Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Effect of the orientation of nitro group on the electronic transport properties in single molecular field-effect transistors

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## Supplementary Information

### Details of thermal average calculation

In Fig. 4, we plot the relative total energy of the free $NO_2$BDT molecule as a function of twist angle $\theta$. Then we fit the curve to a harmonic oscillator potential for $\theta$ ranging from 0˚ to 50˚.

The amplitude of rotation can be written as the standard deviation of $\theta$,

$$\sigma = \sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2},$$

where $\langle \theta \rangle = \dfrac{\mathrm{Tr}(e^{-H/kT}\theta)}{\mathrm{Tr}(e^{-H/kT})}$ is the thermal average.

Hamiltonian of the harmonic oscillator is written as:

$$H = \frac{I\omega^2}{2}\theta^2 + \frac{1}{2I}L^2,$$

where $I$ is the moment of inertia, $\omega = \sqrt{\kappa / I}$ is the vibration frequency, $L = I\dfrac{d\theta}{dt}$ is the angular momentum.

Introduce the raising and lowering operators:

$$\theta = \sqrt{\frac{\hbar}{2I\omega}}(b^+ + b), \quad L = i\sqrt{\frac{\hbar\omega I}{2}}(b^+ - b),$$

which satisfy the following commutation relations:

$$[b, b^+] = bb^+ - b^+b = 1 \quad \text{and} \quad [b, b] = [b^+, b^+] = 0.$$

Then we can obtain:

$$H = \hbar\omega(b^{+}b + \frac{1}{2}).$$

The eigen equation is:

$$H\left|n\right\rangle = E_n\left|n\right\rangle,$$

where $\left|n\right\rangle$ is the eigenvector, $E_n = \hbar\omega(n+\frac{1}{2})$ is the eigenvalue.

Therefore,

$$\begin{cases} \left\langle\theta\right\rangle = \dfrac{\mathrm{Tr}(e^{-H/kT}\theta)}{\mathrm{Tr}(e^{-H/kT})} = \dfrac{\sum_n \left\langle n\right| e^{-H/kT}\theta \left|n\right\rangle}{\sum_n \left\langle n\right| e^{-H/kT} \left|n\right\rangle}, \\ \left\langle\theta^2\right\rangle = \dfrac{\mathrm{Tr}(e^{-H/kT}\theta^2)}{\mathrm{Tr}(e^{-H/kT})} = \dfrac{\sum_n \left\langle n\right| e^{-H/kT}\theta^2 \left|n\right\rangle}{\sum_n \left\langle n\right| e^{-H/kT} \left|n\right\rangle}. \end{cases}$$

Substitute $\theta = \sqrt{\dfrac{\hbar}{2I\omega}}(b^{+}+b)$ into the two equations above, and we can obtain:

$$\begin{cases} \left\langle\theta\right\rangle = 0, \\ \left\langle\theta^2\right\rangle = \dfrac{1}{I\omega^2}\left\langle H\right\rangle = \dfrac{1}{I\omega^2}\dfrac{\hbar\omega}{2}\coth(\dfrac{\hbar\omega}{2kT}). \end{cases}$$

When $kT >> \hbar\omega$, $\left\langle\theta^2\right\rangle \approx \dfrac{kT}{I\omega^2} = \dfrac{kT}{\kappa}$.

At room temperature ($T$ =300K), $kT$ =25.86meV. $\kappa$ can be obtained from the curve fitting of Fig. 4, $\kappa$ =0.154meV/deg$^2$. Take into account these parameters above, we obtain:

$$\sigma = \sqrt{\left\langle\theta^2\right\rangle - \left\langle\theta\right\rangle^2} = \sqrt{\frac{kT}{\kappa}} = 12.96\,\mathrm{deg}.$$