Supplementary Information

On the short and long phosphorescence lifetimes of aromatic carbonyls

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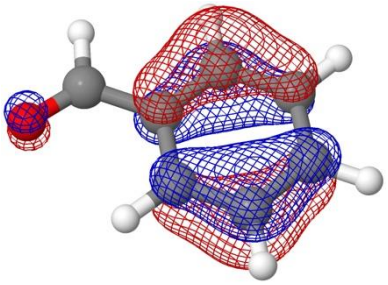
SI-1. Excitation character of the excited electronic states of benzaldehyde

Main orbital transitions in benzaldehyde

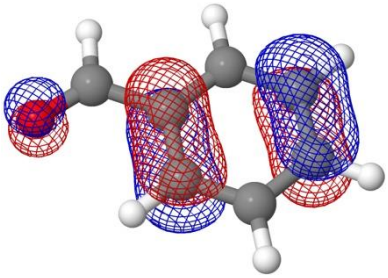
State	ΔE (eV)	Excitation	Character	ΔE (eV)	Excitation	Character
	S_0 minimum			**S_1 minimum**		
S_0	0.0			0.40		
S_1	3.68	28→29: 0.69549 28→31: 0.12554	$n\pi^*$	3.33	28→29: 0.69816 28→31:-0.11278	$n\pi^*$
S_2	4.78	26→29: 0.53542 26→30: 0.13700 27→29:-0.37585 27→30: 0.23048	$\pi\pi^*$	4.97	26→29: 0.64321 27→29: 0.14944 27→30: 0.24943	$\pi\pi^*$
T_1	3.12	28→29: 0.68551 28→31: 0.17163	$n\pi^*$	2.77	28→29: 0.68957 28→31:-0.15977	$n\pi^*$
T_2	3.30	26→29: 0.28343 26→30:-0.22925 27→29: 0.57883 27→30: 0.13537	$\pi\pi^*$	3.05	25→29:-0.11990 25→31: 0.12378 26→30:-0.15201 27→29: 0.68091	$\pi\pi^*$
	T_1 minimum ($n\pi^*$)			**T_1 stationary structure ($\pi\pi^*$)**		
S_0	0.42			0.61		
S_1	3.34	28→29: 0.69809 28→31:-0.11357	$n\pi^*$	3.52	28→29: 0.69842 28→31:–0.11135	$n\pi^*$
S_2	4.95	26→29: 0.64414 27→29:-0.16207 27→30:-0.23849	$\pi\pi^*$	5.07	26→29: 0.58350 27→29: 0.32780 27→30: 0.22166	$\pi\pi^*$
T_1	2.76	28→29: 0.68990 28→31:-0.15930	$n\pi^*$	2.85	24→31: 0.11474 26→30:–0.12072 27→29: 0.69824	$\pi\pi^*$
T_2	3.05	25→29: 0.14125 25→31:-0.12901 26→30: 0.14877 27→29: 0.67637	$\pi\pi^*$	2.96	28→29: 0.69010 28→31:–0.15765	$n\pi^*$

Molecular orbitals of benzaldehyde

S_0 minimum



MO 26: π



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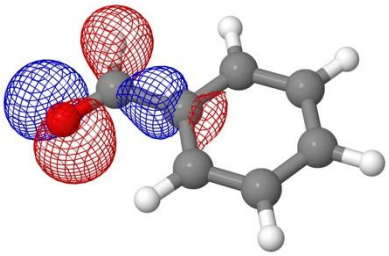
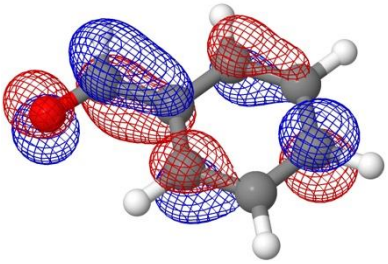
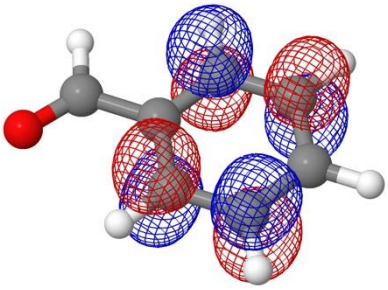


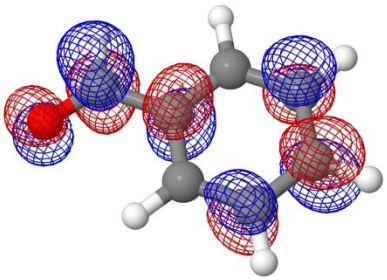
MO 28: nb



MO 29: $\pi^\star$

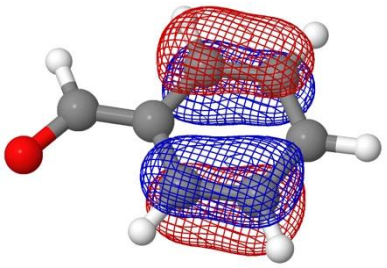


MO 30: $\pi^\star$

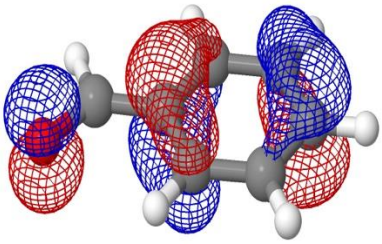


MO 31: $\pi^\star$

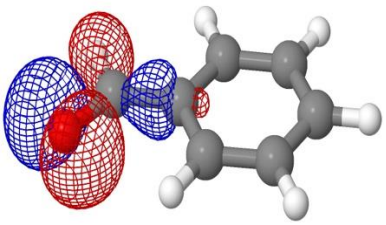
T_1 minimum ($n\pi^\star$)



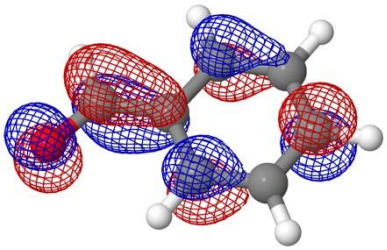
MO 26: π



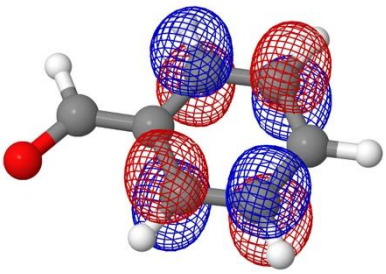
MO 27: π



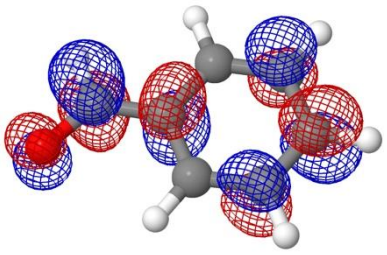
MO 28: nb



MO 29: $\pi^\star$



MO 30: $\pi^\star$



MO 31: $\pi^\star$

SI-2. Geometrical parameters of benzaldehyde in critical points

Table S1: Relevant bond lengths (Å) and bond angles (º) of benzaldehyde in different electronic state minima. The values in parentheses are experimental data with 3σ error bars [1]. The values in square brackets are theoretical data obtained with TDDFT-ωB97X/6-31G(d,p) [2].

Geometry Parameters	S_0 minimum	S_1 minimum	T_1 minimum ($^3n\pi^*$)	T_1 minimum ($^3\pi\pi^*$)
C1-C2	1.403 (1.388 ± 0.004) [1.396]	1.434 [1.410]	1.428 [1.408]	1.481 (1.479 ± 0.029) [1.478]
C2-C3	1.390 (1.381 ± 0.004) [1.387]	1.383 [1.388]	1.385 [1.389]	1.367 (1.322 ± 0.029) [1.360]
C3-C4	1.400 [1.395]	1.404 [1.392]	1.401 [1.391]	1.426 [1.422]
C4-C5	1.397 [1.392]	1.407 [1.397]	1.403 [1.396]	1.445 [1.450]
C5-C6	1.394 (1.381 ± 0.004) [1.390]	1.380 [1.382]	1.383 [1.384]	1.361 (1.322 ± 0.029) [1.352]
C1-C6	1.401 (1.388 ± 0.004) [1.394]	1.433 [1.412]	1.428 [1.409]	1.467 (1.479 ± 0.029) [1.460]
C1-C7	1.480 (1.480 ± 0.005) [1.483]	1.397 [1.431]	1.405 [1.437]	1.394 (1.420 ± 0.045) [1.414]
C7-O	1.216 (1.200 ± 0.002) [1.210]	1.297 [1.293]	1.310 [1.297]	1.305 (1.263 ± 0.031) [1.255]
C1-C7-O	124.7 (126.4 ± 0.3) [124.2]	128.6 [124.3]	126.6 [123.3]	121.3 (125.4 ± 2.6) [122.2]
C2-C1-C7	120.3 [119.7]	121.8 [121.1]	122.4 [121.6]	120.4 [119.4]
O-C7-H	120.8	111.0	111.3	119.5

SI-3. Comparison of vertical excitation energies of benzaldehyde

Table S2: Vertical excitation energies (eV) at the minima of S_0, S_1, S_2, T_1, and T_2 states calculated with TD-B3LYP/6-31G(d,p). The values in parentheses are previously reported CASPT2 results [3]. The values in square brackets are also previously reported data obtained with TD-ωB97X/6-31G(d,p) [2]. Experimental adiabatic excitation energies are given in double brackets [4]. The zero-point energy (ZPE) values are obtained after frequency calculation of the corresponding structures with the same level of theory.

	S_0 minimum	S_1 minimum	S_2 minimum	T_1 minimum ($^3n\pi^*$)	T_1 minimum ($^3\pi\pi^*$)
S_0	0.00	0.40 (0.57) [0.30]	0.31	0.42 (0.48) [0.33]	0.61 (0.37) [0.49]
S_1	3.68 (3.71) [4.01]	3.33 (3.27) [3.75] [[3.34]]	3.76	3.34 (3.29) [3.76]	3.52 (3.76) [4.07]
S_2	4.78	4.97	4.55	4.95	5.07
T_1	3.12 (3.40) [3.45]	2.77 (3.07) [3.18]	3.17	2.76 (3.07) [3.17] [[3.12]]	2.85 (3.52) [3.53]
T_2	3.30 (3.49) [3.78]	3.05 (3.39) [3.64]	3.31	3.05 (3.40) [3.64]	2.96 (3.16) [3.34] [[3.30]]
ZPE	3.00	2.905	2.86	2.906	-

SI-4. C_{2v}-Adapted perturbative expansion

The singlet-triplet transition dipole moments considering the complete first-order perturbative expansion in C_{2v} are given in this section. S_0 is assumed to be A_1.

For T_1 state with A_1 symmetry, we have

$$\begin{bmatrix} \tilde{\boldsymbol{\mu}}^{(x)}_{1_{A_1}0} \\ \tilde{\boldsymbol{\mu}}^{(y)}_{1_{A_1}0} \\ \tilde{\boldsymbol{\mu}}^{(z)}_{1_{A_1}0} \end{bmatrix} = \begin{bmatrix} \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{y}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{y}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{x}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{L_{B_2}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{B_2}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{1_{A_1}} \right\rangle}{{}^1E_{L_{B_2}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{y}_{10} \middle| S_{L_{B_2}} \right\rangle \\ \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{x}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{x}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{y}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{L_{B_1}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{B_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{1_{A_1}} \right\rangle}{{}^1E_{L_{B_1}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{x}_{10} \middle| S_{L_{B_1}} \right\rangle \\ \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{z}_{10} \middle| T_{1_{A_1}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{z}_{10} \middle| T_{1_{A_1}} \right\rangle \end{bmatrix}$$

For T_1 state with A_2 symmetry, we have

$$\begin{bmatrix} \tilde{\boldsymbol{\mu}}^{(x)}_{1_{A_2}0} \\ \tilde{\boldsymbol{\mu}}^{(y)}_{1_{A_2}0} \\ \tilde{\boldsymbol{\mu}}^{(z)}_{1_{A_2}0} \end{bmatrix} = \begin{bmatrix} \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{x}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{x}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{y}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{L_{B_1}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{B_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{1_{A_2}} \right\rangle}{{}^1E_{L_{B_1}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{x}_{10} \middle| S_{L_{B_1}} \right\rangle \\ \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{y}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{y}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{x}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{L_{B_2}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{B_2}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{1_{A_2}} \right\rangle}{{}^1E_{L_{B_2}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{y}_{10} \middle| S_{L_{B_2}} \right\rangle \\ \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{z}_{10} \middle| T_{1_{A_2}} \right\rangle + \sum_{L_{A_1}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{1_{A_2}} \right\rangle}{{}^1E_{L_{A_1}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{z}_{10} \middle| S_{L_{A_1}} \right\rangle \end{bmatrix}$$

For T_1 state with B_1 symmetry, we have

$$\begin{bmatrix} \tilde{\boldsymbol{\mu}}^{(x)}_{1_{B_1}0} \\ \tilde{\boldsymbol{\mu}}^{(y)}_{1_{B_1}0} \\ \tilde{\boldsymbol{\mu}}^{(z)}_{1_{B_1}0} \end{bmatrix} = \begin{bmatrix} \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{z}_{10} \middle| T_{1_{B_1}} \right\rangle \\ \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{z}_{10} \middle| T_{1_{B_1}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{z}_{10} \middle| T_{1_{B_1}} \right\rangle + \sum_{L_{A_1}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{1_{B_1}} \right\rangle}{{}^1E_{L_{A_1}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{z}_{10} \middle| S_{L_{A_1}} \right\rangle \\ \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{x}_{10} \middle| T_{1_{B_1}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{x}_{10} \middle| T_{1_{B_1}} \right\rangle + \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{y}_{10} \middle| T_{1_{B_1}} \right\rangle + \sum_{L_{B_2}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{B_2}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{1_{B_1}} \right\rangle}{{}^1E_{L_{B_2}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{y}_{10} \middle| S_{L_{B_2}} \right\rangle \end{bmatrix}$$

For T_1 state with B_2 symmetry, we have

$$\begin{bmatrix} \tilde{\boldsymbol{\mu}}^{(x)}_{1_{B_2}0} \\ \tilde{\boldsymbol{\mu}}^{(y)}_{1_{B_2}0} \\ \tilde{\boldsymbol{\mu}}^{(z)}_{1_{B_2}0} \end{bmatrix} = \begin{bmatrix} \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{z}_{10} \middle| T_{1_{B_2}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{z}_{10} \middle| T_{1_{B_2}} \right\rangle + \sum_{L_{A_1}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{1_{B_2}} \right\rangle}{{}^1E_{L_{A_1}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{z}_{10} \middle| S_{L_{A_1}} \right\rangle \\ \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{z}_{10} \middle| T_{1_{B_2}} \right\rangle \\ \sum_{K_{B_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(x)}_{K_{B_2}} \right\rangle}{{}^3E_{K_{B_2}} - {}^1E_0} \left\langle T_{K_{B_2}} \middle| \hat{y}_{10} \middle| T_{1_{B_2}} \right\rangle + \sum_{K_{B_1}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(y)}_{K_{B_1}} \right\rangle}{{}^3E_{K_{B_1}} - {}^1E_0} \left\langle T_{K_{B_1}} \middle| \hat{y}_{10} \middle| T_{1_{B_2}} \right\rangle + \sum_{K_{A_2}}^{\{\text{triplets}\}} \frac{\left\langle S_{0_{A_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{K_{A_2}} \right\rangle}{{}^3E_{K_{A_2}} - {}^1E_0} \left\langle T_{K_{A_2}} \middle| \hat{x}_{10} \middle| T_{1_{B_2}} \right\rangle + \sum_{L_{B_1}}^{\{\text{singlets}\}} \frac{\left\langle S_{L_{B_1}} \middle| \hat{H}^{SO} \middle| T^{(z)}_{1_{B_2}} \right\rangle}{{}^1E_{L_{B_1}} - {}^3E_1} \left\langle S_{0_{A_1}} \middle| \hat{x}_{10} \middle| S_{L_{B_1}} \right\rangle \end{bmatrix}$$

In these equations, each vector component indicates the triplet sublevel. The $\hat{x}_{10}$, $\hat{y}_{10}$, and $\hat{z}_{10}$ dipole operators determine the permanent and transition dipole moment directions.

SI-5. Supplementary references

1. Feenstra JS, Park ST, Zewail AH (2005) Excited state molecular structures and reactions directly determined by ultrafast electron diffraction. J Chem Phys 123: 221104
https://doi.org/10.1063/1.2140700
2. Ou Q, Subotnik JE (2013) Electronic Relaxation in Benzaldehyde Evaluated via TD-DFT and Localized Diabatization: Intersystem Crossings, Conical Intersections, and Phosphorescence. J Phys Chem C 117: 19839-19849
https://doi.org/10.1021/jp405574q
3. Molina V, Merchán M (2001) Theoretical Analysis of the Electronic Spectra of Benzaldehyde. J Phys Chem A 105: 3745-3751
https://doi.org/10.1021/jp004041t
4. Ohmori N, Suzuki T, Ito M (1988) Why does intersystem crossing occur in isolated molecules of benzaldehyde, acetophenone, and benzophenone? J Phys Chem 92: 1086-1093
https://doi.org/10.1021/j100316a019