

TD-DFT and DFT/MRCI study of electronic excitations in Violaxanthin and Zeaxanthin

Supporting Information

Jan Philipp Götze and Walter Thiel

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim an der Ruhr

Ring torsional angles

	V _x	Z _{X_{LL}}	Z _{X_{RL}}	Z _{X_{RR}}
1A _g gas phase	81.2 / 81.7	-51.4 / -51.4	-51.8 / 51.0	51.7 / 54.1
2B _u gas phase	81.2 / 81.7	-50.5 / -50.2	-46.5 / 44.2	44.0 / 45.5
1A _g acetone	81.4 / 82.0	-54.0 / -53.7	-52.8 / 53.3	50.1 / 50.6
2B _u acetone	81.4 / 81.9	-45.4 / -44.9	-42.8 / 42.8	41.8 / 42.5

Table S1: Torsional angle (degrees) of the two terminal rings of the V_x and Z_x minimum structures in the gas phase and in acetone. Torsional angle defined as depicted in Figure S1.

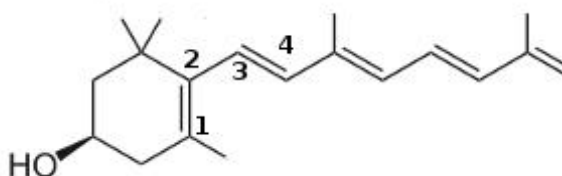


Figure S1: Definition of torsional angle (shown for Z_x, V_x analogous). Angle along atoms 1-2-3-4.

Spectral quality criteria

Model	Gas phase				Acetone	
	V _x		Z _{X_{RR}}		V _x	
Spectrum	Absorption	Emission	Absorption	Emission	Absorption	Emission
Det(J)	0.995	0.995	0.999	0.999	0.999	0.999
C	0.58	0.54	0.63	0.67	0.81	0.77
length(K)	331.16	331.16	173.85	173.86	29.17	29.17
sum(K)/n	2.77	2.77	2.62	2.62	0.50	0.50
E ^{HA}	0.36	0.35	0.33	0.35	0.49	0.44

Table S2: Determinant of the Duschinsky matrix **J**, spectral progression **C**, length of the displacement vector **K**, and harmonic reorganization energies E^{HA} (eV). See main article for definitions.

The Supporting Information addresses quality criteria for the computed time-independent Franck-Condon (TIFC) spectra. Two of these criteria have

already been defined in the main article, namely the determinant of the Duschinsky matrix $\text{Det}(\mathbf{J})$ and the spectral convergence C .

Here we also consider two further criteria. The first one refers to the excited-state energy difference between the optimized $1A_g$ and $1B_u$ geometries: the reference value is calculated directly and is then compared against the reorganization energy in harmonic approximation, E^{HA} , determined as the energy difference on an ideal excited-state harmonic potential surface (using displacements along the excited-state normal modes). Differences between E^{HA} and the directly computed energy difference indicate problems with the chosen harmonic representation of the excited-state surface. The second additional criterion is the size of the displacement vector \mathbf{K} (using Cartesian normal modes), defined either by its $\text{length}(\mathbf{K})$ or by the sum over all elements of \mathbf{K} , divided by the number n of vibrational normal modes ($\text{sum}(\mathbf{K})/n$).

The data in Table S1 confirm that the presented TIFC spectra are reliable. $\text{Det}(\mathbf{J})$ is close to 1 in all cases, and the spectral convergence is acceptable. As expected, there is an inverse relationship between C and $\text{length}(\mathbf{K})$, i.e., a smaller displacement ($\text{length}(\mathbf{K})$) goes along with a larger spectral convergence (C). An analogous relationship is also found between $\text{sum}(\mathbf{K})/n$ and C . For the data presented here, the two \mathbf{K} -based criteria, $\text{length}(\mathbf{K})$ and $\text{sum}(\mathbf{K})/n$, show essentially the same behavior. The E^{HA} values do not correlate as well: for example, for the $1B_u$ excitation of Vx in the gas phase, E^{HA} is 0.36 eV and thus closely corresponds to the reference value of -0.32 eV ($1B_u$ state, Table 2 of the main article), whereas there are larger deviations in the case of Vx in acetone (0.49 eV vs. -0.17 eV); by contrast, the spectral convergence C is lower in the former case (0.58 vs. 0.81, see Table S1).

In the case of the discarded TIFC spectra, the quality criteria were much worse than those reported in Table S1. $\text{Det}(\mathbf{J})$ ranged between 0.998 and 0.953, C was generally below 0.1, $\text{sum}(\mathbf{K})/n$ always exceeded 5.0, and E^{HA} deviated strongly from the directly computed energy difference assuming in some cases values up to several eV (data not shown). These problems are related to the use of Cartesian coordinates in the TIFC treatment (especially in cases involving twisting motions, see main article). We will address these issues in more detail in future work.