Studies of Molecular Interactions and Collective Liquid Motions with Two-Dimensional Raman Spectroscopy

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Abstract. Two-dimensional Raman spectroscopy using femtosecond pulse sequences is used to better understand the interactions between molecules and collective dynamics in liquids.

Multidimensional time domain spectroscopy has been used for several years as a powerful structural and dynamic tool in the field of nuclear magnetic resonance (NMR). The power of multidimensional spectroscopies in studies of condensed phases is their ability to measure the correlation or interaction between different degrees of freedom by virtue of measuring higher correlation functions. Most traditional spectroscopies can be related to an ensemble-averaged two-point (or one-time-variable) correlation function, which is necessarily insensitive to the make-up of the ensemble. Two-dimensional (2-D) Raman spectroscopy [1-6] allows the principles of 2-D NMR to be extended to vibrational frequencies in order to probe the details of molecular dynamics in liquids and peer beneath the ensemble average of the Raman and light scattering spectrum.

Coherent 2-D Raman spectroscopy is a non-electronically-resonant technique that uses 45 fs pulse sequences in order to probe a fifth-order nonlinearity as a function of two time variables. By measuring the full 2-D Raman response, one measures an observable that is directly related to the interactions between Raman active vibrations. For low frequency overdamped motions at light scattering frequencies, the contours in the time domain are characteristic of the ensemble-makeup of the collective liquid dynamics. For higher frequency underdamped vibrational modes, the fifth-order Raman response can be 2-D Fourier transformed in order to obtain a 2-D Raman spectrum, in which interactions between vibration.

The 1-D polarized Raman spectrum of liquid CCl\textsubscript{4} shows three modes that arise from C-Cl stretching and bending motions. These modes are seen in the 2-D spectrum (Fig. 1) as the three features along the frequency diagonal ($\omega_2=\omega_4$). What is also apparent are a number of peaks that lie off the diagonal, which are representative of interaction or couplings between these vibrational modes. Cross peaks between the features on the diagonal (for instance $\omega_2=460$ cm\textsuperscript{-1}, $\omega_4=219$ cm\textsuperscript{-1}) and difference frequency peaks ($\omega_2=-219$ cm\textsuperscript{-1}; $\omega_4=(460-219)$ cm\textsuperscript{-1}) are direct indications of couplings between them [4].
Two-dimensional absolute value Raman spectrum of liquid CCl$_4$

Two possible coupling mechanisms have been shown to lead to cross peaks in the 2-D spectrum [4,5]. One mechanism is mechanical anharmonicity between vibrational modes. In particular, it has been shown that the amplitude of a cross peak is related to the magnitude of a particular cubic anharmonic expansion coefficient for the liquid potential. The other coupling mechanism is the nonlinear polarizability, which reflects the fact that the polarizability along a particular nuclear coordinate can be strongly influenced by the motion of another. A prime example of this is interaction-induced or collision-induced effects in liquids. If the liquid polarizability is expanded in a set of nuclear coordinates it can be shown that the magnitude of the nonlinear polarizability is related to the amplitude of cross peaks.

The same principles that are used to interpret 2-D Raman spectra can also be applied to understanding correlations and heterogeneity within collective motions in liquids. Figure 2 shows the intrinsic heterodyne 2-D Raman response $R^{(5)}(\tau_4)R^{(5)}(\tau_2,\tau_4)$ from liquid CS$_2$ at 165 K, just above its freezing point. The two-dimensional shape of this response forms a basis for understanding the time scales over which motions become averaged and diffusive, and allow a manner of quantifying the cross over from an inhomogeneous system at short-time to a diffusive homogeneous liquid at long times. This data set has been analyzed by breaking up the 1-D response of liquid CS$_2$ into characteristic time scales that are represented by a set of oscillators. The 2-D data can be fit to measure the correlation (or strength of interaction) between the collective liquid motions on these time scales. This analysis indicates a large degree of inhomogeneity on a 1 ps time scale in liquid CS$_2$ at 165 K that is not present at 295 K [6].

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Fig. 2. Two-dimensional heterodyned Raman response $R^{(3)}(t_4)R^{(3)}(t_2,t_4)$ from liquid CS$_2$ at 165 K. The heterodyne technique is discussed in reference 7. The hyperpolarizability contributions at delay times <80 fs have been truncated.

References