<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Disorder and spectral line shapes in two-level systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Shenai, Prathamesh M.; Shi, Wu-Jun; Chernyak, Vladimir; Zhao, Yang</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Shenai, P. M., Shi, W.-J., Chernyak, V., &amp; Zhao, Y. (2013). Disorder and spectral line shapes in two-level systems. Chemical Physics Letters, 582, 66-70.</td>
</tr>
<tr>
<td><strong>Date</strong></td>
<td>2013</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/19723">http://hdl.handle.net/10220/19723</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2013 Elsevier B.V. This is the author created version of a work that has been peer reviewed and accepted for publication by Chemical Physics Letters, Elsevier B.V. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [DOI: <a href="http://dx.doi.org/10.1016/j.cplett.2013.07.032">http://dx.doi.org/10.1016/j.cplett.2013.07.032</a>].</td>
</tr>
</tbody>
</table>
Disorder and spectral line shapes in two-level systems

Prathamesh M Shenai, a Wu-Jun Shi, a Vladimir Chernyak, a,b and Yang Zhao a,∗

a Division of Materials Science, Nanyang Technological University, Singapore 639798
b Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Using a stochastic model, we examine disorder-induced changes in the absorption line shape of a chromophore embedded in a matrix of noninteracting two-level systems (TLSs) with randomly oriented dipole moments. By systematically controlling the degree of TLS positional disorder, a perfectly crystalline, glassy or a combination of the two environments is obtained. The chromophore is assumed to interact with TLSs via long-range dipole-dipole coupling. At long times and in the absence of disorder, Gaussian line shapes are found, which morph into Lorentzian for a completely disordered environment owing to strong coupling between the chromophore and a TLS in close vicinity.

Keywords: Absorption line shape, Two-level systems, Disordered media.

I. INTRODUCTION

With the advent of low-temperature single molecule spectroscopy (SMS), it has become possible to probe the immediate microscopic environment of a single molecule of interest, such as chromophores embedded in organic glasses.1–4 SMS has been employed mostly to measure the absorption spectral line-shape,5–8 typically by fluorescence excitation techniques.9 In the presence of a medium, the transition frequencies of molecules are altered due to the fluctuations of the local environment, resulting in absorption spectrum broadening.10 The optical spectroscopy of chromophores at low concentration can thus play an important role in elucidating the structure and dynamics of solids, especially at very low temperatures. The absorption spectrum of a dilute chromophore in glass or structurally disordered solvents is usually inhomogeneously broadened,11–14 which is related to the local disorder around the chromophore.

The model of a collection of two-level systems (TLSs)15–20 has been satisfactorily employed to study many properties of amorphous systems such as the anomalous specific heat and thermal conductivities.21–27 Within the context of glassy systems, such a TLS is considered to be manifestation of an asymmetric double well potential with respect to some collective configurational coordinate. Typically the two local minima on the potential energy surface are believed to arise from local rearrangements of atomic or molecular clusters.28 Flipping between the two eigenstates is suggested to occur by phonon-assisted tunneling at low temperatures.29–30 Despite decades of research, only a few pointers to interpretations of TLSs such as their speculated relation with the motion of domain walls in glasses31 and possibility of studying the validity32 of standard TLS model with SMS experiments have emerged, and a fundamental understanding of their physical meaning and origin remains largely elusive. In their study of absorption line shape by Orth et al.,27 it was found that the defect density is an important parameter and under the assumption of dipolar-dipolar TLS-chromophore interactions, the line shape changes from Lorentzian to Gaussian form as the defect density is changed from very low to high values, respectively.

In this Letter, we aim to investigate the specific role of disorder on absorption line shape of a chromophore coupled to a collection of noninteracting flipping TLSs. With the introduction of a disorder parameter to simulate different environments, we calculate the absorption line shape as an average over an initial distribution of static TLS configurations. This paper is organized as follows. The details of underlying theoretical model and computational methodology are described in Section II. The results obtained on the analysis of absorption line shapes by both the theoretical and the computational approaches are presented and discussed in Section III. In the final Section IV, conclusions are drawn.

II. THEORETICAL MODEL AND COMPUTATIONAL DETAILS

The chromophore as a TLS with the ground (|g⟩) and excited (|e⟩) electronic states separated by energy equal to ℏωeg, is coupled to a collection of TLSs6,10,33,34 representing the host solid environment. It is essential to note that even though the chromophore and the host matrix are represented as TLSs, they possess distinctly different characteristics. The TLS of the chromophore, which can also be considered as an optical impurity, refers to its two electronic levels (ground state |g⟩ and excited state |e⟩). The TLSs representing the solid matrix, on the other hand, correspond to the double-well potential states. This standard model is depicted schematically in Figure 1. The two zeroth-order states of a TLS localized in the left well |L⟩ and the right well |R⟩ of the potential are separated by an energy barrier justifiably assumed to be infinite, at low temperatures. The Hamiltonian for a TLS can be completely specified by two parameters: A j, the energy asymmetry between the localized
states and \( M_j \), the tunneling matrix element that couples them. The transition frequency of the chromophore depends upon the instantaneous states of the TLSs,\(^{33} \) and thus we can introduce a time-dependent stochastic occupation variable \( \xi_j \) which is set to 0 (1) if the \( j \)th TLS is in its ground (excited) state. With the stochastic sudden jump model, which is among the most popular models employed to study absorption line shape of a chromophore embedded in glassy systems,\(^{33,35–37} \) we can write the renormalized transition frequency of the chromophore as \( \omega_{\text{eg}} = \omega_0 + \sum_j v_j \xi_j \), where \( \omega_0 \) is the unperturbed chromophore transition frequency and \( v_j \) is the perturbation that the \( j \)th TLS in its excited state induces to the chromophore transition frequency. Statistical properties of \( \xi_j \) are determined by the relaxation rate \( K_j = k_j^u + k_j^d \) where \( k_j^u \) (\( k_j^d \)) is the upward (downward) rate. Assuming the relaxation to be dominated by phonon-assisted tunneling, we can write\(^{33} \):

\[
\begin{align*}
k_j^u &= C\epsilon_j M_j^2 \frac{\exp(-\epsilon_j/k_BT)}{1 - \exp(-\epsilon_j/k_BT)} \quad (1a) \\
k_j^d &= C\epsilon_j M_j^2 \frac{1}{1 - \exp(-\epsilon_j/k_BT)} \quad (1b)
\end{align*}
\]

where \( C \) is the TLS-phonon coupling constant, \( T \) is temperature, and \( \epsilon_j = \sqrt{A_j^2 + M_j^2} \) is the energy separation of the eigenstates of the \( j \)th TLS. In thermal equilibrium, the probability of finding the \( j \)th TLS in state \( k \) (\( k = 0, 1 \)) is \( P_j^k \), which is given as:

\[
P_j^k = p_j \delta_{k,1} + (1 - p_j) \delta_{k,0}
\]

where \( p_j = [\exp(\epsilon_j/k_BT) + 1]^{-1} \) is the probability that the \( j \)th TLS is excited, and \( k_B \) is Boltzmann constant.

The approach proposed by Reilly and Skinner is adopted to derive the time-domain response function \( J(t) \) from the product of individual response functions \( J_j(t) \)\(^{6,34} \) and the linear absorption line-shape function \( \sigma(\omega) \) is then given by the Fourier transform of the response function \( J(t) \). The interaction between the chromophore and the \( j \)th TLS has the form

\[
v_j = B f_j \frac{B(n_j \cdot r - 3(n_j \cdot \hat{r}_j)(n \cdot \hat{r}_j))}{r_j^3}
\]

where \( f_j \) is a dimensionless angular factor calculated assuming dipolar coupling between the chromophore and the \( j \)th TLS, whose positions (dipole directions) are \( r_j \) and \( n \) and \( n_j \), respectively: \( r_j = |r_j - r| \) and \( \hat{r}_j = (r_j - r)/r \) are the distance and the direction between them, respectively; \( B = A_j C'/\epsilon_j \) with \( C' \) as the TLS-chromophore coupling constant. The approximation of dipole-dipole coupling between the chromophore and the TLSs is commonly employed in most of the studies of such systems and is well supported by spectroscopic measurements. Such nonresonant coupling between the chromophore and TLSs is thought to be mediated by a strain field resulting from conformational state transitions,\(^{36,38,39} \) thereby implying that a TLS can behave like an ‘elastic dipole moment’.\(^{22,40} \)

We first describe the numerical approach, in which a simple cubic lattice of TLSs with one chromophore at a substitutional site is considered. The dipole directions are randomly distributed, with the azimuthal angle \( \phi \) in the \( xy \) plane and the polar angle \( \theta \) defined in the standard way from the and \( x \) and \( z \) axis, respectively such that \(-1 \leq \cos \theta < 1 \) and \(-\pi \leq \phi < \pi \). The simulation volume is divided into 1331(11 × 11 × 11) unit cells each of a side length of \( a_0 \). The central unit cell is occupied by the sole chromophore, while other cells contain one TLS in each. As shown in Figure 2, the precise position of the chromophore or a TLS is assigned to a randomly selected point inside an even smaller cubic sub-unit of length \( w \).

Figure 1: Schematic of a chromophore modeled as electronic two-level system that is surrounded by a host matrix, which itself is treated as a collection of TLSs effectively modeling the double-well potential states.

Figure 2: The simple cubic lattice structure in which each of the unit cell of length \( a_0 \) is occupied by a TLS except for the central unit cell that is occupied by the chromophore. The precise positions of TLSs/chromophore are ascribed randomly within a smaller cubic sub-unit of length \( w \).
The numerical simulations with the aforementioned parameters correspond to the high-temperature and static regime, which allows us to set, while maintaining accuracy, $p_j = 0.5$ and $K_j = 0$, that yields $J_j(t) = (1 + e^{-iv_jt})/2$, in full accordance with the well-known expression for the static limit.\(^6\)\(^,\)\(^3\)\(^4\) Furthermore, in the presence of disorder, the value $\bar{J}(t) = \langle J(t) \rangle$ that describes the line shape, with angular brackets denoting average over the disorder, as well as the dipole directions, can be represented in a form

$$\bar{J}(t) = \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{n} \prod_j J_j(t; \mathbf{r}, \mathbf{n})$$

$$= \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{n} \bar{J}(t; \mathbf{r}, \mathbf{n}) \quad (4)$$

$$\bar{J}_j(t; \mathbf{r}, \mathbf{n}) = \int d\mathbf{r}_j \rho_j(\mathbf{r}_j) \int d\mathbf{n}_j \frac{1 + e^{-iv_jt}}{2} \quad (5)$$

where $\rho(\mathbf{r})$ and $\rho_j(\mathbf{r}_j)$ are the distributions functions of the chromophore and TLSs positions, respectively, with the homogeneous distributions over the dipole directions, as assumed in our numerical simulations. The integration measures in Eqs. (4) and (5) are normalized

$$\int d\mathbf{n} = \int d\mathbf{n}_j = \int d\mathbf{r}_j \rho_j(\mathbf{r}_j) = \int d\mathbf{r} \rho(\mathbf{r}) = 1 \quad (6)$$

In order to explicitly calculate the integral over $\mathbf{n}_j$ in eq (5), we first represent $\mathbf{v}$ as:

$$v = \frac{B}{\bar{r}_j} [\mathbf{n} - 3(\mathbf{n} \cdot \mathbf{r}_j) \mathbf{r}_j] \cdot \mathbf{n}_j. \quad (7)$$

Using $|\mathbf{n} - 3(\mathbf{n} \cdot \mathbf{r}_j) \mathbf{r}_j| = \sqrt{1 + 3(\mathbf{n} \cdot \mathbf{r}_j)^2}$, we obtain

$$\int d\mathbf{n}_j e^{-iv\mathbf{r}_j} = \frac{1}{4\pi} 2\pi \int_0^\theta \sin \theta d\theta$$

$$= \exp \left(i \frac{Bt}{\bar{r}_j} \sqrt{1 + 3(\mathbf{n} \cdot \mathbf{r}_j)^2} \cos \theta \right)$$

$$= \frac{\sin \left(\frac{\Omega(\mathbf{r}_j)t}{\bar{r}_j} \right)}{\Omega(\mathbf{r}_j)t}, \quad (8)$$

where we have introduced

$$\Omega(\mathbf{r}_j) = \frac{B\sqrt{1 + 3(\mathbf{n} \cdot \mathbf{r}_j)^2}}{\bar{r}_j}. \quad (9)$$

Substituting eq (8) into eq (5) we arrive at

$$\bar{J}_j(t; \mathbf{r}, \mathbf{n}) = 1 - p_j \int d\mathbf{r}_j \rho_j(\mathbf{r}_j) h(\mathbf{r}_j, t), \quad (10)$$

by introducing

$$h(\mathbf{r}_j, t) = 1 - \frac{\sin \left(\frac{\Omega(\mathbf{r}_j)t}{\bar{r}_j} \right)}{\Omega(\mathbf{r}_j)t} = 1 - x \sin \frac{1}{x}, \quad (11)$$

and keeping the arbitrarily valued $p_j$ rather than setting it to 0.5. Note that the function $h(\mathbf{r}_j, t)$ is continuous (although not smooth) at $\mathbf{r}_j = 0$, and $h(\mathbf{r}_j, t) \sim r_j^{-6}$ for large values of $r_j$.

If the distributions $\rho_j(\mathbf{r}_j)$ have the property of $\Omega(\mathbf{r}_j)t \ll 1$ for relevant times $t$, we write $h(x) \sim 1/(6x)^2$ and obtain

$$\bar{J}_j(t; \mathbf{r}, \mathbf{n}) = 1 - g_j(t; \mathbf{r}, \mathbf{n}) \approx \exp(-g_j(t; \mathbf{r}, \mathbf{n})), \quad (12)$$

with

$$g_j(t; \mathbf{r}, \mathbf{n}) = -\sigma_j(\mathbf{r}, \mathbf{n}) \frac{t^2}{2}, \quad (13)$$

and

$$\sigma_j(\mathbf{r}, \mathbf{n}) = \sum_{ab=1}^3 \alpha_j^{ab}(\mathbf{r}) n_a n_b, \quad (14)$$

where $a$ and $b$ label the cartesian coordinates, and

$$\alpha_j^{ab}(\mathbf{r}) = 2p_j B^2 \int d\mathbf{r}_j \rho_j(\mathbf{r}_j) \frac{\delta^{ab} + 3n_a n_b}{6n^2}. \quad (15)$$

If the approximation made to derive eq (12) is valid for all TLSs, we have

$$\bar{J}(t; \mathbf{r}, \mathbf{n}) = \exp \left(-\frac{t^2}{2} \sum_{ab} \alpha_j^{ab}(\mathbf{r}) n_a n_b \right), \quad (16)$$

with

$$\alpha_j^{ab}(\mathbf{r}) = \sum_j \alpha_j^{ab}(\mathbf{r}), \quad (17)$$

which means that under the above assumption and if the position and dipole direction of the chromophore is fixed, the absorption line, even in the presence of positional and dipole-orientational disorder of the TLSs, has a Gaussian shape. Disorder in the chromophore position, as well as random distribution of its dipole orientation will create deviations from the Gaussian shape.

There is still a situation when random orientations of the chromophore dipole do not cause the absorption line...
to deviate from Gaussian shape, namely when the chromophore is fixed at the center of its cell \( r = 0 \), or equivalently, \( \rho(\mathbf{r}) = \delta(\mathbf{r}) \), whereas the distribution functions of the TLS positions preserve the symmetry of the cubic lattice (note that disorder considered in this work obviously satisfies the above property). In this case we deal with \( \alpha^{ab}(0) \), as defined for the general case by eq (17), that can be viewed as a symmetric rank 2 tensor, invariant under the rotations that preserve the cubic lattice. A tensor that satisfies the above property is known to be, up to a scalar multiplicative factor, the Kronecker delta \( \delta^{ab} \), which implies

\[
\alpha^{ab}(0) = \frac{1}{3} \text{Tr}[\alpha(0)] \delta^{ab}.
\]

Taking the trace in eq (15), and making use of Eqs. (17) and (18) we obtain

\[
\bar{J}(t; 0, \mathbf{n}) = \exp \left( -\frac{\sigma t^2}{2} \right),
\]

with

\[
\sigma = \sum_{j} dr_j \rho_j(r_j) \frac{B^2}{3|r_j|^6},
\]

which yields the Gaussian line shape independent of the chromophore dipole orientation \( \mathbf{n} \), and therefore, invariant upon any averaging over the latter.

Figure 3 shows the frequency-domain absorption line shapes calculated numerically for \( \alpha = 0.0, 0.4, 0.8 
\text{and} 1.0 \), as well as their fitting by Gaussian (G) and Lorentzian (L) functions with the same FWHM and their linear combinations \( \alpha L + (1 - \alpha) G \). For the perfectly crystalline environment (\( \alpha = 0.0 \)), as seen in Figure 3(a), the line shape is of Gaussian profile, in agreement with our theoretical prediction and previous results.\(^{27,42}\) Furthermore, we have verified that the value of \( \sigma = 1.956 \times 10^{-5} \text{ps}^{-2} \) obtained by applying eq 20 to our model, yields a satisfactory fit to the averaged response function \( \bar{J}(t) \).

With an increase in \( \alpha \), a change in line shape as well as an increase in the full width at half-maximum (FWHM) can be observed in Figures 3(b)-(d). As the finite FWHM results from the chromophore-TLS interactions, it is apparent that the stronger the interaction, the greater its influence on the broadening. This implies that as \( \alpha \) increases, the average chromophore-TLS separation will tend to decrease thereby leading to an increase in FWHM. Evident from the Figure 3(d), for \( \alpha = 1.0 \) which represents the glassy environment, the line shape is fitted well by a Lorentzian. For this case, as the TLSs are completely disordered in both spatially and sterically sense within their residence cells. Therefore, after averaging over a large number of initial conditions, the distribution of the TLSs around the chromophore should be statistically isotropic, and one can observe homogeneous broadening which can induce the Lorentzian profile. In the intermediate regime, the degree of spatial disorder increases gradually thereby leading to a gradual change from inhomogeneous to homogeneous influence of the environment, and thus the absorption line shape can be approximately fitted by a superposition of the individual G and L components, \( \alpha L + (1 - \alpha) G \) [see Figure 3 (b) to (c)]. In essence, we observe a smooth transition of the line shape from Gaussian to Lorentzian with an increase in spatial disorder of the host medium to the chromophore.

To gain further insights into disorder-induced changes in the line shapes, we examined the binning-statistics of chromophore-TLS pairwise distances, especially in the regime of pairwise distances equal to or less than \( a_0 \). Whereas for \( \alpha = 0 \) the minimum separation is equal to \( a_0 \), that for \( \alpha = 1 \) can even be vanishingly small. The presence of TLSs in such close proximity of the chromophore implies a much stronger perturbation to the transition frequency of the chromophore as compared that due to the relatively distant TLSs. We carried out constrained simulations such that the chromophore and its 6 nearest neighbors are fixed to the corresponding lattice points, while allowing their transition dipoles to be randomly oriented. The rest of the TLSs are subjected to the condition of \( \alpha = 1 \), and thus, the smallest possible separation is \( \sqrt{2} a_0 \) (see inset in Figure 4). The resulting absorption line shape depicted in Figure 4 is found to be Gaussian. This implies that the aforementioned transition from Gaussian to Lorentzian line shape when \( \alpha \) is changed from 0 to 1 can be ascribed to the strong
effect exerted by the TLSs in the immediate vicinity of
the chromophore. This argument is further supported by
Figure 5 in which the absorption line shapes for
the chromophore. This argument is further supported by
Figure 4: The absorption line shape and its fitting by a Gaus-
ian (G) and Lorentzian (L) functions when $\alpha = 1.0$, and the
chromophore and its 6 nearest neighbor TLSs are fixed at
the centers of their unit cells. The inset shows the pairwise
distance distribution.

Figure 5: For $\alpha=1.0$, the unrenormalized absorption line
shapes for different lattice sizes of $3\times3\times3$, $5\times5\times5$, $7\times7\times7$,
$9\times9\times9$ and $11\times11\times11$. The inset shows the correspond-
ing maximum peak intensities (crosses) and FWHM (hollow
stars).

with the dimensionless factor

$$
\zeta = \frac{4\pi}{3} \int_0^1 d\tau \sqrt{1 + 3\tau^2} \int_0^\infty dx \left( 1 - x \sin \frac{1}{x} \right) 
= \frac{\pi^2}{3} \int_0^1 d\tau \sqrt{1 + 3\tau^2}.
$$

Finally we arrive at

$$
\bar{J}(t) = (\bar{J}(t))^N = e^{-\gamma t}, \gamma = \zeta p B n,
$$

where $n = N/V$ is the TLS concentration, which imme-
diately leads to the Lorentzian line shape. Note that
$Bn$ has a meaning of a typical dipole coupling, i.e.,
the value of the dipole coupling at the average distance
$\bar{a}_0 = (n)^{-1/3}$ between the chromophore and a TLS, and
$\zeta$ is a dimensionless factor of the order of 1 that reflects
a particular model of disorder.

We are now in a position to consider the model of dis-
order that has been used in our numerical simulations,
and thus introduce the line shape function $g(t)$ so that

$$
\bar{J}(t) = e^{-g(t)}.
$$

The short-time asymptotic corresponding to $\gamma t =
Bt/\bar{a}_0^3 \ll 1$ can be computed by noting that the contribu-
tion to $\bar{J}(t)$ in this case is dominated by configurations
with $|r_j - r| \ll \bar{a}_0$, which is possible only if both $r_j$ and
$r$ are located in the close vicinity of the chromophore
cell border. The major contribution from each face thus
comes from the coupling between the chromophore and
the TLS that resides in the cell on the opposite side of the
face. The line shape function can then be obtained by
performing the integration in this restricted regime. On
the other hand, for calculating the long-time asymptotic,
we employ the fact that each of the cells containing a
TLS contributes to $J(t)$ and thus integration can be performed over the whole Euclidian space $\mathbb{R}^3$. Thus, for our $\alpha = 1$ model of disorder we finally obtain:

\[
g(t) = \zeta_c (\gamma_0 t)^{3/4}, \text{ for } \gamma_0 t \ll 1, \\
g(t) = \zeta_L (\gamma_0 t), \quad \text{for } \gamma_0 t \gg 1.
\] (26)

where

\[
\zeta_L = -\frac{4\pi}{3} \int_0^1 d\tau \sqrt{1 + 3\tau^2} \\
\times \int_0^\infty dx \ln \left( 1 - p + px \sin \frac{1}{x} \right), 
\] (27)

and

\[
\zeta_s = 4\pi p \int_0^1 d\tau (1 + 3\tau^2)^{2/3} \\
\times \int_0^\infty dx x^{1/3} \left( 1 - x \sin \left( \frac{1}{x} \right) \right).
\] (28)

For the model used in this work, we have evaluated eq (27) and eq (28), and the obtained value of $\zeta_s \gamma_0^{3/4} = 2.26 \times 10^{-3}$ ps$^{-3/4}$ is found yield a satisfactory fit to the $\bar{J}(t)$, in the short-time limit. At long times, on the other hand, the calculated value of $\zeta \gamma_0 = 7.36 \times 10^{-3}$ ps$^{-1}$ is roughly two times smaller than that obtained by fitting $\bar{J}(t)$ in the long-time limit.

**IV. CONCLUSIONS**

In summary, we have systematically investigated the influence on the absorption line shape of a chromophore of the disorder in the solid matrix in which it is embedded. In the absence of disorder, the absorption line shape is revealed to be of inhomogeneously broadened Gaussian form, whereas in a glassy environment, it is found to be of homogeneously broadened Lorentzian profile. We have demonstrated both theoretically and numerically that the origin of the Lorentzian line shape in glassy systems lies in enhanced chromophore-TLS coupling due to close proximity. An interesting parallel can be drawn from our earlier studies of finite sized single-domain micromagnetic particle arrays, in which disorder was found to lead to an increase in the coercivity. Our results thus emphasize on a broader perspective, that the disorder in the environment of a system of interest can significantly impact its macroscopic observables and provide insights in elucidating the nature of immediate microscopic environment of a chromophore from studying its absorption line shapes.

**Acknowledgements**

Support by the Singapore National Research Foundation through the Competitive Research Programme (CRP) under Project No. NRF-CRP5-2009-04 is gratefully acknowledged. This work is also supported in part by the US National Science Foundation under Grant No. CHE-1111350.