Stochastic simulation of chemical exchange in two dimensional infrared spectroscopy

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The stochastic Liouville equations are employed to investigate the combined signatures of chemical exchange (two-state jump) and spectral diffusion (coupling to an overdamped Brownian oscillator) in the coherent response of an anharmonic vibration to three femtosecond infrared pulses. Simulations reproduce the main features recently observed in the OD stretch of phenol in benzene. © 2006 American Institute of Physics. [DOI: 10.1063/1.2205367]

I. INTRODUCTION

Chemical exchange processes cause time-dependent spectral jumps between stable configurations of molecular complexes. These are accompanied by coherence transfer which has distinct spectroscopic signatures. NMR line shapes are commonly analyzed in terms of chemical exchange on the millisecond time scale.1–4 As the exchange rate is increased the line shapes first broaden and become narrower for faster rates. This motional narrowing reflects an averaging of fluctuations. Recent experiments demonstrated that two dimensional infrared (2D IR) line shapes can probe the picosecond dynamics of chemical exchange by observing coherence transfer in molecular vibrations.5,6

The 2D IR spectrum is obtained using three pulses (Fig. 1).6–10 The first pulse creates a vibrational coherence, whose evolution (free induction decay) during the first interval \( t_1 \) is related to the absorption line shape by a Fourier transform. During the second \( t_2 \) interval (population time) the vibrational frequency changes stochastically by complexation with the solvent. Finally vibrational coherence is again created by the third pulse and the signal is heterodyne detected after the third interval \( t_3 \). The correlations of the line shapes in the first and the third intervals provide information on chemical exchange processes which take place during the second interval.

Due to the spatial coherence in the optical response the signal is generated along phase-matching directions which correspond to the various Liouville space pathways of the vibrational density matrix. Certain combinations of these pathways11,12 give absorptive 2D line shapes which are more clearly resolved. Chemical exchange dynamics is clearly seen by a two dimensional Fourier transform of the signals with respect to \( t_1 \) and \( t_3 \) and plotting them versus the conjugate frequencies \( \omega_1 \) and \( \omega_3 \) for various values of \( t_2 \).

A recent experiment6 looked at the OD stretching mode of phenol in benzene whose frequency fluctuates between 2665 cm\(^{-1}\) (free) and 2631 cm\(^{-1}\) (complexed). The 2D line shapes monitored the dynamics of complex formation and dissociation.5 For short delays \( t_2 \approx 100 \text{ fs} \) two diagonal peaks broadened by spectral diffusion were observed at the linear-absorption frequencies for short delays. For longer times \( t_2 \approx 10 \text{ ps} \) additional off-diagonal cross peaks were induced by chemical exchange. Similar effects were seen in the overtone region. The rate constants for complexation were directly measured from the peak kinetics.

Similar hydrogen-bonding dynamics was reported for the CN stretch of acetonitrile in methanol.7 The relative intensity of the two peaks attributed to free and hydrogen-bonded CN shows strong temperature dependence. The reaction coordinate profile in both ground and excited vibrational states was found to be very similar.

The weak variation of the chemical-exchange rates with changes in the vibrational state justifies the application of stochastic chemical exchange models13 for vibration frequency fluctuations. The stochastic Liouville equations (SLEs) describe the dynamics of a quantum system (vibrational coherence) perturbed by a stochastic process (chemical exchange and spectral diffusion) described by a Markovian master equation. This formalism was recently applied to model the signatures of conformational fluctuations in trialanine in water17 using a Brownian oscillator coordinate model of fluctuations. The SLEs were also used to compare the Brownian oscillator and the four-state-jump model of hydrogen bonding fluctuation on the photon echo of the OH stretch of HOD in DOD.18 In the present paper we use the SLE to simulate the effects of chemical exchange14–16 and spectral diffusion in 2D line shapes of an anharmonic vibration. Our simulations reproduce all the effects observed recently5 in the study of complexation dynamics of the OD stretch.

In Sec. II we introduce our model which consists of an anharmonic vibration subjected to fluctuations due to a two-state chemical exchange and a Brownian oscillator coordinate. Expressions for the 2D IR signals are given in Sec. III.
The stochastic Liouville equation for the two-state-jump (TSJ) model is introduced in Sec. IV. In the TSJ model of Kubo and Anderson et al. bath-assisted (incoherent) chemical exchange is described by kinetic equations. The model shows several distinct dynamical regimes depending on the motional narrowing parameter (ratio of the frequency shift and relaxation rate) and the 2D IR signals are calculated for the limiting cases of slow and fast fluctuations and for short and long-time delays between pulses. Spectral diffusion is incorporated by coupling to an overdamped Brownian oscillator coordinate, whose coupling to the vibration through the parameters \( \Omega_2 \) and \( \Delta_2 \) causes spectral diffusion. \( \Omega_2 \) and \( \Delta_2 \) allow the spectral diffusion to have a different magnitude in the two spin states.

We shall divide the Hamiltonian [Eq. (1)] into three parts \( H = H_S + H_Q + H_{QS} \), where \( H_S \) includes the first two (spin + vibration) terms in Eq. (2) which do not depend on \( Q \), and \( H_Q \) and \( H_{QS} \) include the third and fourth terms in Eq. (2), respectively. The dipole interaction with the electric field \( E(t) \) is

\[
H_{\text{int}} = -\mu E(t)(B^3 + B^2).
\]

Three vibrational levels (Fig. 1) are accessible in a three-pulse experiment: the ground state \( |g\rangle \), the first excited \( |e\rangle \) \( = B^\dag |g\rangle \), and the doubly excited \( |f\rangle = (1/\sqrt{2})B^\dag B^\dag |g\rangle \) state. Their energies are \( 0, \Omega, \) and \( \Omega + \Delta \), respectively. The corresponding nine-component Liouville space basis set for the density matrix is denoted \( |v v'\rangle = |v\rangle\langle v'| \); \( v = e, f, g \). The dipole moment matrix elements are \( \mu_{eg} = \mu \) and \( \mu_{ef} = \sqrt{2}\mu \).

### III. THE THIRD ORDER RESPONSE AND 2D SIGNALS

We consider an impulsive four wave mixing process whereby the electric field [Eq. (1)] consists of three impulsive optical pulses with intervals \( t_1, t_2, \) and calculate the response at \( t_3 \) (see Fig. 1). Interactions with the field can create or annihilate one vibrational quantum at a time [Eq. (3)]. The equilibrium distribution is

\[
|\rho(0)\rangle_{\mathcal{H}} = |\rho(0)\rangle_{\mathcal{S}}|0\rangle_{Q}\langle gg|.
\]

where \( |\rho(0)\rangle_{\mathcal{S}} \) represents the spin state and \( |0\rangle_{Q} \) [Eq. (3)] represents the Brownian coordinate. The space \( \mathcal{H} \) is a direct product of the vibrational, spin, and the Brownian oscillator space.

The polarization generated in this experiment is described by the third order response function,

\[
S^{(3)}(t_1, t_2, t_3) = \left( \frac{i}{\hbar} \right)^3 \langle \theta(t_1) \theta(t_2) \theta(t_3) \rangle
\]

\[
\times \langle \langle j_l \mu(\xi) \hat{G}(t_3) \mu(\xi) \hat{G}(t_2) \mu(\xi) \hat{G}(t_1) \mu(\xi)|\rho(0)\rangle \rangle_{\mathcal{H}},
\]

where \( \mu(\xi) = \mu[B + B^\dag, \xi] \) (\( \xi \) is an arbitrary Hilbert space operator). Summing over final states is represented by \( \langle \langle j_l \rangle \rangle_{\mathcal{H}} \), where \( \langle I \rangle_{\mathcal{S}} = \langle I \rangle_{\mathcal{S}}|0\rangle_{Q} \langle 0|_{Q} \), and the trace is over the vibrational degrees of freedom \( \text{Tr} = \langle \langle gg \rangle + \langle ee \rangle \rangle + \langle \langle ff \rangle \rangle \). The time evolution between pulses is described by

\[
\Omega = \Omega_0 + \Omega_1 \sigma_z + \Omega_2 Q + \Omega_3 \sigma_z Q,
\]

\[
\Delta = \Delta_0 + \Delta_1 \sigma_z + \Delta_2 Q + \Delta_3 \sigma_z Q.
\]
Green’s function $G(t)$ of the SLE in the space $H$.

The vibrational state cannot change between pulses, so that the Green’s functions are block diagonal and the response functions can be separated into six contributions from different Liouville space pathways.

$$R_i(t_3,t_2,t_1) = \langle |G_{e_g,e_g}(t_3)G_{e,e,e}(t_2)G_{e_g,e_g}(t_1)|\rho(0)\rangle_\text{QS},$$

$$R_{ii}(t_3,t_2,t_1) = \langle |G_{e_g,e_g}(t_3)G_{e,e,e}(t_2)G_{e_g,e_g}(t_1)|\rho(0)\rangle_\text{QS},$$

$$R_{ii}(t_3,t_2,t_1) = \langle |G_{e_g,e_g}(t_3)G_{e,e,e}(t_2)G_{e_g,e_g}(t_1)|\rho(0)\rangle_\text{QS},$$

$$R_{ii}(t_3,t_2,t_1) = \langle |G_{e_g,e_g}(t_3)G_{e_e,e_e}(t_2)G_{e_g,e_g}(t_1)|\rho(0)\rangle_\text{QS},$$

$$R_{ii}(t_3,t_2,t_1) = \langle |G_{f,e,f}(t_3)G_{e,e,e}(t_2)G_{f,e,f}(t_1)|\rho(0)\rangle_\text{QS},$$

$$R_{ii}(t_3,t_2,t_1) = \langle |G_{f,e,f}(t_3)G_{e,e,e}(t_2)G_{f,e,f}(t_1)|\rho(0)\rangle_\text{QS},$$

These may be graphically represented by the Feynman diagrams given in Fig. 1. For the stochastic models of frequency fluctuations considered here we have $R_{ii}=R_{ii}$ and $R_{ii}=R_{ii}$ so that we only need to consider four independent pathways.

Green’s function matrix elements $G_{f,e,f}(t_3)$, etc., are now matrices in the joint spin and Brownian oscillator space.

We shall display the signal using the mixed time-frequency representation,

$$R_{ii}(t_3,t_2,t_1) = \int_0^\infty \int_0^\infty \exp(i\omega_1 t_1 + i\omega_2 t_2) R_{ii}(t_3,t_2,t_1) dt_1 dt_2,$$

Eq. (6) then reads

$$R_i(\omega_3,\omega_2,\omega_1) = \langle |G_{e_g,e_g}(\omega_3)G_{e,e,e}(t_2)G_{e_g,e_g}(\omega_1)|\rho(0)\rangle_\text{QS},$$

and similarly for other pathways, where

$$G(\omega) = \int_0^\infty G(t) e^{i\omega t} dt$$

is the Green’s function in the frequency domain.

We consider the coherent nonlinear signals generated in the $k_i=-k_1+k_2+k_3$ and $k_{ii}=k_1-k_2+k_3$ phase-matching directions. Invoking the rotating wave approximation the $k_i$ (photon echo) signal is

$$S_i(\omega_3,\omega_2,\omega_1) = \left(\frac{i}{\hbar}\right)^3 \left\{\mu_{eg}^4[R_{ii}(\omega_3,\omega_2,\omega_1) + R_{ii}(\omega_3,\omega_2,\omega_1)] \right.$$  

$$+ \mu_{eg}^2 \mu_{ee}^2 R_{ii}(\omega_3,\omega_2,\omega_1)\},$$

and for the $k_{ii}$ signal we have

$$S_{ii}(\omega_3,\omega_2,\omega_1) = \left(\frac{i}{\hbar}\right)^3 \left\{\mu_{eg}^4[R_{ii}(\omega_3,\omega_2,\omega_1) + R_{ii}(\omega_3,\omega_2,\omega_1)] \right.$$  

$$+ \mu_{eg}^2 \mu_{ee}^2 R_{ii}(\omega_3,\omega_2,\omega_1)\}. $$

We shall also display the following combination of the two signals which shows absorptive peaks:11,12

$$S_A(\omega_3,\omega_2,\omega_1) = -\text{Im}[S_i(\omega_3,\omega_2, -\omega_1) + S_{ii}(\omega_3,\omega_2,\omega_1)].$$

When during the interval $t_3$ the system has no memory about its state in $t_1$, the third order response functions are factorized into products of the linear response functions $K(t)$,

$$R_{ii}(t_3,t_2,t_1) = K(t_3)K(t_1),$$

$$R_{ii}(t_3,t_2,t_1) = K(t_3)K'(t_1),$$

$$R_{ii}(\omega_3,\omega_2,\omega_1) = K(\omega_3)K'(- \omega_1).$$

For the stochastic model $R_i$ and $R_{ii}$ are factorized in the same way. Neglecting the overtone contributions $R_{ii}$ and $R_{ii}$ it follows that the $S_A$ signal is given by the product of the linear absorption line shapes $W_A$ [Eq. (A1)]

$$hS_A(\omega_3,\omega_1) = W_A(\omega_1)W_A(\omega_3).$$

### IV. STOCHASTIC LIOUVILLE EQUATIONS FOR THE TWO-STATE-JUMP MODEL

The stochastic Liouville equations13,26 are constructed by combining the Liouville equation, the dynamics of a quantum coherence, and a Markovian master equation describing a stochastic process,

$$\frac{dp}{dt} = \hat{L} \rho(t) = -\frac{i}{\hbar} [H, \rho(t)] + \hat{L} \rho(t).$$

Stochastic models are closely related to microscopic models of bath variables.8,23 Their optical response corresponds to the real part of the microscopic line broadening function8 [see also Eq. (C6)]. Due to the fluctuation-dissipation theorem, the real part dominates at high temperatures, where the stochastic model becomes exact. (Limitations are discussed below.)

We first focus on the TSJ model4,19,20 by neglecting the spectral diffusion (setting $\Delta_2$, $\Delta_3$, $\Omega_2$, $\Omega_3=0$). The total density matrix $\rho$ has 18 components $|\nu\nu's'>)$ given by the direct product of nine Liouville space states $|\nu\nu'>)$ and the two spin states, $s=u,d$. The Liouville operator $\hat{L}$ is diagonal in the vibrational Liouville space variables, and is thus given by nine $2 \times 2$ diagonal blocks in spin space,

$$[\hat{L}]_{\nu\nu's'u',s'>} = \delta_{\nu\nu} \delta_{\nu's'} [\hat{L}_S]_{s's'} + \delta_{\nu'1} \delta_{\nu's'} [\hat{L}_3]_{\nu'1\nu's'},$$

where $\hat{L}_S$ describes the two-state-jump kinetics and $\hat{L}_3$ represents the coherent vibrational evolution that depends parametrically on the spin state.

Chemical exchange is described by the rate matrix $\hat{L}_3$ for the spin,

$$[\hat{L}_3] = \begin{pmatrix} -k_d & k_u \\ k_d & -k_u \end{pmatrix}. $$

The up (down) jump rates $k_u(k_d)$ are connected by the detailed-balance relation $k_u/k_d = \exp(\beta(\varepsilon_d - \varepsilon_u))$, where $\varepsilon_d - \varepsilon_u$ is the energy difference between the $u$ and $d$ states.
The equilibrium density matrix is

$$|\rho(0)\rangle = |gg\rangle |\rho(0)\rangle_s, \quad |\rho(0)\rangle_s = \frac{1}{k_u + k_d} \langle k_u |.$$  \hspace{1cm} (16)

We next turn to the coherent part \(\hat{L}_s=-(i\hbar)[H_s,\ldots].\) For the \(|gg\rangle, |ee\rangle,\) and \(|ff\rangle\) blocks, \([\hat{L}_s]_{gg,gg} = [\hat{L}_s]_{ee,ee} = 0.\) The other blocks of \(L_s\) are

\[
\begin{align*}
[\hat{L}_s]_{gg,gg} &= \begin{pmatrix} -i(\Omega_0 + \Omega_1) & 0 \\ 0 & -i(\Omega_0 - \Omega_1) \end{pmatrix}, \\
[\hat{L}_s]_{gf,fg} &= \begin{pmatrix} -i(\Omega_0 + \Delta_0) - i(\Omega_1 + \Delta_1) & 0 \\ 0 & -i(\Omega_0 - \Delta_0) + i(\Omega_1 + \Delta_1) \end{pmatrix}, \\
[\hat{L}_s]_{gg,fe} &= \begin{pmatrix} -i(2\Omega_0 + \Delta_0) - i(2\Omega_1 + \Delta_1) & 0 \\ 0 & -i(2\Omega_0 - \Delta_0) + i(2\Omega_1 + \Delta_1) \end{pmatrix}.
\end{align*}
\]

The remaining blocks are obtained by taking complex conjugates \([\hat{L}_s]_{gg',gg'} = [\hat{L}_s]_{ee',ee'}\).

These matrices may be represented in a compact form by defining the energy \(\hbar \epsilon_0\) and splitting \(\hbar \epsilon_1\) parameters \(\epsilon_0^{(e)} = 0, \epsilon_0^{(f)} = 2\Omega_0 + \Delta_0, \epsilon_1^{(e)} = \Omega_1,\) and \(\epsilon_1^{(f)} = 2\Omega_1 + \Delta_1.\) We then have

\[
[\hat{L}_s]_{gg',gg'} = \delta_{gg'} \delta_{gg'}^{\prime}
\]

\[
\begin{pmatrix} -i(\epsilon_0^{(e)} - \epsilon_0^{(f)}) - i(\epsilon_1^{(e)} - \epsilon_1^{(f)}) & 0 \\ 0 & -i(\epsilon_0^{(e)} - \epsilon_0^{(f)}) + i(\epsilon_1^{(e)} - \epsilon_1^{(f)}) \end{pmatrix}.
\]

The Green’s function solution of Eq. (13) is given by 2 \times 2 blocks for each vibrational state \(|\nu\nu'\rangle\) of the density matrix,

\[
[\mathcal{G}]_{\nu\nu',\nu\nu'}(t) = [\exp(\hat{L}_s)]_{\nu\nu',\nu\nu'} = \delta_{\nu\nu'} \delta_{\nu\nu'}^{\prime} \times \begin{pmatrix} \eta_1 & 0 \\ 0 & \eta_2 \end{pmatrix} \exp(\eta_1 t) \\
\left( \begin{pmatrix} \eta_1 & 0 \\ 0 & \eta_2 \end{pmatrix} - \begin{pmatrix} \eta_1 & 0 \\ 0 & \eta_2 \end{pmatrix} \hat{L}_{\nu\nu',\nu\nu'} \right) \exp(\eta_2 t),
\]

where \(\eta_j\) are the eigenvalues of each block of \(\hat{L}.\)

\[
\eta_1 = -\frac{k_d + k_u}{2} - i(\epsilon_0^{(e)} - \epsilon_0^{(f)})
\]

\[
+ \sqrt{\frac{(k_d + k_u)^2}{4} - (\epsilon_0^{(e)} - \epsilon_0^{(f)})^2 + i(\epsilon_1^{(e)} - \epsilon_1^{(f)})(k_d - k_u)}.
\]

\[
\eta_2 = -\frac{k_d + k_u}{2} - i(\epsilon_0^{(e)} - \epsilon_0^{(f)})
\]

\[
- \sqrt{\frac{(k_d + k_u)^2}{4} - (\epsilon_0^{(e)} - \epsilon_0^{(f)})^2 + i(\epsilon_1^{(e)} - \epsilon_1^{(f)})(k_d - k_u)}.
\]

For the \(gg, ee,\) and \(ff\) spaces \(\hat{L}_s=0,\) and Eq. (18) reads

\[
\begin{align*}
\[\mathcal{G}]_{gg,gg}(t) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \\
\[\mathcal{G}]_{ee,ee}(t) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \\
\[\mathcal{G}]_{ff,ff}(t) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.
\end{align*}
\]

\[
\begin{align*}
\[\mathcal{G}]_{gg,gg}(t) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \\
\[\mathcal{G}]_{ee,ee}(t) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \\
\[\mathcal{G}]_{ff,ff}(t) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.
\end{align*}
\]
The linear response is given in Appendix A. Closed expressions for the various pathways are given in Appendix B. Below we discuss the 2D signals for limiting cases.

Figures 2(a) and 2(b) show the 2D signals $S_4$ [Eq. (10)] in the slow bath limit $\Omega_1 \gg k$ ($k = k_d = k_u$) where no spin jumps occur during the $t_1$ and $t_3$ intervals. In all figures we shift frequencies by setting $\Omega_0 = 0$ and normalize the signal to have maximum absolute value of 1. For $k t_2 \ll 1$ no spin jumps occur during the $t_2$ interval and we only see four peaks [Fig. 2(a)], two diagonal at $\omega_1 = \omega_3 = \Omega_2 \pm \Omega_1$, and two overtones at $(\omega_1, \omega_3) = (\Omega_0 + \Omega_1, \Omega_0 + \Delta_0 + \Omega_1 + \Delta_1)$ and $(\Omega_0 - \Omega_1, \Omega_0 + \Delta_0 - \Omega_1 - \Delta_1)$. In the opposite $k t_2 \gg 1$ limit we see eight peaks [Fig. 2(b)]. The additional four cross peaks at $(\omega_1, \omega_3) = (\Omega_0 + \Delta_0, \Omega_0 - \Delta_0)$, $(\Omega_0 - \Delta_0, \Omega_0 + \Delta_0)$, $(\Omega_0 - \Omega_1, \Omega_0 + \Omega_1 + \Delta_0)$, and $(\Omega_0 + \Omega_1, \Omega_0 - \Omega_1 - \Delta_0)$ are induced by the spin jumps. Diagrams i, ii, iii, and iv in Fig. 1 describe the $g \rightarrow e$ peaks at $\omega_1, \omega_3 \sim \Omega$. Diagrams v and vi show the $e \rightarrow f$ peaks at $\omega_1 \sim \Omega + \Delta$.

Note that the relation [Eq. (B5)], similar to Eq. (12), is valid for individual peaks in the short time regime since peak shapes are not connected with any inhomogeneity which carries memory. However, Eq. (12) does not apply for the entire 2D line shape, since the memory of spin state erases the cross peaks. In contrast, for long $t_2$ [Fig. 2(b)] this memory is lost and Eq. (12) applies (apart from the the overtone contributions).

In Fig. 2(c) we display $S_1$ [Eq. (10)] in the fast $k_d, k_u \gg \Omega_1$ limit. We see a fundamental peak at $\omega_1 = \omega_3 = \Omega_0$ and an overtone at $\omega_1 = \Omega_1$ and $\omega_3 = \Omega_0 + \Delta_0$. Linear response in the fast regime shows one peak (motional narrowing\ref{19}). Any memory of the $t_1$ interval is lost in the $t_3$ interval and the factorization [Eq. (11)] holds resulting in Eq. (12) as observed in Fig. 2(c).

V. TWO-STATE JUMP WITH SPECTRAL DIFFUSION

Spectral diffusion is described by a dimensionless overdamped Brownian oscillator coordinate $Q$ [Eq. (1)] with unit variance whose dynamics is given by the Fokker-Planck operator,\ref{27}

$$L_Q = \Lambda \frac{\partial}{\partial Q} \left( Q + \frac{\partial}{\partial Q} \right),$$

where $\Lambda$ is the relaxation rate. For fast fluctuations $\Omega_2 / \Lambda \ll 1$, spectral diffusion may be accounted for by simply adding dephasing rates $\Omega_2^2 / \Lambda$ to the line shapes. However, the
complete solution of the Fokker-Planck equation is required
for arbitrary fluctuation time scales.

We define \( \epsilon_i^{(p)} = 0, \epsilon_i^{(q)} = \Omega_i, \) and \( \epsilon_i^{(r)} = 2\Omega_i + \Delta_i, \) and \( \epsilon_i^{(s)} = 0, \epsilon_i^{(t)} = \Omega_i, \) and \( \epsilon_i^{(u)} = 2\Omega_i + \Delta_i. \) The coupling of \( Q \) to the vibration is given by the Liouville operator

\[
\hat{L}_S^{eq} = \hat{L}_S + \hat{L}_Q + \hat{L}_{QS} + L_Q,
\]

where \( \hat{L}_S \) is given by Eq. (15), \( \hat{L}_Q \) by Eq. (17), \( \hat{L}_Q \) and \( \hat{L}_{QS} \) by Eqs. (21), and \( L_Q \) by Eq. (20).

The response function for the spectral diffusion model alone\(^{20}\) (neglecting the spin, setting \( \Omega_1 = 0, \Delta_1 = 0 \)) can be calculated using the second order cumulant expansion\(^{25}\) and is given in Appendix C.

We next turn to the third order response [Eq. (6)]. The equilibrium distribution is

\[
|\rho(0)\rangle_{QS} = |\rho(0)\rangle_{S} |\rho(0)\rangle_{Q},
\]

where \( |\rho(0)\rangle_{S} \) is given by Eq. (16) and \( |\rho(0)\rangle_{Q} \) by Eq. (D1) and the final averaging should run over all degrees of freedom.

\[
\langle \hat{d}_{QS} \rangle = \langle \hat{d}_{S} \rangle |\rho(0)\rangle_{Q}.
\]

The Green’s function matrix elements \( G_{ee,fg}(t_2) \) are now matrices in the joint spin and Brownian oscillator space,

\[
G(t_2) = (\hat{L}_Q \exp(\hat{L}_Q t_2))^{-1}.
\]

During \( t_2 \) the evolution is in the ee, gg, and ff spaces where \( \hat{L}_Q \exp(\hat{L}_Q t_2) \) and the Green’s function may be factorized as

\[
G_{ee,fg}(t_2) = G_{ee,gg}(t_2) \exp(\hat{L}_Q t_2) \exp(\hat{L}_Q t_2).
\]

The first factor is given by Eq. (19) and the second is the propagator of Fokker-Planck equation\(^{25}\) expanded in its eigenmodes [Eq. (D1)].

\[
[\exp(\hat{L}_Q t_2)]_{ab} = \delta_{ab} \exp(-\alpha t_2).
\]

For slow chemical exchange (compared to the spectral diffusion \( k_{sp}, k_d \ll \alpha, \lambda \)) the TSJ peaks are well resolved and their line shapes are determined by the spectral diffusion. Chemi-

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**FIG. 5.** (Color) 2D signals for \( S_1 \) generated along \( k_1 \) [Eq. (8)], and \( S_n \) generated along \( k_n \) [Eq. (9)]: (a) \( k_1 \) and \( \Lambda_2 = 0, \) (b) \( k_1 \) and \( \Lambda_2 = 0, \) (c) \( k_1 \) and \( \Lambda_2 = 5, \) and (d) \( k_1 \) and \( \Lambda_2 = 5. \) Other parameters same as in Fig. 4.

**FIG. 6.** (Color) 2D signal \( S_1 \) [Eq. (10)] with spectral diffusion and TSJ. Spectral diffusion linewidth is varied \( (\Delta_2 \neq 0). \) Slow spectral diffusion in ee state and fast diffusion in overtone ef: \( \Omega_2/\Omega_1 = 2, \) \( \Delta_2/\Omega_1 = 0.6, \) \( k_1 = k_2 = 0.002 \Omega_1, \) \( \Delta_2 = -41 \Omega_1, \) \( \Omega_1 = \Delta_1 = \Delta_2 = 0. \) (a) \( \Lambda_2 = 0, \) (b) \( \Lambda_2 = 15 \) (i.e., \( k_d = 0.1 \)), and (c) \( k_d = 1. \)
tained by the growth rate of the cross peaks.

FIG. 7. (Color online) Absorption line shape for our model Eq. (22) with different spectral diffusion widths in the $u$ and $d$ states ($\Omega_1 \neq 0$). $\Omega_2$ is fixed at $0.5 \, \text{fs}^{-1} \, \Lambda = 0.4 \, \text{ps}^{-1}$, $\Omega_3 = 0.33 \, \text{ps}^{-1}$, $\Omega_1 = -0.07 \, \text{ps}^{-1}$, $k_d = 0.125 \, \text{ps}^{-1}$, $k_u = 0.1 \, \text{ps}^{-1}$, $\Delta_1 = 2.0 \, \text{ps}^{-1}$, $\Delta_2 = 0$, and $\Delta_3 = 0$.

cal exchange occurs on a much longer time scale and affects the cross peaks.

We start by setting $\Omega_1$ and $\Delta_1$ to 0 and examine fast and the slow spectral diffusion. The fast (motional narrowing) limit ($\Lambda \gg \Omega_2$) gives a Lorentzian absorption line shape. Since the bath has no memory, peak shapes are less sensitive to $t_2$ and cross peaks due to chemical exchange only appear as $t_2$ is increased. Effects of fast fluctuations may be accounted for by adding dephasing rates $\Omega_2^2 / \Lambda$. 2D line shapes $S_{\Lambda}$ [Eq. (10)] shown in Fig. 3 are similar to the TSJ model (Fig. 2); both are given by a product of Lorentzian line shapes (in $\omega_0$ and $\omega_3$). The important difference is that for fast spectral diffusion, the linewidth is determined by both exchange and dephasing rates $(k_d + \Omega_2^2 / \Lambda)^{-1}$, i.e., it is different from the cross-peak time scale. In contrast the linewidth of the TSJ model must be equal to the exchange rate $k$ obtained by the growth rate of the cross peaks.

$S_{\Lambda}$ in the static $\Lambda \ll \Omega_2$ limit (Fig. 4) shows Gaussian linear line shapes. Static disorder is eliminated in the photon echo $k_1$ experiment. 2D peaks are elliptic with different “diagonal” and “antidiagonal” linewidths [Fig. 4(a)]. The intermediate regime may be observed at $\Lambda^{-1} < t_2 < k^{-1}$ when the bath loses memory [Fig. 4(b)], and the 2D peaks become symmetric. For long times $k_d t_2 \gg 1$ we see cross peaks induced by chemical exchange. Note the circular contours of Fig. 4(c), compared to the starlike contours for fast fluctuations (Fig. 3). These may be understood by noting that the product of two Gaussians (which represent the linear line shape for the slow case) is rotationally invariant, unlike the Lorentzian line shapes in the fast limit.

Figure 5 shows the $k_1$ and $k_2$ signals [Eqs. (8) and (9)]. The $k_1$ contribution dominates at short times, and shows effective rephasing (photon echo). The 2D IR spectrum is similar to the dominant $k_1$ contribution [see Fig. 4(a)]. For longer $t_3 \gg \Lambda^{-1}$ (right panels), the $k_1$ and $k_2$ contributions become comparable and $S_{\Lambda}$ is symmetric (see Fig. 4).

We next explore some more general cases. First we take $\Delta_2 \neq 0$. The overtone peaks may now have different widths along $\omega_1$ and $\omega_0$. Overtone photon echoes are expected at $\Omega_2 t_3 = (\Omega_1 + \Delta_2) t_1$. Note that we have a slow bath ($\Lambda < \Omega_2$) for the $\epsilon g$ and a fast bath for the $e^f$ transition ($\Lambda > \Omega_2 + \Delta_2$). These line shapes are shown in Fig. 6.

The inclusion of $\Omega_3$ does not require additional numerical effort. This parameter allows the $u$ and $d$ peaks to have different widths due to spectral diffusion. To demonstrate these effects and relate them to the recent experiments we have simulated the spectral diffusion using a single overdamped Brownian oscillator coordinate allowing a different width for $u$ and $d$ peaks. We used the splitting $2 \Delta_0 = 34 \, \text{cm}^{-1}$ (i.e., $\sim 1.01 \, \text{ps}^{-1}$) and the exchange rates $k_u = 0.1 \, \text{ps}^{-1}$ and $k_d = 0.125 \, \text{ps}^{-1}$ as determined in Ref. 5 from the cross peak growth. Three regimes similar to those of Fig. 5 were observed suggesting that the bath is not fast. The intermediate regime, where the memory of the Brownian oscillator coordinate is lost (circular line shape) but the cross peaks are still weak, was found on the 2 ps time scale. We thus assumed for the relaxation rate $\Lambda \sim 0.4 \, \text{ps}^{-1}$. Knowing $\Lambda$, $\Omega_1$ and $\Omega_3$ are connected to the peak linewidth in linear spectra and can be estimated using the Padé approximant of a two-level system. We have simulated the absorption spectra in Fig. 7 and found line shapes similar to experiment for $\Omega_2 = 0.33 \, \text{ps}^{-1}$ and $\Omega_3 = -0.07 \, \text{ps}^{-1}$. This completely determines the model for 2D IR spectroscopy (neglecting dynamics in the overtone), we have no additional free param-

FIG. 8. (Color) The 2D signal $S_{\Lambda}$ [Eq. (10)] for the same parameters of Fig. 7 at various time delays. (a) $t_2 = 0$, (b) $t_2 = 2 \, \text{ps}$, and (c) $t_2 = 10 \, \text{ps}$. These spectra closely resemble the experimental results of Ref. 5.
eter. The predicted 2D IR line shapes shown in Fig. 8 are in qualitative agreement with experiment. We reproduce all three regimes, rephasing elliptic shapes, the relaxed Brownian oscillator with circular shape, and chemical exchange cross peaks at the proper time scales. The peaks have also the correct relative intensity (the lower frequency peak is weaker but broader).

In conclusion, we have demonstrated that the SLE may be used to model chemical exchange in 2D IR spectroscopy. Spectral diffusion may not be accounted for by simply adding dephasing rates, when its time scale may be observed in experiment. Its proper description must be combined with the two-state jump which describe chemical exchange. The high temperature overdamped Brownian oscillator model for spectral diffusion with arbitrary fluctuation time scale reproduces all the regimes observed in recent experiments.15

In contrast with calculations based on the cumulant expansions18,25,32 our high temperature bath does not respond to the state of system, and its evolution in the ground and excited states is same.25 This is why the bath does not respond to the state of system, and its evolution is observed in 2D signals. However, the Stokes shift is often negligible in the infrared, and the chemical exchange rates do not change with the vibrational state of molecule.7 This limitation may be overcome by introducing a vibrational state dependent stochastic bath.38,39 The lack of phase factors during the $t_2$ interval reduces the dynamics to classical level and allows large scale molecular-dynamics (MD) simulations of environmental dynamics.

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APPENDIX A: THE ABSORPTION LINE SHAPE

The linear response function is given by25

$$S^{(1)}(t_1) = \theta(t_1) \frac{i}{\hbar} \langle \langle \mu^{-}(\omega_1) \mu^{+}(\omega_0) \rangle \rangle_{\mu}.$$ 

We define the contribution

$$K(t_1) = \langle \langle \mu_{ee}(t_1) \mu_{gg}(0) \rangle \rangle_{QS}.$$ 

This response function is connected to absorption line shape,

$$W(\omega_1) = \mu_{ee}^2 \omega_1^{-1} \Re \int_0^{\infty} \exp(i\omega_1 t_1) K(t_1) dt_1.$$ (A1)

For the TSJ model ($\Omega_{2,3}=0$) the result of Kubo19 is recovered,

$$W(\omega) = \frac{1}{(k_d + k_u)} \times \frac{4k_d k_u \Omega^2_{1}}{\left(\omega - \Omega_1 - \Omega_2 \right)^2 + \left(\omega - \Omega_0 \right) \left(k_d + k_u \right) + \Omega_1 \left(k_d - k_u \right)^2}.$$ 

For the spectral diffusion model we set $\Omega_1=0$ and the linear response function is given by the second order cumulant expression [see Eq. (C6)].

$$K(t_1) = \exp(-g_{uu}(t_1)).$$

APPENDIX B: RESPONSE FUNCTIONS FOR TWO-STATE-JUMP SPIN DYNAMICS

In the frequency domain the Green’s function [Eq. (18)] matrix elements are

$$G_{\nu\nu',\nu'\nu}(\omega) = -\left( i\omega \hat{\mathcal{L}} \right)^{-1}_{\nu\nu',\nu'\nu} = \left( \omega - \epsilon_0^{(p)} + \epsilon_0^{(r')} \right) - \delta_{\nu\nu'} \delta_{\nu'\nu'}$$

$$\times \left( k_u - i(\omega - \epsilon_0^{(p)} + \epsilon_0^{(r')} + \epsilon_1^{(r')} - \epsilon_1^{(r)}) \right) \left( k_d - i(\omega - \epsilon_0^{(p)} + \epsilon_0^{(r')} - \epsilon_1^{(r)} + \epsilon_1^{(r)}) \right).$$ (B1)

$R_{i}$ and $R_{ii}$ [Eq. (6)] are given by

$$R_{ii}(\omega_3,\omega_2,\omega_1) = \frac{1}{(\omega + \Omega_0)^2 - \Omega_1^2 + i(\omega_1 + \Omega_0)(k_d + k_u) \pm i\Omega_1(k_d - k_u)}$$

$$\times \frac{1}{(\omega_3 - \Omega_0)^2 - \Omega_1^2 + i(\omega_3 - \Omega_0)(k_d + k_u) \pm i\Omega_1(k_d - k_u)}$$

$$\times \left( k_u + k_d \right)^3 - \left( \omega_3 - \Omega_0 \right) \left( \omega_1 + \Omega_0 \right) \pm \Omega_1^3 \left( k_u + k_d \right) \pm \left( \omega_3 - \Omega_0 \right) \Omega_1 \pm \left( \omega_3 - \Omega_0 \right) \Omega_1 \pm \left( \omega_3 - \Omega_0 \right) \Omega_1 \left( k_d - k_u \right)$$

$$- i \left[ \left( \omega_3 - \Omega_0 \right) \left( \omega_1 + \Omega_0 \right) \left( k_u + k_d \right)^2 - \left( \Omega_1 \pm \Omega_0 \right) \left( k_u^2 - k_d^2 \right) \right] \pm 4\Omega_1^2 k_d k_u \left( 1 - \exp(-k_d + k_u) \right),$$

where the upper (lower) sign in for $R_{1}$ ($R_{i}$). Since the evolution in the excited $|ee\rangle$ and in the ground $|gg\rangle$ state is the same for stochastic jumps (where the bath is not affected by the system) we have
\[ R_{ii}(\omega_1, t_2, \omega_1) = R_i(\omega_1, t_2, \omega_1), \quad R_{ii}(\omega_2, t_2, \omega_1) = R_{ii}(\omega_3, t_2, \omega_1). \]  
(B2)

We further have for \( R_v \) and \( R_{vi} \),

\[
R_{vi}(\omega_3, t_2, \omega_1) = - \frac{1}{(\omega_1 - \Omega_0)^2 - \Omega_1^2 + i(\omega_1 - \Omega_0)(k_d + k_u) \pm i\Omega_1(k_d - k_u)} \times \left( (\omega_3 - \Omega_0 - \Delta_0)^2 - (\Omega_1 + \Omega_2)^2 + i(\omega_3 - \Omega_1 - \Delta_1)(k_d + k_u) + i(\Omega_1 + \Omega_2)(k_d - k_u) \right) \times \left( \frac{1}{k_u + k_d} \right) \times \left[ \left( (\omega_3 - \Omega_0 - \Delta_0)(\omega_1 \mp \Omega_0) \pm \Omega_1(\omega_1 + \Delta_1) \right) (k_u + k_d) + \left( \Omega_1 + \Omega_2 \right)(k_d - k_u^2) \right] \\
\times \left( (k_d - k_u) - \frac{i}{2} \left( (\omega_3 - \Omega_0 - \Delta_0)(\omega_1 \mp \Omega_0) \pm \Omega_1(\omega_1 + \Delta_1) \right) (k_u + k_d) - (\Omega_1 + \Omega_2)(k_d - k_u^2) \right) \\
\pm \frac{4i}{\Omega_1(\Omega_1 + \Delta_1)} \frac{k_u k_d}{k_d + k_u} \frac{1 - \exp[-(k_d + k_u)t_2]}{k_d + k_u},
\]

where the upper (lower) sign is for \( R_v \) (\( R_{vi} \)).

1. High temperature spin dynamics

In the high temperature limit we set \( k_u = k_d = k \). We first analyze the \( R_i \) and \( R_{ii} \) contributions. Here

\[
G_{ex,ex}(t) = e^{-i(\Omega_1 \eta)t} \begin{pmatrix} \cosh(\eta t) - \frac{i\Omega_1}{\eta} & \frac{k}{\eta} \\ \frac{k}{\eta} & \cosh(\eta t) + \frac{i\Omega_1}{\eta} \end{pmatrix},
\]
and

\[
G_{ex,ex}(t) = G^*_{ex,ex}(t),
\]

where \( \eta = \sqrt{k^2 - \Omega_1^2} \). When \( \Omega_1 > k \) we use analytic continuation [e.g., (\( \cosh(ix)=\cos x \) and \( \sinh(ix)=i \sin x \)] and after some algebra we get for \( \alpha = i, ii \);

\[
R_{ii}(t_3, t_2, t_1) = \frac{e^{-i(k(t_1+t_3))}}{2} \left[ \left( 1 + \frac{k^2}{\eta} \right) \cosh[\eta(t_1+t_3)] + \left( 1 - \frac{k^2}{\eta} \right) \cosh[\eta(t_1-t_3)] + \frac{2k}{\eta} \sinh[\eta(t_1+t_3)] \right] \\
+ \frac{e^{-i(k(t_1+2t_2+t_3))}}{2} \frac{\Omega_0^2}{\eta} \left[ \cosh[\eta(t_1+t_3)] - \cosh[\eta(t_1-t_3)] \right],
\]

where the upper (lower) sign stands for \( R_i \) (\( R_{ii} \)). Equation (7) then gives

\[
R_{ii}(\omega_3, t_2, \omega_1) = \frac{1}{(\omega_1 + \Omega_0)^2 - \Omega_1^2 + 2i(\omega_1 + \Omega_0)k(\omega_3 - \Omega_0)^2 - \Omega_1^2 + 2i(\omega_3 - \Omega_0)^2} \\
\times \{ 4k^2 - (\omega_3 - \Omega_0)(\omega_1 + \Omega_0) \pm \Omega_1^2 - 2i(\omega_3 - \Omega_0 + \omega_1 + \Omega_0)k \pm \Omega_1^2 \{ 1 - \exp[-2kt_2] \} \}.
\]

We further have \( R_{ii} = R_i \) and \( R_{vi} = R_{ii} \). For \( \alpha = v, vi \) we get

\[
R_{vi}(\omega_3, t_2, \omega_1) = \frac{1}{(\omega_1 + \Omega_0)^2 - \Omega_1^2 + 2i(\omega_1 + \Omega_0)k(\omega_3 - \Omega_0)^2 - \Omega_1^2 + 2i(\omega_3 - \Omega_1 - \Delta_1)^2} \\
\times \{ 4k^2 - (\omega_3 - \Omega_0)(\omega_1 + \Omega_0) \pm \Omega_1^2 - 2i(\omega_3 - \Omega_0 - \Delta_0 + \omega_1 + \Omega_0)k \pm \Omega_1(\Omega_1 + \Delta_1)(1 - \exp[-2kt_2]) \},
\]

where the upper (lower) sign corresponds to \( R_v \) (\( R_{vi} \)).

2. Slow spin dynamics

When \( \Omega_1 \gg k_u, k_d \) no spin jumps occur during the \( t_1 \) and \( t_3 \) intervals. Then

\[
G_{v'v, t_1, t_1}(\omega) = \delta_{v'v} \delta_{t_1, t_1} \begin{pmatrix} k_d + i(\epsilon_{0}^{(v')} - \epsilon_{0}^{(v)} + \epsilon_{1}^{(v')} - \epsilon_{1}^{(v)} - \omega) & 0 \\ 0 & k_u + i(\epsilon_{0}^{(v)} - \epsilon_{0}^{(v')} + \epsilon_{1}^{(v)} - \epsilon_{1}^{(v')} - \omega) \end{pmatrix}^{-1}
\]

The Green’s function for \( t_2 \) is still given by Eq. (19).

In the vicinity of the peaks [Fig. 2(a)] at, e.g., \( \omega_i = \Omega_0 + \Omega_1 \), and \( \omega_3 = \Omega_0 - \Omega_1 \), we have
The response functions may now be factorized into products of frequency fluctuations. The response functions may now be factorized into products of second order cumulant expansion25,33 which represents stochastic Gaussian fluctuations. The response functions may then be expressed in terms of the following four-point correlation functions:34

\[ F_1(t_{\tau}, t_3, t_2, t_1) = (B(t_{\tau})B^\dagger(t_3)B(t_2)B^\dagger(t_1)), \]

\[ F_2(t_{\tau}, t_3, t_2, t_1) = (B(t_{\tau})B(t_3)B^\dagger(t_2)B^\dagger(t_1))/2. \]

We then have34-36

\[ R_i(t_{t_1}, t_{t_2}, t_{t_3}) = F_1(t_{t_1}, t_{t_2}, t_{t_3}, t_{t_4}) + t_{t_5}, \]

(\text{C2})

Here

\[ F_1(t_{\tau}, t_3, t_2, t_1) = \exp(i(-\Omega_0 t_{\tau} + \Omega_0 t_3 - \Omega_0 t_2 + \Omega_0 t_1)), \]

(\text{C3})

with

\[ f_1(t_1, t_2, t_3, t_4) = g_{ee}(t_2 + t_3 + t_4), \]

(\text{C4})

\[ g_{ee}(t_2) = \exp[-i(\Omega_0 t_2 + \Omega_0 t_3) + \Omega_0 t_4) - f_2(t_{\tau}, t_3, t_2, t_1)]. \]

\[ g_{ee}(t_2) = \exp[-i(\Omega_0 t_2 + \Omega_0 t_3) + \Omega_0 t_4) - f_2(t_{\tau}, t_3, t_2, t_1)]. \]

\[ g_{ee}(t_2) = \exp[-i(\Omega_0 t_2 + \Omega_0 t_3) + \Omega_0 t_4) - f_2(t_{\tau}, t_3, t_2, t_1)]. \]

(\text{C5})

\[ g_{ab} \] are the line broadening functions,25,34

\[ g_{ee}(t) = \Omega_2^2[\exp(-\Lambda t) + \Lambda t - 1], \]

(\text{C6})

\[ g_{ee}(t) = (\Omega_2 + \Delta_2)\Omega_2[\exp(-\Lambda t) + \Lambda t - 1], \]

Note that \( R_i = R_{ii} \) and \( R_{ij} = R_{ij} \) as expected for stochastic models of frequency fluctuations.
APPENDIX D: SPECTRUM OF THE FOKKER-PLANCK EQUATION

The eigenvectors of the Fokker-Planck operator \([\text{Eq. (20)}]\) with eigenvalue \(-\alpha \Lambda\) are given by \(^{27}\)
\[
|\alpha\rangle_Q = \frac{\exp[-(Q^2/2)]}{2^n \sqrt{2\pi n!}} H_n \left( \frac{Q}{\sqrt{2}} \right), \quad \alpha = 0, 1, 2, \ldots .
\] (D1)
where \(H_n\) is the Hermite polynomial,
\[
H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}.
\]
The matrix representation of bath densities and evolution matrices refer to to the basis \(|\alpha\rangle_Q\). The matrix elements of \(L_Q\) are
\[
(L_Q)_{\beta,\alpha} = -\alpha \Lambda \delta_{\alpha,\beta}.
\] (D2)
We use the recurrence relation,
\[
QH_n(Q) = \frac{H_{n+1}(Q)}{2} + nH_{n-1}(Q).
\] (D3)
The \(Q\) coordinate is then represented by the tridiagonal matrix \([\text{Eq. (D4)}]\).
\[
[Q]_{\beta,\alpha} = \beta \sqrt{2} \delta_{\beta,\alpha+1} + \frac{1}{\sqrt{2}} \delta_{\beta,\alpha-1}.
\] (D4)

APPENDIX E: MATRIX CONTINUED-FRACTION SOLUTION OF THE FOKKER-PLANCK EQUATION

The complete Liouville superoperator is an \(18 \times 18\) matrix in the joint vibrational and spin space. The \(Q\) variable is tridiagonal in the Fokker-Planck eigenbasis and the complete Liouvillean may be thus arranged in the tridiagonal block structure in the Brownian coordinate variable,
\[
i \omega + \hat{L} = \begin{pmatrix}
Q_0 & Q_0^+ & 0 & 0 & \cdots & \cdots \\
Q_1^- & Q_1 & Q_1^+ & 0 & \cdots & \cdots \\
0 & \cdots & Q_m^- & Q_m & Q_m^+ & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\end{pmatrix}.
\] (E1)

For Eq. (22) the blocks are
\[
Q_n = i \omega + \hat{L}_S + \hat{L}_S - n \Lambda \hat{1},
\]
\[
Q_n^- = \frac{1}{\sqrt{2}} \hat{L}_{QS},
\]
\[
Q_n^+ = \sqrt{2}(n + 1) \hat{L}_{QS}.
\]
The SLE may be solved in the frequency domain using a matrix continued fraction.\(^{17,27,29}\) The Green’s function is given by the inverse \([\text{Eq. (24)}]\) of the tridiagonal matrix Eq. (E1). Starting with
\[
[i \omega + \hat{L}] \mathcal{G}(\omega) = -\hat{1}.
\]
For the off-diagonal \(n \neq m\) elements we have
\[
Q_{n}^{+} G_{n-1,m} + Q_{n} G_{n,n} + Q_{n}^{+} G_{n+1,m} = 0.
\] (E2)
The diagonal \(n=m\) elements are
\[
Q_{n}^{+} G_{n-1,n} + Q_{n} G_{n,n} + Q_{n}^{+} G_{n+1,n} = -1.
\] (E3)
The recursion relation Eq. (E2) is independent of the index \(m\). Consequently we can introduce the matrices \(S^+\) and \(S^-\),
\[
G_{n+1,0,1,2,\ldots,n}^\mp = S_n^\mp G_{n,n},
\] (E4)
Using Eq. (E2) these matrices may be solved iteratively,
\[
S_n^n = Q_{n+1} + Q_{n+1}^+ + Q_{n}^+ Q_{n+1}^- = Q_{n+1}^-.
\] (E5)
Combined with Eq. (E3) we obtain for the diagonal terms,
\[
G_{n,n} = \frac{-1}{Q_{n+1}^+ + Q_{n} Q_{n+1}^- + Q_{n}^+ Q_{n+1}^- + Q_{n}^+ Q_{n+1}^-}.
\] (E6)
while the off-diagonal \(G_{\omega_{nm}}\) are obtained from Eqs. (E5) and (E4). For \(n > m\),
\[
G_{n,m}(\omega) = S_n^{n-1}(\omega) S_n^{n-2}(\omega) \cdots S_m(\omega) G_{m,m}(\omega),
\] (E7)
and for \(n < m\),
\[
G_{n,m}(\omega) = S_n^{n+1}(\omega) S_n^{n+2}(\omega) \cdots S_m(\omega) G_{m,m}(\omega).
\] (E8)

The full Green’s function \(G(\omega)\) can be calculated by using Eq. (E5) to find the connection matrices \(S^\pm\). We note that \(S_n^\pm\) is zero and truncate the recurrence relation for \(S^\pm\) at some level \(n\) by setting \(S_n^\pm\) equal to zero. The matrix elements \(G(\omega)_{nm}\) can then be obtained using Eq. (E6). All other matrix elements \(G(\omega)_{nm}\) are calculated from Eq. (E4).