Supporting Information

Validity of Franck-Condon approximation in semi-classical Marcus Theory

Semi-classical Marcus theory is commonly used to describe charge transfer between conjugated organic molecules. The rate of charge transfer is given by [1]

$$k = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta\varepsilon + \lambda)^2}{4\lambda k_B T}\right) \tag{1}$$

where λ is the reorganisation energy, J is the transfer integral between the initial and final state and $\Delta\varepsilon$ is the change in energy.

Marcus theory is valid in the non-adiabatic limit where charges can be considered to be highly localised on individual molecules. This is not the case for naphthalene because λ is only $\simeq$100 meV, a similar value to the largest J. Moreover, Marcus theory predicts a charge mobility with a positive temperature dependence whereas experimental mobilities in naphthalene show a negative temperature dependence [5]. Although not valid for charge transfer in naphthalene, our results provide a useful point from which to analyse the Franck-Condon approximation that is implicit in the derivation semi-classical Marcus theory. This approximation states that J is independent of nuclear coordinates and can therefore be treated as a constant in equation 1. This assumption is usually justified by noting that during charge transfer, the reorganisation of the molecules is small and along high energy intramolecular modes which do not greatly change J. However, we have shown in figures 4 and 6 that small distortions along high energy modes can significantly alter J. In the light of these results we analyse the validity of the Franck-Condon approximation for naphthalene.

Table 1: The most important modes involved in the reorganisation of a molecule from the anionic to neutral geometry.

Anion mode (cm^{-1})	Equivalent neutral mode (cm^{-1})	Distortion (Å)
498	508	0.098
1353	1385	-0.036
1563	1576	-0.032

Table 2: The most important modes involved in the reorganisation of a molecule from the cationic to neutral geometry.

Cation mode (cm^{-1})	Equivalent neutral mode (cm^{-1})	Distortion (Å)
1390	1385	-0.025
1586	1576	-0.037

We optimised the geometry of the anion and cation with PW91 [4] and the 6-311G* basis set. By comparing these geometries with that of the neutral geometry, we decomposed the molecular reorganisation that occurs during charge transfer into contributions from each of the normal modes. Tables 1 and 2 shows the largest of these distortions for the anion and cation respectively. The total λ for anion and cation are 105 meV and 70 meV respectively. These are in good agreement with similar calculations in references [3, 2], with small discrepancies arising from our use of the PW91 functional instead of the B3LYP functional. The modes 1385 cm^{-1} and 1576 cm^{-1} (mode frequencies for the neutral molecule) account for most of the relaxation in both the cation and anion. These are the modes that alter the lengths of the C-C bonds on which the HOMO and LUMO are localised. These modes also make a large contribution to $\sigma\left(\Delta\varepsilon_{HOMO}\right)$ (figure 6).

During the reaction in which a cation gains an electron, J_{HOMO} varies by $\simeq 0.1$ meV along each of these modes. When an anion loses an electron, the change in J_{LUMO} is bigger because of the large distortion along the mode at 508 cm^{-1} (frequency for the neutral molecule); this distortion changes J_{LUMO} by nearly 1.8 meV. The modes at 1385 cm^{-1} and 1576 cm^{-1} change J_{LUMO} by $\simeq 0.5$ meV and $\simeq 0.2$ meV respectively.

For the optimised geometry of the two molecules, the values of J_{HOMO} and J_{LUMO} are -8.4 meV and -53.9 meV respectively. The total changes to J_{HOMO} and J_{LUMO} during charge transfer are $\simeq 0.2$ meV and $\simeq 2.5$ meV respectively. Therefore, to a first approximation, it appears that the Franck-Condon approximation would be valid for naphthalene.

Although the Franck-Condon approximation is reasonable for charge transfer in naphthalene, we have demonstrated that it is not necessarily true that small fluctuations along high energy modes will have negligible effects on J (figures 4 and 6). In other molecules it may be that the Franck-Condon approximation is not be valid during the charge transfer reaction. In this case, the Marcus rate equation may not be the most appropriate description of intermolecular charge transfer.

References

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