

Supplemental Material for
“Modeling the effects of torsional disorder on the spectra of poly-
and oligo-(*p*-phenyleneethynylenes)”

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This supplement examines the sensitivity of the predicted spectra to the model parameters. In fitting the model parameters to experiment, we began with a fit to the $N = 3$ oligomer, since the line shape reflects contributions from both the planar cusp and the entropy generated peak. The best fit for $N = 3$ is obtained with a ground-state (GS) rotational barrier of 1.18 Kcal/mol, which is about twice that of tolane; an excited-state (ES) transfer integral of 1.6 times that from INDO theory, β_o^{INDO} in Table II of the main text, and linewidths, LW , equal to those extracted from the emission spectrum of an $N = 3$ oligomer in Table III of the main text.

The left panel of Fig. (S1) shows the spectra predicted with the GS barrier varying from 0.0 to 2.2 V_{tolane} ($V_{tolane} = 0.59$ Kcal/mol), and with β_o and LW frozen at the above best fit values (Best fit value of LW is the vibronic structure extracted from the emission spectrum). Changing the GS rotational barrier alters the relative intensities of the two lowest-energy peaks. As the GS barrier increases, planar configurations become more favored and the low energy peak increases in intensity. The observed relative intensity of this peak thereby provides an indirect measure of the GS rotational barrier in solution. Increasing the GS barrier also narrows the overall spectrum.

The right panel of Fig. (S1) shows the effect of changing the ES transfer integral, β_o , from β_o^{INDO} to 1.7 β_o^{INDO} ($\beta_o^{INDO} = 3804.23$ cm^{-1}), with V and LW fixed at the above best fit values. As the ES transfer integral increases, the separation between the first and second peak increases. The observed separation between these peaks thereby provides an indirect measure of the ES transfer integral, with the best fit value being 1.6 β_o^{INDO} .

Fig. (S2) shows the effect of scaling the line widths of the vibronic structure in Table III of the main text by a constant factor, LW . The best fit is achieved with unscaled line widths, $LW = 1.0$.

We next consider the dependence of the absorption spectra on oligomer length. Fig. (S3) compares results obtained using each of the three methods discussed in the main text for obtaining the chain-length dependence of β_o . The three methods differ primarily in their predictions for how the origin of the electronic transition varies with chain length. Case (b), which multiplicatively scales β_o by 1.6 from the INDO/SCI predictions, leads to poor agreement with the observed spectra. Reasonable agreement is obtained using either case (a), which holds the slope of β_o at the INDO/SCI value, or case (c), which assumes β_o is independent of chain length. Both case (a) and case (c) lead to similar agreement with experimental

data and case (c) is taken in the fit. Apparently, although β_o must be increased from the INDO/SCI value to obtain good agreement with the observed spectra, the dependence of β_o on chain length is reasonably well predicted by INDO/SCI theory.

The left panel of Fig. (S4) shows the influence of the GS barrier on the spectra predicted for various oligomer lengths. As the barrier is increased, the ensemble of GS structures becomes more planar, causing the spectra to shift to the red. The line shape also narrows and exhibits increasingly well resolved vibronic structure. The best fit of the GS barrier was chosen primarily from agreement with the width and vibronic resolution of the observed spectra. The best value for the GS barrier decreases with chain length, from five times that of tolane for $N = 2$ to the tolane value for the polymer.

The right panel of Fig. (S4) compares various models for the vibronic structure. The vibronic structure was first extracted from the emission spectrum of various length oligomers. Since the molecule planarizes in the ES before emission, this reflects the vibronic structure of more nearly planar oligomers. To include the effects of the torsional disorder on the vibronic structure, we invoke an argument based on effective conjugation lengths. Torsional disorder is expected to reduce the effective conjugation length, and so it is reasonable to use the vibronic structure extracted from a short planar oligomer to model the vibronic structure of a longer disordered oligomer. The figure shows the results obtained using the vibronic structure extracted from various length oligomers. The best fit to the lower energy portion of the spectra is obtained using the vibronic structure extracted from the $N = 3$ oligomer for all oligomers with $N \geq 3$.

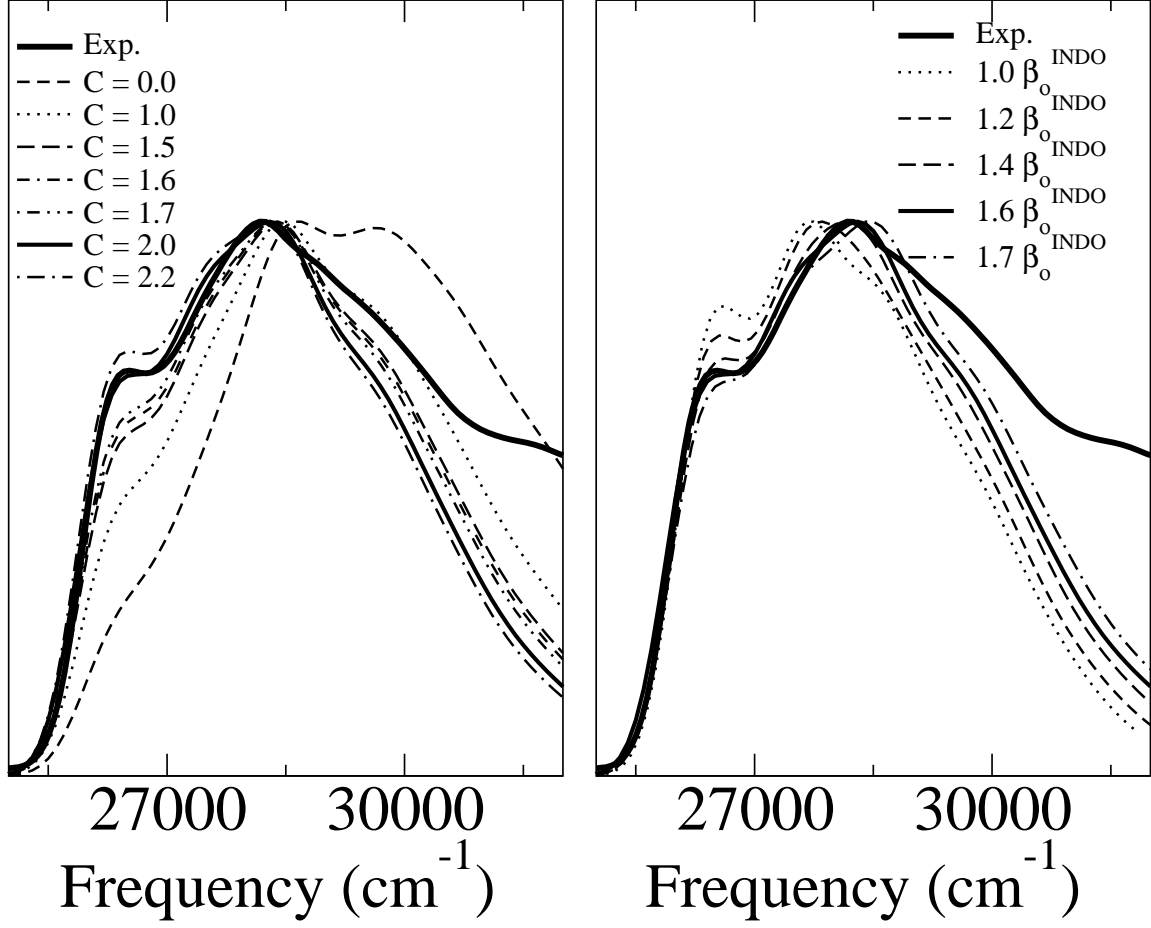


FIG. S1: The best fit to an oligomer with 3 rings is obtained with $\beta_o = 1.6$ times that of INDO theory (β_o^{INDO}) and a ground state barrier twice that measured for gas phase toluene, $C = 2$. The left panel shows the effect of varying the ground state barrier, holding β_o at the best-fit value. The right panel shows the effect of varying β_o holding the ground state barrier at its best-fit value.

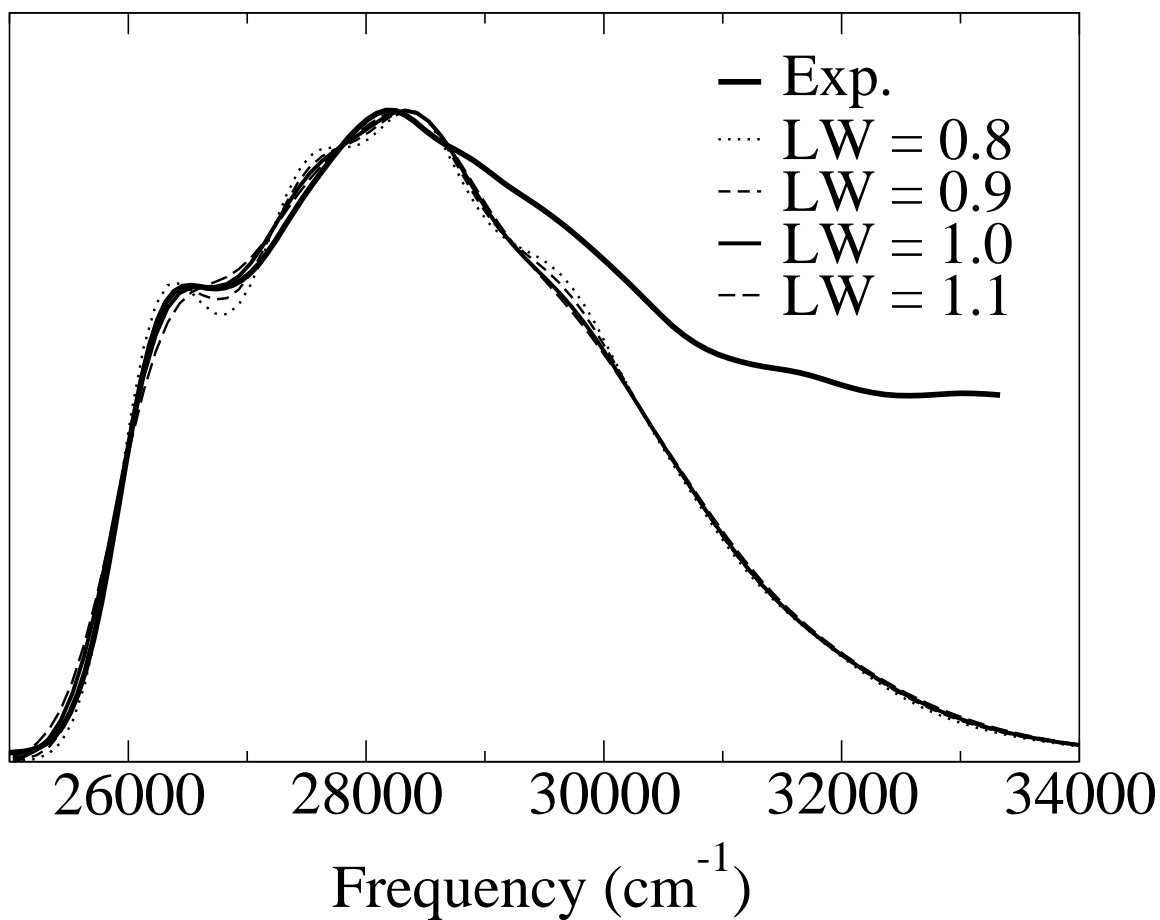


FIG. S2: The sensitivity to the choice of linewidths, holding other parameters at their best fit values. The plot shows the effect of multiplying the line widths obtained from the emission spectra by the constants shown, for an oligomer with $N = 3$.

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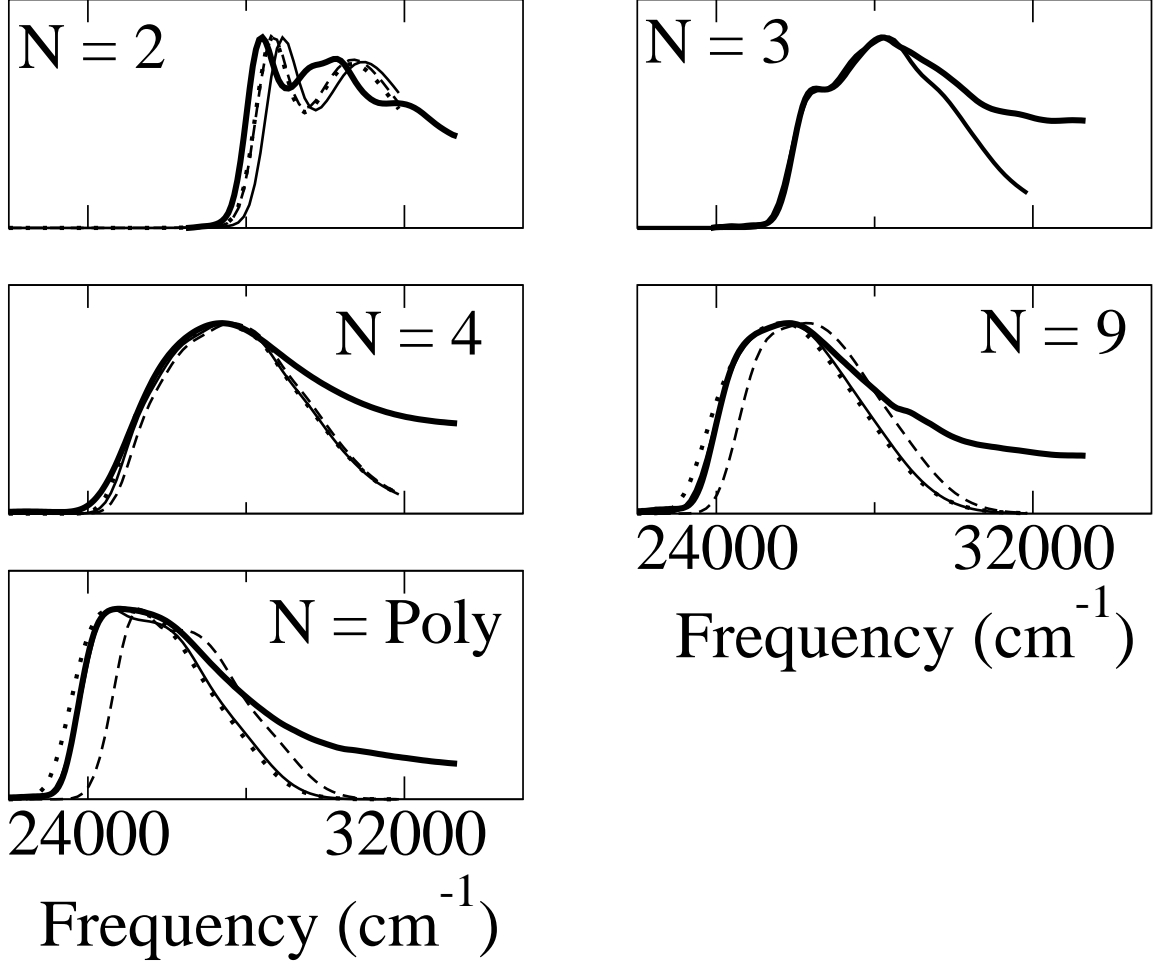


FIG. S3: Comparison of the three methods used to obtain the chain-length dependence of β_o discussed in Sec. IV of the main text. The experimental spectrum (thick solid) is compared with (a) additive scaling (solid), (b) multiplicative scaling (dash), and (c) no chain length dependence (dot). The GS barrier and vibronic structure are those from the best fit to the spectra.

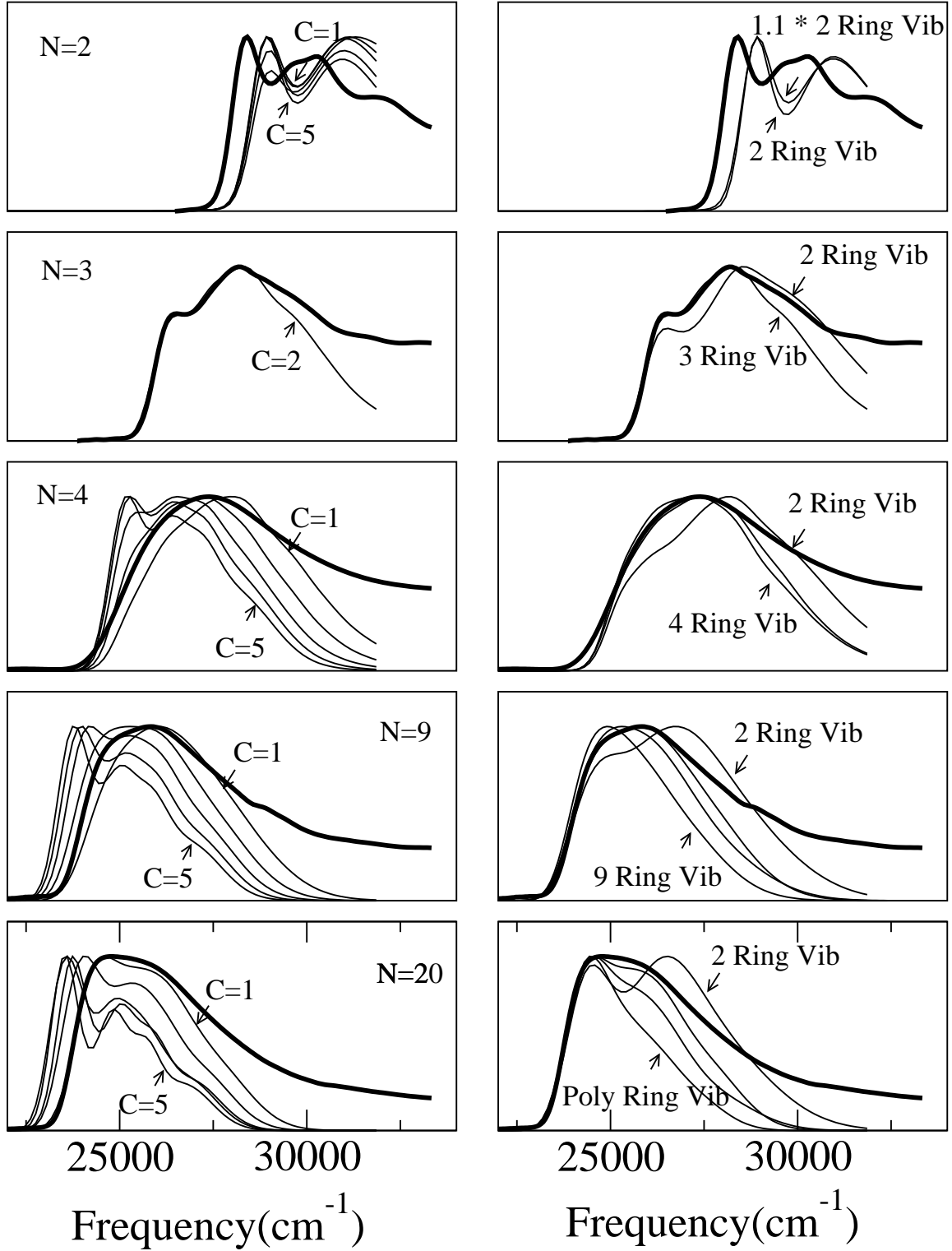


FIG. S4: The left column shows the effects of varying the GS barrier from that of tolane ($C = 1$) to five times that of tolane ($C = 5$). The right column shows the effects of using the vibronic structure for chain lengths less than or equal to the physical length of the oligomer. This models the effects of disorder, which can cause the effective conjugation length of an oligomer to be less than its physical length.