65971823554233 2.286734315383 c
0.00000000000000 -2.67165472069636 -2.25056228491017 n
0.00000000000000 2.67165472069636 -2.25056228491017 n
0.00000000000000 1.33982622873228 -4.33893321844487 c
0.00000000000000 -1.33982622873228 -4.33893321844487 c
0.00000000000000 2.36641046716173 -6.11641565124786 h
0.00000000000000 -2.36641046716173 -6.11641565124786 h
0.00000000000000 4.70524646880327 2.2380739016897 h
0.00000000000000 2.34078894813222 6.30069856802307 h
0.00000000000000 -2.34078894813222 6.30069856802307 h
0.00000000000000 -4.70524646880327 2.2380739016897 h
$user-defined bonds
$end

Quinazoline

$coord
-1.36377830593764 0.02164891624333 0.00000000000000 c
1.32358004466339 -0.00642782560434 0.00000000000000 c
-2.67344557760090 2.35111102112969 0.00000000000000 c
-1.34210560585668 4.57650051698381 0.00000000000000 c
1.33118157888386 4.55054284673907 0.00000000000000 c
2.64773551616107 2.31460626473841 0.00000000000000 c
2.62027853734640 -2.23232554321978 0.00000000000000 n
-2.55361790292543 -2.37354727839355 0.00000000000000 c
-1.29008728275860 -4.50630971626298 0.00000000000000 n
1.27443449300352 -4.3085968746912 0.00000000000000 c
-4.6066030571199 -2.49662580101590 0.00000000000000 h
2.2958361341275 -6.08655825695464 0.00000000000000 h
-4.72287386788293 2.35172083639553 0.00000000000000 h
-2.33128955432688 6.36844044222261 0.00000000000000 h
2.3466893885953 6.32863938189363 0.00000000000000 h
4.69249305982863 2.26136784419168 0.00000000000000 h
$user-defined bonds
$end

*****************************************************************************
Pyranthione

$coord
0.00000000000000 0.00000000000000 -5.41280084911143  s
0.00000000000000 0.00000000000000 -2.27610234375952  c
2.28239911071821 0.00000000000000 0.00000000000000  c
-2.28239911071821 0.00000000000000 0.00000000000000  c
1.7921770453302 0.00000000000000 0.00000000000000  c
-1.7921770453302 0.00000000000000 0.00000000000000  c
2.19281770453302 0.00000000000000 0.00000000000000  c
-2.19281770453302 0.00000000000000 0.00000000000000  c
0.00000000000000 0.00000000000000 3.10029625536432  o
4.09779134136361 0.00000000000000 0.00000000000000  c
-4.09779134136361 0.00000000000000 0.00000000000000  c
3.81569058976344 0.00000000000000 0.00000000000000  c
-3.81569058976344 0.00000000000000 0.00000000000000  c

$user-defined bonds
$end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Dithiin

$coord
-2.86580686520235 0.06685457466165 -0.58761113643798  c
-1.74686625152159 -0.9349975340578 -3.58743264371355  s
1.74686625152159 0.9349975340578 -3.58743264371355  s
2.86580686520235 -0.06685457466165 -0.58761113643798  c
1.3494386294333 -0.2646520176855 1.43325076748021  c
-1.3494386294333 0.2646520176855 1.43325076748021  c
4.88043546579430 -0.4204691325140 0.4773225730807  h
2.19170307049153 -0.81587368262624 3.21985735926151  h
-2.19170307049153 0.81587368262624 3.21985735926151  h
-4.88043546579430 0.4204691325140 0.4773225730807  h

$user-defined bonds
$end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
Bithiophene

coord
-3.96988778421768 1.08891220762545 0.86140126635055 s
-0.74152793302954 1.15246315166230 0.1713671343972 c
0.02013601870388 3.59049859122632 -0.30037764090575 c
-1.96658915178120 5.38569505078307 -0.13126800701727 c
-4.23600721856751 4.31664305664117 0.46548485545081 c
0.74152793302954 -1.15246315166230 0.1713671343972 c
-0.02013601870388 -3.59049859122632 -0.30037764090575 c
1.96658915178120 -5.38569505078307 -0.13126800701727 c
4.23600721856751 -4.31664305664117 0.46548485545081 c
3.96988778421768 -1.08891220762545 0.86140126635055 s
6.04440759167992 -5.22731659581586 0.69687312532149 h
-6.04440759167992 5.22731659581586 0.69687312532149 h
-1.71756381233833 7.3826074025362 -0.45753873320741 h
1.94373787470285 4.07268383409784 -0.79726048539097 h
-1.94373787470285 -4.07268383409784 -0.79726048539097 h
1.71756381233833 -7.3826074025362 -0.45753873320741 h

$user-defined bonds$
$end$

Nitromethane

$coord$
1.39335214705160 -0.76295979932813 0.00000000000000 n
1.28450387612169 -3.06285847571066 0.00000000000000 o
3.3286182243600 0.49273279279710 0.00000000000000 o
-1.08606004843182 0.62725172762346 0.00000000000000 c
-0.69904605232834 2.63955977340387 0.00000000000000 h
-2.11071587242454 0.03583699060714 -1.68078913533078 h
-2.11071587242454 0.03583699060714 1.68078913533078 h

$user-defined bonds$
$end$

71
Nitrobenzene

$coord
0.00000000000000 0.00000000000000 1.60347294530390  c
0.00000000000000 0.00000000000000  3.59896025534619  c
2.29878831137124 0.00000000000000 0.33655081995768  c
-2.29878831137124 0.00000000000000 0.33655081995768  c
-2.28322846111443 0.00000000000000 2.28896805815391  c
 2.28322846111443 0.00000000000000 2.28896805815391  c
 4.04004564954374 0.00000000000000 1.40275883089641  h
-4.04004564954374 0.00000000000000 1.40275883089641  h
-4.05541523981593 0.00000000000000 -3.31160564246933 h
 4.05541523981593 0.00000000000000 -3.31160564246933 h
 0.00000000000000 0.00000000000000 -5.64617215317262 h
 0.00000000000000 0.00000000000000 4.40465230335952 n
2.04887036382285 0.00000000000000 5.47976762969691 o
-2.04887036382285 0.00000000000000 5.47976762969691 o

$user-defined bonds
$end

Dithiosuccinimide

$coord
0.00000000000000 -1.45666900594610 -1.66620418588077  c
0.00000000000000 -2.21034538961508  1.10066498364750  c
0.00000000000000 0.00000000000000  2.46084368279514 n
0.00000000000000 2.21034538961508  1.10066498364750  c
0.00000000000000 1.45666900594610 -1.66620418588077  c
0.00000000000000 5.04724275757076  2.32512196784998 s
0.00000000000000 -5.04724275757076  2.32512196784998 s
0.00000000000000 0.00000000000000  4.37458631463165 h
1.65477054116251 -2.26812361781069 -2.5886488216505 h
-1.65477054116251 -2.26812361781069 -2.5886488216505 h
-1.65477054116251  2.26812361781069 -2.5886488216505 h
 1.65477054116251  2.26812361781069 -2.5886488216505 h

$user-defined bonds
$end

|
--- | --- | --- |
| 72 | 72 | 72 |
Methionine

$coord
4.76099430895915 -1.7133782672988 1.79001120037847 c
4.44195060765592 -2.57337548311441 4.17681740779049 o
6.73547550894334 -0.87343024066359 1.03129552889427 o
6.03384721355275 -2.33959388425558 5.05836468986696 h
2.3223111761168 -1.83336199077757 0.26252246897826 c
3.01191601137541 -2.24565242658838 -2.37088018598580 n
1.25452267943939 -3.46488828582037 0.93136353597730 h
0.78326112962969 0.59026860172462 0.85795464483749 c
1.50001951379748 -2.08106869788800 -3.52885842715726 h
4.36762180027747 -1.00791439640966 -2.92238815854439 h
-1.82234113037246 0.55764684457247 -0.37825550229080 c
0.55704472603566 0.75684654251706 2.90554979877657 h
1.85046680753457 2.23982186123099 0.21438436052467 h
-3.58938225022865 3.40382269096334 0.48331018053293 s
-1.66355429116183 0.50012898279821 -2.43637847953666 h
-2.88650199322567 -1.10159950300212 0.23926972954955 h
-6.46776499311525 2.85263434307328 -1.31680416127601 c
-7.71857857571236 4.44536166753883 0.94532193712846 h
-6.07612816129063 2.77019011069814 -3.33892928668144 h
-7.40310002970565 1.11750109013264 -0.71302740750607 h

$user-defined bonds
$end

*******************************************************************************

73
Isoalloxazine

$coord

2.51988147835166  -1.36384049945196  0.00000000000000  c
4.57172112766037  -2.70142876166231  0.00000000000000  n
6.87887313585653  -1.46785020644587  0.00000000000000  c
6.85196359523531   1.21173040580103  0.00000000000000  n
4.7918998631520   2.8126154742180   0.00000000000000  c
2.33542437604255   1.39534955869551  0.00000000000000  c
0.24197822755524  -2.5871214357286   0.00000000000000  n
-2.05105524911613  -1.36512882582954  0.00000000000000  c
-2.00997620849890  1.31100618503416  0.00000000000000  c
0.22684912824209   2.62521091683690  0.00000000000000  n
-4.35206876488726  -2.66514536632553  0.00000000000000  c
-6.58317892927744  -1.30417219401142  0.00000000000000  c
-6.57340285963868   1.34837992430289  0.00000000000000  c
-4.30974932946563   2.63989017414723  0.00000000000000  c
 8.88925948139859  -2.55529606892658  0.00000000000000  o
 4.97576345077364   5.09131875662744  0.00000000000000  o
-8.34351156204724   2.37249377528319  0.00000000000000  h
 0.32588952491405  -4.50054276596776  0.00000000000000  h
-8.36597090104112  -2.3098604609086   0.00000000000000  h
-4.37233213191804   -4.71294314907122  0.00000000000000  h
-4.22485476781693   4.68341199676864  0.00000000000000  h
 8.57651329975121   2.04188095074323  0.00000000000000  h

$user-defined bonds

$end

*******************************************************************************
References

[1] C. Marian, Spin–orbit coupling in molecules, in Reviews In Computational Chemistry, edited by K. Lipkowitz and D. Boyd, Vol. 17, pp. 99–204, Wiley-VCH, Weinheim (2001).
[2] J.G.G. Simon, N. Mnzel and A. Schweig, Chem. Phys. Lett. 170 (23), 187 (1990).
[3] K.N. Walzl, C.F. Koerting and A. Kuppermann, J. Chem. Phys. 87, 3796 (1987).
[4] S. Taylor, D.G. Wilden and J. Comer, Chem. Phys. 70, 291 (1982).
[5] J.E. Mentall, E.P. Gentieu, M. Krauss and D. Neumann, J. Chem. Phys. 55, 5471 (1971).
[6] P. Brint, J.P. Connerade, C. Mayhew and K. Sommer, J. Chem. Soc., Faraday Trans. 2 81, 1643 (1985).
[7] C. Drury and D. Moule, J. Mol. Spectrosc. 92, 469 (1982).
[8] R. Judge, C. Drury-Lessard and D. Moule, Chem. Phys. Lett. 53, 82 (1978).
[9] S.Y. Chiang and I.F. Lin, J. Chem. Phys. 122, 094301 (2005).
[10] M.H. Palmer, I.C. Walker, C.C. Ballard and M.F. Guest, Chem. Phys. 192, 111 (1995).
[11] K.R. Asmis, Ph.D. thesis, University of Freiburg, Switzerland 1996.
[12] W.M. Flicker, O.A. Mosher and A. Kuppermann, J. Chem. Phys. 64, 1315 (1976).
[13] E.V. Veen, Chem. Phys. Lett. 41 (3), 535 (1976).
[14] J. Roebber, D. Gerrity, R. Hemley and V. Vaida, Chem. Phys. Lett. 75 (1980).
[15] M.H. Palmer, I.C. Walker and M.F. Guest, Chem. Phys. 241, 275 (1999).
[16] R.W. Glass, L.C. Robertson and J.A. Merritt, J. Chem. Phys. 53, 3857 (1970).
[17] J. Aaron, A. Tine, M. Gaye, C. Parkanyi, C. Boniface and T. Bieze, Spectrochim. Acta A: Mol. Spectrosc. 47, 419 (1991).
[18] M. Szymanski, R. Steer and A. Maciejewski, Chem. Phys. Lett. 135, 243 (1987).
[19] E. Block, M. Birringer, R. DeOrazio, J. Fabian, R.S. Glass, C. Guo, C. He, E. Lorance, Q. Qian, T.B. Schroeder, Z. Shan, M. Thiruvazhi, G.S. Wilson and X. Zhang, J. Am. Chem. Soc. 122, 5052 (2000).
[20] S. Siegert, F. Vogeler, C.M. Marian and R. Weinkauf, Phys. Chem. Chem. Phys. 13, 10350 (2011).
[21] R.S. Becker, J. Seixas de Melo, A.L. Maçanita and F. Elisei, J. Phys. Chem. 100, 18683 (1996).
[22] I.C. Walker and M.A. Fluendy, Intern. J. Mass Spectrom. 205, 171 (2001).
[23] W.M. Flicker, O.A. Mosher and A. Kuppermann, J. Chem. Phys. 72, 2788 (1980).
[24] W.D. Taylor, T.D. Allston, M.J. Moscato, G.B. Fazekas, R. Kozlowski and G.A. Takacs, Int. J. Chem. Kinet. 12, 231 (1980).
[25] S. Nagakura, Mol. Phys. 3, 152 (1960).
[26] S. Nagakura, M. Kojima and Y. Maruyama, J. Mol. Spectrosc. 13, 174 (1964).
[27] S.C. Meskers, T. Polonski and H.P. Dekkers, J. Phys. Chem. 99, 1134 (1995).
[28] M. Sun, T.A. Moore and P.S. Song, J. Am. Chem. Soc. 94, 1730 (1972).