Signatures of Chemical Exchange in 2D Vibrational Spectroscopy; Simulations Based on the Stochastic Liouville Equations

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Abstract. The Stochastic Liouville Equations are employed to investigate the combined signatures of chemical exchange and spectral diffusion in coherent vibrational spectroscopy molecular complexes and of hydrogen bonding fluctuations in water.

Recent experiments have demonstrated that 2D IR lineshapes can probe the picosecond dynamics of chemical exchange by observing coherence transfer in molecular vibrations through time-dependent spectral jumps. In this three-pulse experiment, the first pulse creates a coherence, whose decay during the first interval t_1 is related to the absorption lineshape by a Fourier transform. In the second interval t_2 the vibrational frequency changes by complexation with the solvent. Finally vibrational coherence is again created and detected during the third interval t_3. The correlation of the lineshapes in the first and the third intervals provides information on chemical exchange during the second interval.

The Stochastic Liouville Equations (SLE) developed by Kubo [1] describe the dynamics of a quantum system coupled to a stochastic Markovian process.

The equations are constructed by combining the Liouville equation and the Markovian master equation

$$\frac{\partial}{\partial t}\rho(Q,s,t) = -\frac{i}{\hbar}\mathrm{L}(Q,s)\rho(Q,s,t) - \Gamma_i(Q)\rho(Q,s,t) + \Gamma_J(s)\rho(Q,s,t)$$

where ρ is the density matrix describing the state of the system and $\mathrm{L}(t)\rho(t) = -i/\hbar[H_0(t),\rho(t)]$ is the Liouvillian for the isolated system. We consider two types of stochastic processes:

1, Γ_i is a Fokker-Planck operator representing a continuous Gaussian coordinate Q

$$\Gamma_i \equiv \Lambda_i \frac{\partial}{\partial Q_i}\left(Q_i + \gamma_i^2 \frac{\partial}{\partial Q_i}\right)$$

where Λ_i is the relaxation rate and γ_i is the magnitude of bath fluctuations, and

2, Γ_J represents a stochastic jump between discrete states.

We consider the Hamiltonian describing a single anharmonic vibrational mode

$$H_0 = \hbar\Omega B^+ B + \tfrac{1}{2}\hbar\Delta B^+ B^+ BB$$

where both frequency and anharmonicity fluctuate as

$$\Omega = \Omega_0 + \Omega_1\sigma_z + \Omega_2 Q$$
$$\Delta = \Delta_0 + \Delta_1\sigma_z + \Delta_2 Q$$

where σ_z is Pauli matrix which describes chemical shift. Chemical exchange is described by a two state jump model and spectral diffusion is described by the Fokker-Planck equation [2]. A simulation of chemical exchange using this model is described in Fig 1.

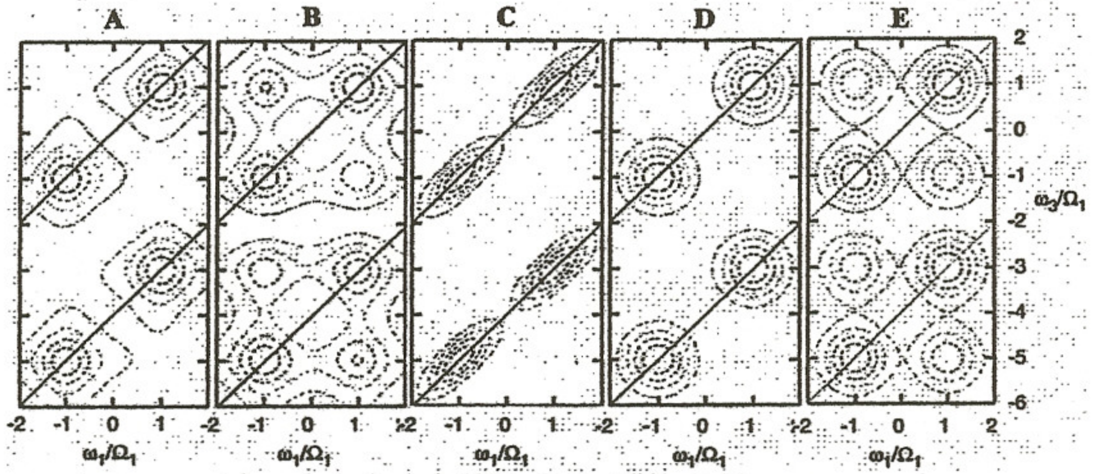


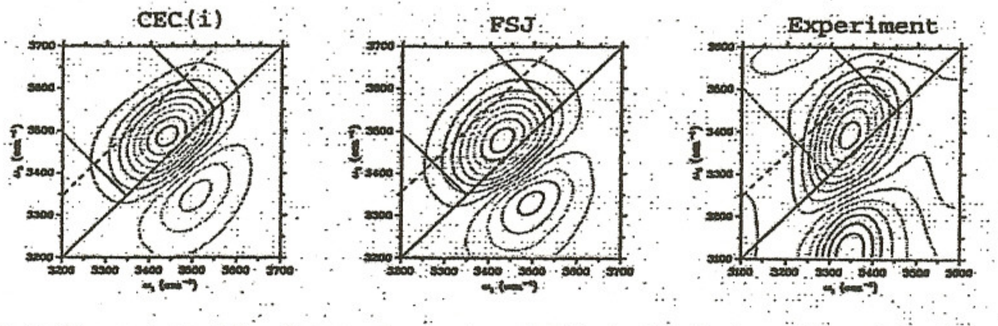
Fig 1:The SLE simulated 2D absorptive signals for a system undergoing two state chemical exchange and spectral diffusion. A (t_2=0)and B (t_2>>0) are for a fast bath motion, the peaks have lorentzian shapes and are less sensitive to t_2. C(t_2=0),D(t_2 intermediate) and E(t_2>>0) are for the slow bath limit, where the peaks have gaussian lineshapes. For C, the signals are elliptic because of the rephasing effect. The intermediate regime (D) may be observed when the bath lost memory and signals become symmetric . For long times (E) cross peaks appears caused by chemical exchange.

We have further used the SLE to simulate the photon echo spectrum of HOD in D_2O. The fluctuating frequency of the OH stretching are generated by classical MD simulations [3]. Two models were employed toward the simulation of the effects of hydrogen bonding fluctuations on the lineshapes. In the first we use two (continuous) collective electronic coordinate (CEC(i)) to describe fast and slow fluctuations and set Γ_J =0. In the second we use four state jump model (FSJ) for slow fluctuations. Fast fluctuation are still described using CEC.

The anti-diagonal linewidth in CEC(i) is about the same at the low and the high frequency while the linewidth for FSJ is 23 cm^{-1} larger for higher frequencies, despite the fact that the distribution of frequencies is broader for the low frequency configuration I which has two hydrogen bonds to O and one hydrogen bond to H (see Table 2 of Ref. 3). The blue slice in the experiment is 19 cm^{-1} broader than the red. We define the asymmetry parameter η as the fwhm line widths of the red and the blue anti-diagonal slices (Fig. 2)

$$\eta = \frac{\mathrm{fwhm(blue)} - \mathrm{fwhm(red)}}{\mathrm{fwhm(blue)} + \mathrm{fwhm(red)}}.$$

The FSJ asymmetry parameter η (0.125) was in better agreement with experiment (0.0848) than CEC(i) (0.0138). The experimental η suggests that the shorter lifetime of the high frequency hydrogen bond species gives rise to a considerable line broadening [4]. The hydrogen bond kinetics must be much faster than the slow dynamics giving rise to the frequency distribution of the individual species. The triangular shape of the diagonal photon echo peak is due to the fast femtosecond hydrogen bonding kinetics. The FSJ model which explicitly accounts for the hydrogen bonding kinetics reproduces this triangular shape and has a simulated 23 cm^{-1} broader linewidth in the blue than in the red, in good agreement with the 20 cm^{-1} reported from hole-burning studies [3]. This suggests that the non-Gaussian nature of the hydrogen bonding dynamics is responsible for the asymmetry of the spectrum.


CEC(i)

FSJ

Experiment

Fig. 2: Comparison of the photon echo spectra calculated using the two SLE models with experiment [4]. The full black line illustrate the diagonal, the dashed line is displaced 100 cm^{-1} above the diagonal. The red and blue lines show where the anti-diagonal slices are taken on the red and blue side, respectively to calculate the asymmetry parameter η .

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