

Nuclear Dynamics of Liquids; possible probe by 2D femtosecond off-resonant spectroscopy

Abstract

The nonlinear nuclear optical response of liquids subjected to a series of N off-resonant femtosecond laser pulses is calculated using the N 'th order non-Condon response function for a multimode Brownian oscillator model. This multidimensional spectroscopy can be used to unveil the homogeneous or the inhomogeneous nature of the spectral density observed in impulsive Raman and birefringence measurements.

Introduction

Nuclear motions in liquids take place over a broad range of time scales. It is therefore not clear whether spectral lineshapes can be classified as either homogeneous or inhomogeneous. Even when such classification is possible by virtue of separation of timescales, it is not easy to firmly establish it experimentally. Early picosecond coherent Raman measurements were assumed to have the capacity of selectively eliminating inhomogeneous vibrational dephasing and revealing the homogeneous component. [Kaiser and Laubereau (1978); Zinth, et al. (1981); Oxtoby (1979); George et al., (1984)].

Loring and Mukamel (1985) have formulated the problem using a multitime correlation function approach and proved that this electronically off-resonant Raman technique, which contains only a single time variable is equivalent to linear absorption and is thus non selective in principle. They pointed out that only multitime techniques such as the Raman echo can address this issue. Several experiments have been subsequently carried out in order to measure the homogeneous vibrational linewidth [Vanden Bout, Muller, and Berg (1993); Muller, Wynne, and van Voorst (1988)]. These experiments were conducted on isolated intramolecular high frequency vibrations. In these applications the light pulses were longer than the vibrational periods. As such they did not have the time resolution to observe directly the vibrational motions. The decay of the signal with the delay between the excitation and the probe pulses then reflects vibrational dephasing.

Recent development of femtosecond techniques made it possible to probe

intermolecular vibrations in the frequency range 0-700[cm⁻¹] using an impulsive excitation with pulses short compared with the vibrational periods. Under these conditions the time resolved signal can show the coherent vibrations as well as their dephasing. It is tempting to analyze the spectral densities obtained [Nelson, et. al (1985-1990); McMorrow, et al. (1987, 1988, 1991); Cho, et al. (1993b)] in terms of instantaneous normal mode analysis of liquids [Keyes (1984); Chen and Stratt (1991)]. However, since impulsive birefringence and stimulant Raman techniques have only a single time variable, the limitations of the picosecond Raman measurements apply here as well; the homogeneous and the inhomogeneous nature of nuclear motions cannot be addressed.

In this article we present a closed form expression for the nuclear response function to third and fifth order in the field, using a harmonic model for nuclear motions with a nonlinear coupling to the radiation field (i.e. through the nonlinear dependence of the polarizability on nuclear coordinates).

This multimode Brownian oscillator model provides a convenient means for incorporating nuclear degrees of freedom in optical response functions. We have recently used a path integral approach to develop exact closed expressions for the nuclear wavepackets in phase space and for the nonlinear response functions for this model, including a coordinate dependent dipole interaction (non-Condon dipole interaction). Inhomogeneous broadening is incorporated by assuming a static distribution of the oscillator parameters (Fried and Mukamel, 1993). As an illustration, we analyze the possible application of a 5-pulse ($P^{(5)}$) measurement to a model liquid with a typical optical birefringence spectral density.

Off-Resonant Non-Condon Response Functions

We consider off-resonant spectroscopy of liquids in which all optical frequencies and their combinations are far detuned off any electronic excitation.

The external field consists of a train of N pairs of simultaneous pulses, followed by a final (probe) pulse,

$$E(\mathbf{r}, t) = \sum_{i=1}^N E_j(\mathbf{r}, t) + E_T(\mathbf{r}, t), \quad (1)$$

where

$$E_j(\mathbf{r}, t) = E_j(t) \{ \exp[i(\Omega_j t - \mathbf{k}_j \mathbf{r})] + \exp[i(\Omega'_j t - \mathbf{k}_T \mathbf{r})] \} + c.c., \quad (2)$$

and

$$E_T(\mathbf{r}, t) = E_T(t) \exp[i(\Omega_T t - \mathbf{k}_T \mathbf{r})] + c.c.. \quad (3)$$

Here $E_j(t)$ denotes the temporal profile of the j 'th pulse. We assume that the pulse pairs are well separated in time. We further assume that the system is initially in thermal equilibrium in the ground electronic state.

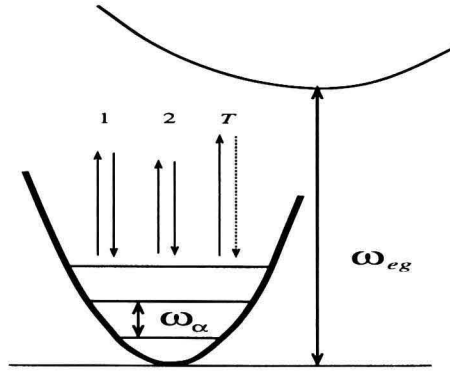


Fig. 1. The potential surfaces of the ground state and the first excited state for an α 'th Brownian oscillator. Shown also in the pulse interaction scheme for a $P^{(5)}$ ($N = 2$) process. Two off-resonant pairs of the pulses labeled 1 and 2 perturb the nuclear motion in the ground state. The fifth pulse labeled T then creates the polarization and generates the signal. This experiment has two time intervals and can therefore distinguish between inhomogeneous and homogeneous spectral densities.

Off resonant measurements have the following attractive characteristics.

(i) Excited state populations are limited by the Heisenberg relation to very short times $\Delta t \approx 1/\Delta\omega$, where $\Delta\omega$ is the off-resonant detuning. As $\Delta\omega$ is increased, these populations become practically negligible and the measurements probe only ground state dynamics. (ii) The time the system spends in an electronic coherence is also limited by the same Heisenberg relation, and consequently nuclear dynamics can be neglected during the coherence periods. We can then perform time integrations over these periods and describe the interaction of the liquid with the laser fields by an effective Hamiltonian

$$H_{eff} = H_g(\mathbf{p}, \mathbf{q}) - \alpha(\mathbf{q}) E(\mathbf{r}, t), \quad (4)$$

where $H_g(\mathbf{p}, \mathbf{q})$ is the ground state Hamiltonian and $\alpha(\mathbf{q})$ is the electronic polarizability that depends parametrically on the nuclear coordinates \mathbf{q} (Hellwarths, 1977; Yan and Mukamel, 1991; and Tanimura and Mukamel, 1993). We assume the following model for the electronic polarizability,

$$\alpha(\mathbf{q}) = \exp\left(\sum_s A_s a q_s\right), \quad (5)$$

where A_s is the dipole coupling constant for the s 'th oscillator. The dimension of A_s is chosen to be m^{-1} , therefore, a is a dimensionless coupling parameter. The coordinate q dependence of s may arise from the coordinate dependence of the dipole moment and of the electronic energies.

For off resonant excitation, the $2N + 1$ 'th polarization is then expressed as

$$P^{(2N+1)}(t) = 2^{N+1} E_T(t) \exp(i\Omega_T t - i\mathbf{k}_T \mathbf{r}) \left\{ \prod_{j=1}^N \int_0^\infty d\tau_j E_j^2 \left(t - \sum_{k=j}^N \tau_k \right) \right. \\ \left. \times \left[2 \cos \left(\Delta\Omega_j \left(t - \sum_{k=j}^N \tau_k \right) - \Delta\mathbf{k}_j \mathbf{r} \right) + 1 \right] \right\} R^{(2N+1)}(\{\tau_j\}), \quad (6)$$

where $\Delta\mathbf{k}_j \equiv \mathbf{k}_j - \mathbf{k}'_j$, $\Delta\Omega_j \equiv \Omega_j - \Omega'_j$.

For H_g , we assume a multimode Brownian oscillator model.

$$H_g(\mathbf{p}, \mathbf{q}) = \sum_s \left\{ \frac{p_s^2}{2m_s} + \frac{m_s \omega_s^2 q_s^2}{2} + \sum_k \left[\frac{(p_k^s)^2}{2m_k^s} + \frac{m_k^s (\omega_k^s)^2}{2} \left(x_k^s - \frac{c_k^s q_s}{m_k^s (\omega_k^s)^2} \right)^2 \right] \right\}. \quad (7)$$

Here, x_k^s , p_k^s , m_k^s , and ω_k^s , are the coordinate, the momentum, the mass and the frequency of the k 'th bath oscillator for s 'th mode, respectively. We assumed that the optically active vibrations are linearly coupled to a heat bath. The heat-bath system may represent optically inactive vibrational modes, phonons, solvent modes, etc.

We can think of the system in terms of a few Brownian oscillators q_s , or an infinite number of harmonic oscillators (with no damping). The two pictures are mathematically equivalent. The former may provide a better physical insight regarding the relevant collective nuclear motions.

Expanding in powers of a^2 , the lowest term in the third order response function is given by

$$R^{(3)}(\tau_1) = \frac{2}{\hbar} a^2 \int d\Gamma S(\Gamma) C''(\tau_1; \Gamma), \quad (8)$$

where

$$C''(t; \Gamma) = \int d\omega J(\omega; \Gamma) \sin(\omega t). \quad (9)$$

Here, we introduce the spectral distribution function

$$J(\omega; \Gamma) = \sum_s \eta_s f(\omega; \omega_s, \gamma_s), \quad (10)$$

where $\Gamma \equiv \{\eta_s, \omega_s, \gamma_s\}$ represents the parameters of the model namely the strength of the interaction (η_s), the frequency (ω_s), and the relaxation rate (γ_s) of the s 'th mode and

$$f(\omega; \omega_s, \gamma_s) = \frac{1}{2\pi} \frac{\omega \gamma_s}{(\omega_s^2 - \omega^2)^2 + \omega^2 \gamma_s^2}. \quad (11)$$

The effect of the heat bath is expressed by the spectral distribution, $\gamma_s(\omega)$ will represents the friction induced by the bath on the s 'th oscillator,

$$\gamma_s(\omega) \equiv \sum_k \frac{(c_k^s)^2}{2m_k^s(\omega_k^s)^2} \delta(\omega - \omega_k^s). \quad (12)$$

In this study we assume a frequency-independent friction $\gamma_s(\omega) = \gamma_s$, which represents a Gaussian-white noise on the nuclear system. The coupling strength is given by

$$\eta_s \equiv \frac{\hbar A_s^2}{m_s}. \quad (13)$$

This model can be used to represent specific coordinates, whether local (e.g. intramolecular) or collective in nature. Even if we do not have a clear idea of the nature of the modes of the system, it can be used as a convenient parameterization. In the liquid phase, the distribution of the values of $\{\eta_s, \omega_s, \gamma_s\}$ may reflect different slowly interconverting local environments. Similar problems of inhomogeneity are of current interest in the studies of dissipative kinetics observed in charge transfer in the photosynthetic reaction center (Walker, et.al. 1992, 1993).

Consider the following form for the birefringence (Kerr) amplitude

$$R^{(3)}(\tau_1) = \frac{2}{\hbar} a^2 \int d\Gamma S(\Gamma) \int d\omega J(\omega; \Gamma) \sin(\omega\tau_1), \quad (14)$$

where

$$\begin{aligned} R^{(3)}(\omega) &\equiv \int d\tau_1 e^{i\omega\tau_1} R^{(3)}(\tau_1) \\ &= \frac{\omega A_1 C_1}{2\pi[(B_1^2 - \omega^2)^2 + \omega^2 C_1^2]} + \frac{\omega A_2 C_2}{2\pi[(B_2^2 - \omega^2)^2 + \omega^2 - C_2^2]}. \end{aligned} \quad (15)$$

Here A_1, B_1, C_1 , etc. are chosen to represent the experimental birefringence spectral density of CH_3CN of these parameters (in $[\text{cm}^{-1}]$) are given by (Cho et.al, 1993b)

$$A_1 = 0.01, B_1 = 50, C_1 = 100, A_2 = 0.04, B_2 = 350, C_2 = 25. \quad (16)$$

$R^{(3)}$ depends on the homogeneous J and inhomogeneous S components only through the combination

$$\int d\Gamma S(\Gamma) J(\omega; \Gamma). \quad (17)$$

There are therefore infinite number of choices of inhomogeneous distribution

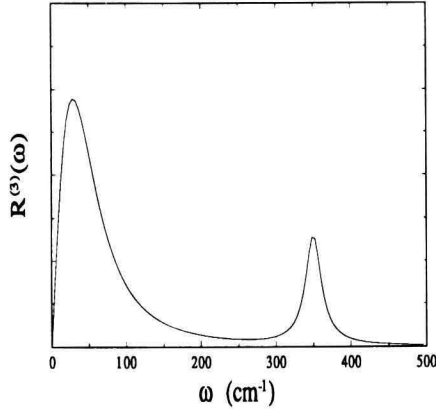


Fig. 2. The spectral density $R^{(3)}(\omega)$ of CH_3CN obtained from the optical Kerr experiment (Cho et al., 1993).

$S(\Gamma_s)$ and homogeneous spectral distribution $J(\omega; \Gamma_s)$, that gives the same optical Kerr signal,

$$I^{(3)}(T_1) = |R^{(3)}(T_1)|^2, \quad (18)$$

where $R^{(3)}$ is given by Eq. (15). Hereafter we adopt the two extreme choices; (i) a purely homogeneous two oscillator case, where spectral density is attributed to the two oscillator modes

$$S(\Gamma_1, \Gamma_2) = \prod_{x=1}^2 \delta(\eta_x - A_x) \delta(\omega_x - B_x) \delta(\gamma_x - C_x), \quad (19)$$

$$J(\omega; \Gamma_1, \Gamma_2) = \eta_1 f(\omega; \omega_1, \gamma_1) + \eta_2 f(\omega; \omega_2, \gamma_2) \quad (20)$$

(ii) purely inhomogeneous one oscillator case, where a single harmonic frequency is inhomogeneously distributed

$$S(\Gamma_1) = \lim_{\varepsilon \rightarrow 0} \delta(\eta_1 - 1) \delta(\gamma_1 + \varepsilon) [A_1 f(\omega_1; \beta_1, C_1) + A_2 f(\omega_1; B_2, C_2)], \quad (21)$$

$$J(\omega; \Gamma_1) = \eta_1 f(\omega; \omega_1, \gamma_1). \quad (22)$$

As can be seen from Eq. (14), the third order signal, which corresponds to the optical Kerr (birefringence) experiments, is identical for the two models. This is in agreement with our previous analysis to the effect that we cannot distinguish between homogeneous and inhomogeneous contributions from experiments based on the third order response function.

Let us consider now the fifth order signal. The 5'th order off-resonant response function is given by

$$R^{(5)}(\tau_2, \tau_1) = \frac{4a^4}{\hbar^2} \int d\Gamma S(\Gamma) C''(\tau_2; \Gamma) [C''(\tau_1; \Gamma) + C''(\tau_1 + \tau_2; \Gamma)], \quad (23)$$

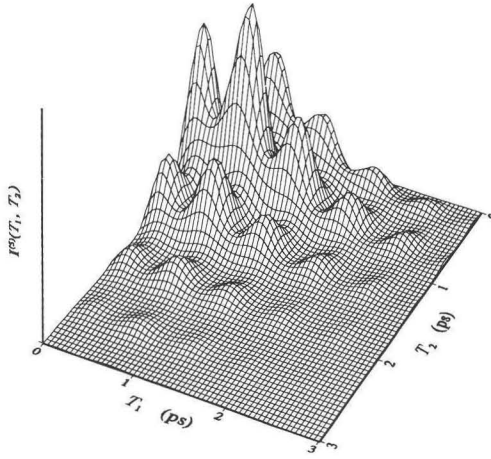


Fig. 3. The time domain 2D signal $I^{(S)}(T_1, T_2)$ for the pure homogeneous case (i) using the spectral distribution of Fig. 2.

or alternatively,

$$R^{(S)}(\tau_2, \tau_1) = \frac{4}{\hbar^2} a^4 \int d\Gamma S(\Gamma) \left[\int d\omega J(\omega; \Gamma) \sin(\omega\tau_2) \right] \times \left\{ \int d\omega J(\omega; \Gamma) [\sin(\omega\tau_1) + \sin(\omega(\tau_1 + \tau_2))] \right\}. \quad (24)$$

For impulsive pump probe experiments, such that $E_T(t) = \delta(t - T_1 - T_2)$,

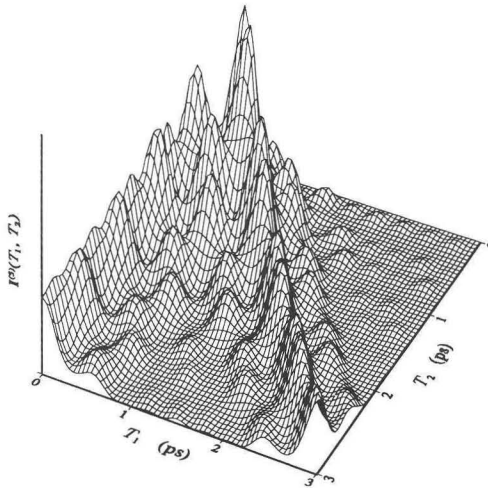


Fig. 4. The time domain 2D signal $I^{(S)}(T_1, T_2)$ for the pure inhomogeneous case (ii) using the spectral distribution of Fig. 2.

$E_1(t) = \delta(t)$, and $E_2(t) = \delta(t - T_1)$ for the 5'th order, we can perform the time integrations over τ_j . Then the total signal intensity related the square of the polarization is given by (up to a proportionality constant)

$$I^{(5)}(T_1, T_2) = |R^{(5)}(T_2, T_1)|^2. \quad (25)$$

$R^{(5)}$ depends on $J(\omega; \Gamma)$ and $S(\Gamma)$ separately and not merely through the combination Eq. (17). This opens up the possibility of observing the difference between the homogeneous and the inhomogeneous contributions to the spectral density obtained from birefringence $R^{(3)}$ experiments (Figs. 3-6). The two models Eq. (19) together with Eq. (20) or Eq. (21) together with Eq. (22) have dramatically different predictions for $R^{(5)}$. This is illustrated in the following numerical calculations. For (i) the pure homogeneous and (ii) the pure inhomogeneous cases. As seen from the figures, the fifth order (3-pulse) signal is very different for the two cases. The $I^{(5)}$ signal constitutes a two-dimensional spectroscopy with a two independent time periods during which the nuclear coherence evolves.

A different perspective on these results can be obtained by performing two-dimensional (2D) Fourier transformation, as follows,

$$I(\omega_2, \omega_1) = \left| \int_0^\infty dT_1 \int_0^\infty dT_2 e^{i\omega_1 T_1 + i\omega_2 T_2} I(T_2, T_1) \right|^2. \quad (26)$$

Calculations were made using a two-dimensional fast Fourier transform (FFT) routine on a 256 by 256 grid. Figs. 7 and 8 show, respectively, the 2D Fourier

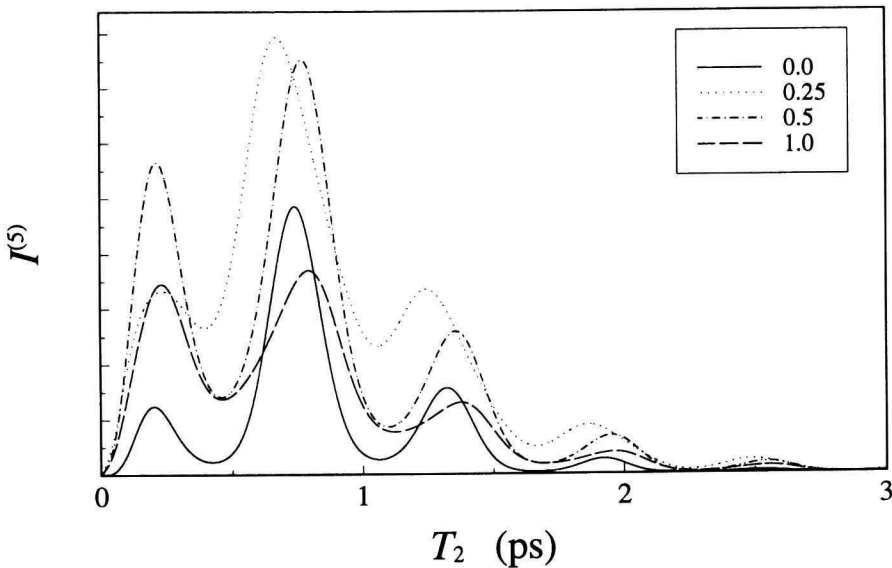


Fig. 5. Sections of Fig. 3 for different value of T_1 as indicated (in ps).

transform of (i) the pure homogeneous (Figs. 3 and 5) and (ii) the pure inhomogeneous cases (Figs. 4 and 6). In Fig. 7, we observe peaks whose positions are determined by the products $[\sin(\omega_a T_2) + \sin(\omega_b T_2)][\sin(\omega_a T_1) + \sin(\omega_b T_1)]$ and $[\sin(\omega_a T_2) + \sin(\omega_b T_2)]\{\sin[\omega_a(T_1 + T_2)] + \sin[\omega_b(T_1 + T_2)]\}$, however, since their spectral width at $(\omega_1, \omega_2) = (\pm 50, \pm 50)$ [cm^{-1}] are broad ($\gamma_a = 100$ [cm^{-1}]), we cannot distinguish them from the zero frequency peak at $(\omega_1, \omega_2) = (0, 0)$. In the purely homogeneous case, one can observe coherent modes of the ground states as shown in this Figure.

Fig. 8 represents the pure inhomogeneous case, where we can rewrite the response function as

$$R^{(5)}(T_2, T_1) = \int d\omega_1 [A_1 f(\omega_1; B_1, C_1) + A_2 f(\omega_1; B_2, C_2)] \times \{ \cos[\omega_1(T_1 - T_2)] + \cos[\omega_1 T_1] - \cos[\omega_1(T_1 + T_2)] - \cos[\omega_1(T_1 + 2T_2)] \}. \quad (27)$$

Thus, the response function consists of functions of the form $f(T_1 - T_2)$, $g(T_1 + T_2)$, $j(T_1 + T_2)$ and $k(T_1)$. Since we performed the Fourier transformation over T_1 , $T_2 \geq 0$, the contributions of $f(T_1 - T_2)$ and $k(T_1)$ are large compared with the contribution from $g(T_1 + T_2)$ and $j(T_1 + 2T_2)$ and show maxima along the lines $\omega_1 = -\omega_2$ and $\omega_2 = 0$. The distribution of the ground state mode frequency can be observed on these lines as the peaks at $(\omega_1, \omega_2) = (\pm \omega_b, 0)$ and $(\omega_1, \omega_2) = \pm(\omega_b, -\omega_b)$. The functions $g(T_1 + T_2)$ and $j(T_1 + 2T_2)$ also

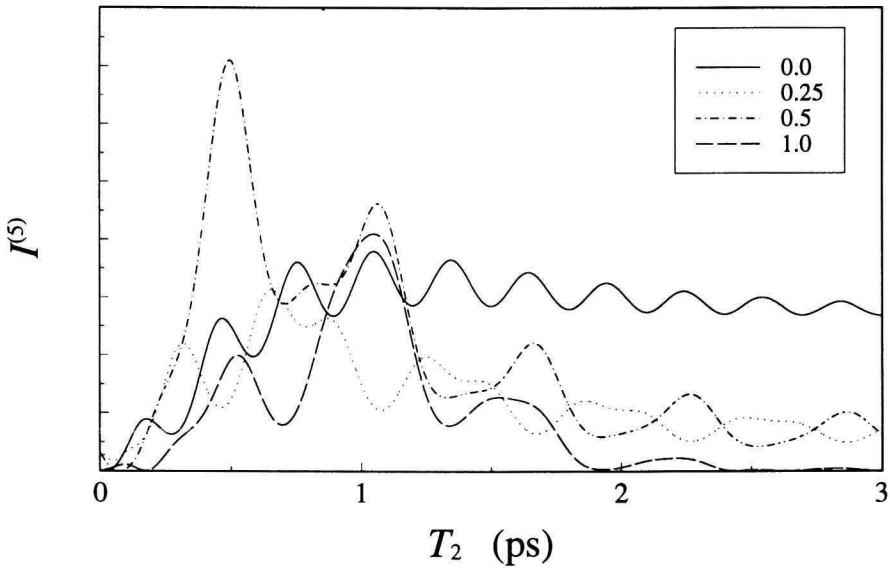


Fig. 6. Sections of Fig. 4 for different value of T_1 as indicated (in ps).

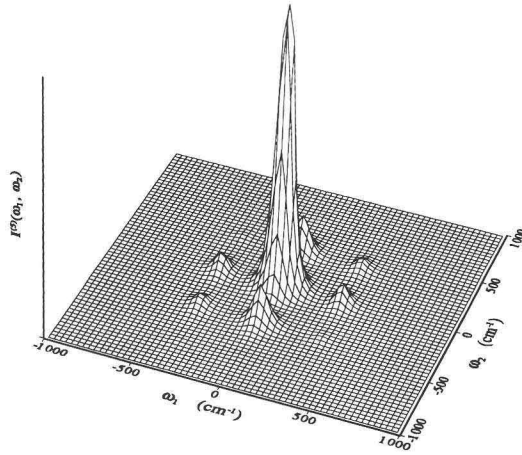


Fig. 7. The frequency domain 2D signal $I^{(S)}(\omega_1, \omega_2)$ corresponding to Figs. 3 and 5.

show small peaks at $(\omega_1, \omega_2) = \pm(\omega_b, \omega_b)$ and $(\omega_1, \omega_2) = \pm(\omega_b, 2\omega_b)$, however, the contribution from ω_a cannot be distinguished from the central peak.

In conclusion, the two models, which have an identical 1D (birefringence) spectrum clearly show very different 2D spectra. Realistic situations of the liquid spectral density are expected to be intermediate between these purely homogeneous and inhomogeneous cases. Separately of $J(\omega; \Gamma)$ and $S(\Gamma_s)$ may thus be probed by performing higher order measurements in addition to the optical Kerr experiment.

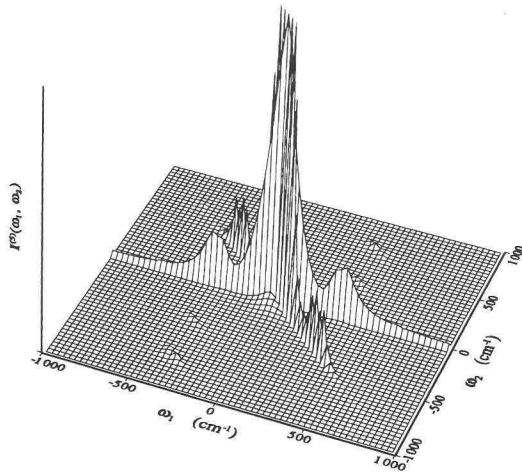


Fig. 8. The frequency domain 2D signal $I^{(S)}(\omega_1, \omega_2)$ corresponding to Figs. 4 and 6.

Acknowledgements

We wish to thank J. Buontempo, S. Palese, and D. Miller, V. Chernyak, M. Cho and G. Fleming for most useful discussions. The support of the National Scientific Foundation and the Air Force Office of Scientific Research is gratefully acknowledged.

References

- Chen, A., and Stratt, R.M., *J. Chem. Phys.* **95**, 2669, 1991.
- Cho, M., Fleming, G.R., and Mukamel, S.J., *Chem. Phys.* **98**, 5314, 1993a; Cho, M., Du, M., Scherer, N.F., Fleming, G.R., and Mukamel, S., submitted to *J. Chem. Phys.*, 1993b.
- Egelstaff, P.A., *An Introduction to the Liquid State* (Academic, New York), 1967.
- Ernst, R.R., Bodenhausen, G., and Wokaun, *Principles of nuclear magnetic resonance in one and two dimensions*, (Clarendon press, Oxford, 1987), 1987.
- Fried, L.E. and Mukamel, S., *Adv. Chem. Phys.* **84**, 435, 1993.
- Fayer, M.D.
- George, S.M., Harris, A.M., Berg, M., and Harris, C.B., *J. Chem. Phys.* **73**, 5573, 1984.
- Hallwarth, R.W., *Prog. Quant. Electr.* **5**, 1, 1977.
- Keyes, T., and Ladanyi, B.M., *Adv. Chem. Phys.* **56**, 411, 1984.
- Laubereau, A., and Kaiser, W., *Rev. Mod. Phys.* **50**, 607, 1978.
- Loring, R.F., and Mukamel, S., *J. Chem. Phys.* **83**, 2116, 1985.
- Muller, L.J., Vavid, D., and Berg, M., submitted to *J. Chem. Phys.*, 1993.
- Muller, M., Wynne, K., and van Voorst, J.D.W., *Chem. Phys.* **128**, 549, 1988.
- MacMorrow, D., Kalpouzos, and C. Kenney-Wallace, G.A., *Chem. Phys. Lett.* **137**, 323, 1987; MacMorrow, D., Lotshaw, W.T., Kenney-Wallace, G.A., *IEEE J. Quantum Electron* **QE24**, 443, 1988; Lotshaw, W.T. McMorrow, D., and Lotshaw, W.T., *J. Phys. Chem.* **95**, 10395, 1991.
- Nelson, K.A. and Ippen, E.F., *Adv. Chem. Phys.* **75**, 1, 1989; Weiner, A.M., Leaird, D.E., Wiederrecht, G.P., and Nelson, K.A., *Science* **247**, 1317, 1990; Yan, Y.X., Gamble, E.B., and Nelson, K.A., *J. Chem. Phys.* **83**, 5391, 1985; Ruhman, S., Joly, A.G., Kohler, B., Nelson, K.A., and Williams, L.R., *Rev. De. Phys.* **22**, 1717, 1978; Ruhman, S., Joly, A.G., Kohler, B., Nelson, K.A., and Williams, L.R., *J. Phys. Chem.* **91**, 2237, 1987.
- Noda, I., *J. Am. Chem. Soc.* **111**, 8116, 1989; Noda, ., *Appl. Spectrosc.* **44**, 550, 1990.
- Oxtoby, D.W., *Adv. Chem. Phys.* **40**, 1, 1979.
- Scherer, N.F., Ziegler L.D., and Fleming, G.R., *J. Chem. Phys.* **96**, 5544, 1992.
- Tanimura, Y., and Mukamel, S., *Phys. Rev.* **E47**, 118, 1993a; *ibid.*: to be published in *J. Opt. Soc. Am.* **B**, 1993b; *ibid.* submitted to *J. Chem. Phys.*, 1993c.
- Yan Y.J., Mukamel, S., *J. Chem. Phys.* **94**, 997, 1991.
- Vanden Bout, D., Muller, L.J., and Berg, M., *Phys. Rev. Lett.* **67**, 3700, 1991.

Walker, G.C., Akesson, E., Johnson, A.E., Levinger N.E., and Barbara, P.F.; *J. Phys. Chem.* **90**, 3128, 1992; Tominaga, K., Kliner, D.A.V., Johnson, A.E., Levinger, N.E., and Barbara, P.F., *J. Chem. Phys.* **98**, 1228, 1992.
Zinth, W., Polland, H.-J., Laubereau, A., and Kaiser, W., *Appl. Phys.* **B26**, 77, 1981; Zinth, W., Leonhardt, R., Holzapfel, H., and Kaiser, W., *IEEE J. Quantum Electron.* **24**, 455, 1988.

Author's address

Department of Chemistry
University of Rochester
Rochester, New York 14627
USA