A note on the fitting of the displacement (δ) of the S_0 torsional potential.

As the intensity fits were carried out individually to each of the five spectra, slightly different values for the displacement δ of the S_0 minimum with respect to the S_1 minimum were obtained. These displacements are δ=13.9° in the case of the fluorescence excitation spectrum, δ=15.0° for the 0^0 SVLF spectrum, δ=15.1° for the T^1 SVLF spectrum, δ=16.2° for the T^2 SVLF spectrum and δ=17.3° for the T^3 SVLF spectrum. It should be noted that the simulated intensities of all spectra were very sensitive to the exact value of the displacement. We preferred, however, not to display here simulations of all spectra at, e. g., a mean value between δ=13.9° and δ=17.3° because of the artificial character of these differences between the displacement values of different spectra, which is explained below. Especially noteworthy is the monotonic increase of the displacement values in the series of SVLF spectra. This finding can be rationalized as being due to the neglect of the small non-planarity of the S_1 equilibrium geometry (ϕ ~ 2° according to the CIS potential energy scans, see **Table 4**) and, consequently, slight asymmetry of the S_1 potential well. (This asymmetry was neglected in the torsional analysis as the use of the sine/cosine potential showed only slight contributions from the odd terms of the expansion on the overall shape and energy level spacings of the potential.) This neglect also accommodates the decreasing quality of the fits, especially that to the T^3 SVLF spectrum, with increasing torsional quantum number. One can, thus, conceive of the need to best represent different spectra with different displacement values as an artificial means to take account of the small asymmetry of the S_1 potential well. The narrow distribution of these displacement values around a mean value of ϕ ~ 15° can, nonetheless, be interpreted as convincingly indicating the appropriateness and validity of our assumptions about the near-planarity of the S_1 equilibrium geometry and the near-symmetry of the S_1 potential well underlying the fit procedure.

The best-fit S_0 torsional potential with a minimum at ϕ=15.0° has potential parameters $V_2^e = 948\ \mathrm{cm}^{-1}$, $V_4^e = -195\ \mathrm{cm}^{-1}$, $V_2^o = -162\ \mathrm{cm}^{-1}$ and $V_4^o = -268\ \mathrm{cm}^{-1}$. They should be regarded as being representative for any torsional potential function with the energetic features, i. e. frequency spacings and barrier height, given in **Tables 4** and **5**. The potential parameters pertinent to a different equilibrium angle ϕ′ can be easily

determined according to eqs. (1) from those given above after setting the displacement to $\delta=\phi'-\phi$.]

$$V_2^e{}' = V_2^e \cos(2\delta) - V_2^o \sin(2\delta)$$

$$V_4^e{}' = V_4^e \cos(4\delta) - V_4^o \sin(4\delta)$$

$$V_2^o{}' = V_2^e \sin(2\delta) + V_2^o \cos(2\delta)$$

$$V_4^o{}' = V_4^e \sin(4\delta) + V_4^o \cos(4\delta) \qquad (1)$$