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Two-Dimensional Optical Correlation Spectroscopy Applied to Liquid/Glass Dynamics

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Abstract. Correlation spectroscopy was used to study the effects of temperature and phase changes on liquid and glass solvent dynamics. By assessing the eccentricity of the elliptic shape of a 2D optical correlation spectrum the value of the underlying frequency–frequency correlation function can be retrieved through a very simple relationship. This method yielded both intuitive clues and a quantitative measure of the dynamics of the system.

How the properties of a material, once the freezing point is passed with a high enough quenching rate, can suddenly change so drastically at the glass transition without a major structural rearrangement on a molecular level is a fundamental scientific issue. Below some cross-over temperature in the super-cooled liquid regime macroscopic observables connected to molecular motion show strong deviations from an Arrhenius type temperature dependence [1,2].

The effects of temperature and phase changes on liquid and glass solvents are typically studied by measuring the dephasing rate of a coherently excited ensemble of chromophores. As this rate is set by the evolution of the solvent environments of the individual chromophores, its temperature dependence serves as a good indicator of the temperature-effected dynamical properties of the solvent. The amount of dephasing is expressed by the two time frequency–frequency correlation function (FFCF). In this paper, a novel, simple but quantitative method of deriving the correlation function directly from 2D optical correlation spectra (2DCS) is presented.

It has been long recognized that the 2DCS shapes in the frequency domain yield intuitive qualitative clues about the evolution of the individual microscopic environments [3,4]. They are quite sensitive to details of the system–bath interactions and the corresponding timescales. 2DCS can reveal the fluctuations of the electronic energy gap of the chromophores in the same way that 2D NMR follows spins in the COSY arrangement [5]. The correspondence between the eccentricity of the spectrum and the amount of coherence, i.e. the value of the system-bath correlation function, has been known for some time but this qualitative assessment has never been quantified [6].

We do this by assuming a FFCF $M(t)$ that is nearly constant on the time scale of delay τ_1 between a first and second pulse that is applied to the sample. It is also constant on the scale of delay τ_3 between a third and a fourth pulse, but not on the time scale of the waiting time t_w (i.e. the delay in between the two pulse pairs). We first consider the case of no Stokes shift. The photon echo signal can be evaluated through the well know formalism of nonlinear response functions [7],

and the result is double Fourier transformed to yield the following absorptive part of the 2D spectrum:

$$\text{Re}[S(\omega_1, t_w, \omega_3)] \propto \exp\left[-\frac{\omega_1^2 + \omega_3^2 - 2M(t_w)\omega_1\omega_3}{2\Delta^2(1-M^2(t_w))}\right]. \quad (1)$$

Here the frequencies ω_1 and ω_3 correspond to the time intervals τ_1 and τ_3 respectively. The equilateral contours of the 2D spectrum are ellipses tilted by 45° with a major axis $a = \eta\sqrt{1+M(t_w)}$ along the $\omega_1 = \omega_3$ direction, and a minor axis $b = \eta\sqrt{1-M(t_w)}$ along the orthogonal direction (here η is a common normalization coefficient constant). Therefore, the correlation function becomes:

$$M(t_w) = \frac{a^2 - b^2}{a^2 + b^2} = \frac{\varepsilon^2}{2 - \varepsilon^2}, \quad (2)$$

where ε is the ellipse eccentricity.

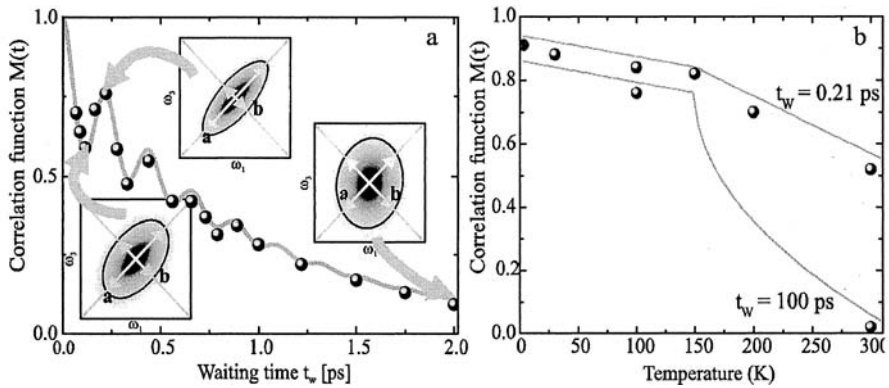


Fig.1. (a): The model correlation functions of the fluctuations of the resonance frequency of the dissolved chromophores (grey line). The 2D spectra are calculated using the full mathematical expressions (insets). The values of the correlation function (circles) are recalculated using Eq.(2). (b): The correlation function as calculated from a global analysis using a closed set of parameters at two waiting times (grey lines) as compared the same function calculated from the 2DCS using Eq.(2) (black balls).

In the more general case with the Stokes shift included, the equilateral contours are not simple ellipses any longer because the appearance of the spectrally shifted emission. In fact, they are represented by a sum of two ellipses with their centers shifted by the value of the momentarily Stokes shift. However, even in this case Eq. (2) has been shown to yield the right result on the correlation function.

Fig. 1a shows a realistic model correlation function for which the corresponding 2DCS are calculated using the complete expressions. Subsequently, the values of the FFCF at these times were derived according to Eq. (3). The proposed method produces excellent results even when the emission is Stokes shifted.

The experimental temperature dependent data on a dye DTTCI in a 1,2 propanediol/ethanol matrix is presented in Fig. 2. All data are taken for a waiting time $t_w = 210$ fs, where the first recurrence of the main vibrational mode at

150 cm^{-1} occurs. Whereas at 3 K the frequency off-sets of the chromophores seem to be nearly static, with increasing temperature the frequency excursions become evidently faster. The peak shape is more circular at higher temperatures, indicating that the correlation function has decayed further, and the transition is more and more homogeneously broadened.

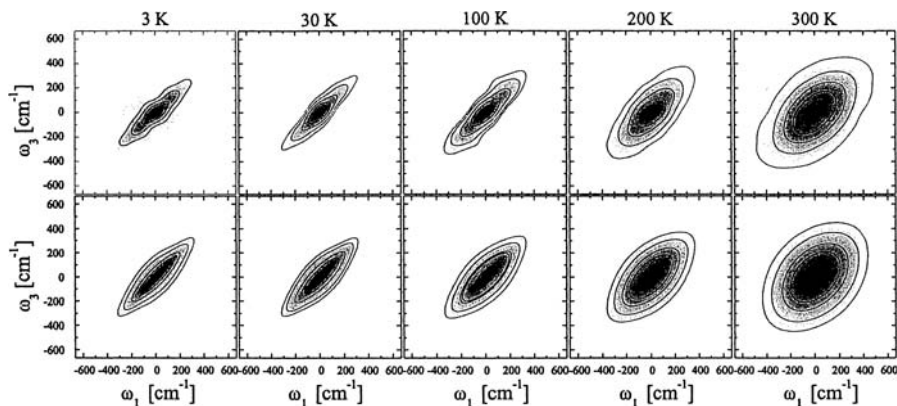


Fig.2. 2DCS of DTTCl dissolved in a 1,2 propanediol ethanol mixture at a waiting time $t_w = 210$ fs (upper plots). The bottom row of plots shows the corresponding simulated spectra. The simulations were performed with a global set of parameters.

This qualitative analysis was quantified by measuring the eccentricity of the spectral contours. The values of the FFCF as retrieved from the axes lengths are compared to the values of the correlation function as determined from a global fitting of all experiments done at various waiting times and temperatures in Fig. 1b. The correspondence between the values of the correlation function derived through the eccentricity of the ellipses and determined from the global analysis is excellent.

This shows that 2D correlation spectroscopic techniques present a constructive and insightful means of representing the data. The new method for analyzing 2DCS can also be extended to the IR vibrational spectroscopy where the 2D spectra have both positive and negative features arising from the lower and higher vibrational transitions [6].

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