Temperature dependence of hydrogen-bonding dynamics via ultrafast 2D-IR spectroscopy

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Introduction

Ultrafast 2D-IR spectroscopy has been applied to study the dynamics of hydrogen-bonding interactions between acetylacetonato-dicarbonyl rhodium (RDC) and 1,7 heptanediol. Analysis of the 2D-IR spectral lineshape as a function of temperature provides new insights into the rate of hydrogen bond fluctuations.

Ultrafast 2D-IR has become well-established as a powerful probe of molecular structure and vibrational dynamics. By spreading the molecular response over two frequency axes to produce a spectrum in which off-diagonal peaks reveal couplings between vibrational modes, 2D-IR circumvents the main drawback of conventional IR spectroscopy, namely the loss of information due to the projection of an ensemble-averaged response onto one frequency axis [1-3].

It has also been shown 4-6 that the 2D-IR spectral lineshape enables a direct measurement of the frequency correlation function $C(\tau)=\langle\delta\omega(\tau)\delta\omega(0)\rangle$ (where $\delta\omega(\tau)=\omega(\tau)-\langle\omega\rangle$), which characterizes the magnitude and rate of frequency fluctuations and spectral diffusion [4]. These arise in solution phase systems from changes in the local environment leading to fluctuations in the interaction with the solvent bath and so changes in the vibrational energy of a given mode. If this process is slow in relation to the temporal resolution of the experiment then this leads to inhomogeneous broadening and a diagonal elongation of the 2D lineshape. In the limit of homogeneous broadening, the lineshape is observed to be circular in profile.

Many ultrafast techniques have attempted to measure $C(\tau)$ [7-9] but it has been shown that the 2D-ellipticity, a metric which monitors the temporal evolution of the 2D-IR lineshape from diagonally-elongated to circular provides a direct measurement of spectral diffusion and thus $C(\tau)$ [4].

In this study, the 2D-IR spectrum of RDC was recorded as a function of waiting time at different temperatures; the evolution of the 2D lineshape was then monitored to obtain information on the fluctuations of the hydrogen bond network.

Experimental

2D-IR spectra were obtained using a modification [10] of the quasi-frequency domain double resonance (narrowband pump-broadband probe) technique [11,12]. The experiment has been described elsewhere [10,13]. Briefly, two OPAs, equipped with difference frequency generation were used
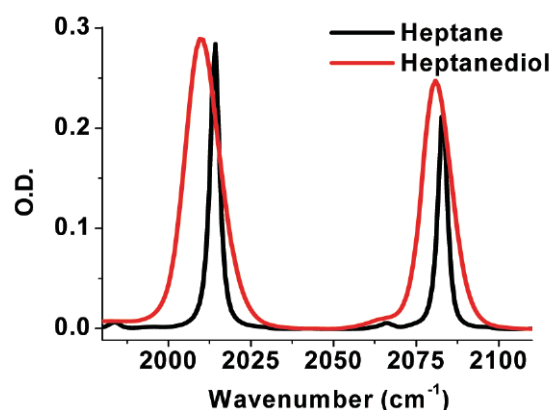

Figure 1. FTIR spectrum of a 1mM solution of RDC in heptanediol, as compared with a similar solution in heptane.

to generate radiation centred at ~2000 cm^{-1} with a bandwidth of ~150 cm^{-1} and pulse-duration of ~200 fs. The major modification to the established double resonance method was the use of a pulse-shaping device to produce the tuneable narrow bandwidth (~10 cm^{-1}) pump radiation [10]. This yields pump pulses with an approximately Gaussian temporal profile versus the single-sided exponential produced by the widely-used Fabry-Perot filter. Pump-probe delay times are analogous to the photon echo terminology 'waiting time' referred to below.

Results and discussion

The FTIR spectrum of RDC in heptanediol is shown in figure 1, where it is compared to that in heptane. The symmetric and antisymmetric stretching modes of the dicarbonyl moiety, appear at 2084 and 2015 cm^{-1} respectively in heptane but become broadened and red-shifted as expected when exposed to the hydrogen-bonding solvent.

Figure 2 (a) shows the 2D-IR spectrum of RDC in heptanediol at 303 K with a waiting time of 2 ps. The pairs of negative and positive peaks on the diagonal of the spectrum correspond to bleach and stimulated emission from the v=0-1 transitions and from transient absorptions from the v=1-2 transitions of the two carbonyl stretching modes respectively. The off-diagonal peaks, indicated by crossing points of the thin dashed lines, reveal the vibrational coupling of these modes.

In contrast to the 2D-IR spectrum of RDC in alkane solvents [1] the 2D-IR lineshape in figure 2(a) is elongated
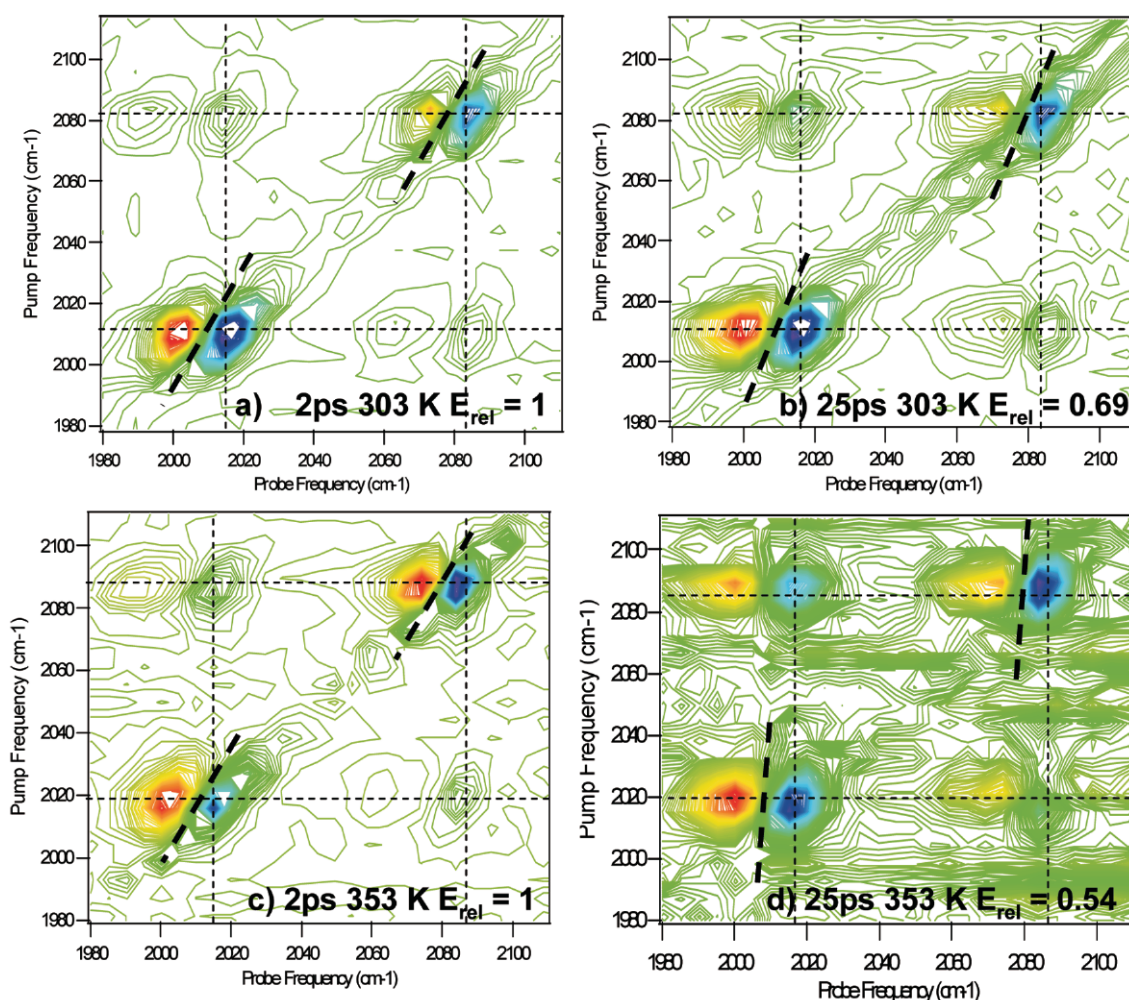
Figure 2: 2D-IR spectra of a 1mM solution of RDC in heptanediol recorded at a) 303K with a pump-probe time delay of 2 ps, b) 303K with a pump-probe time delay of 25 ps, c) 353K with a pump-probe time delay of 2 ps, d) 353K with a pump-probe time delay of 25 ps.

along the diagonal, indicating inhomogeneous broadening. This can be examined in two ways, qualitatively, through the rotation of the nodal plane between the bleach and transient absorption halves of the lineshape toward the spectrum diagonal (see the bold dashed line) and quanitatively, through fitting the diagonal lineshapes to 2D-Gaussian lineshape functions [14] to determine the ellipticity of the lineshape. The latter is given by $E=(a^2-b^2)/(a^2+b^2)$ where a and b are the diagonal and anti-diagonal linewidths [4].

Figure 2(b) shows the effect of increased (25 ps) waiting time at 303 K. A slight decrease in the ellipticity of the lineshape occurs to a value of 0.69 relative to that obtained at a waiting time of 2 ps. Fitting was carried out on the diagonal feature at 2014 cm^{-1} but it can be seen that similar results were obtained for both diagonal lineshapes. This is also evidenced by a slight rotation of the nodal plane towards the vertical.

Increasing the temperature of the system to 353 K leads to the observation of a similar lineshape at a waiting time of 2 ps (figure 2(c)) but by 25 ps (figure 2(d)) it is clear that

the line displays much more circular character; the relative ellipticity falls from to 0.54 by 25 ps and the nodal plane has rotated almost to the vertical in figure 2(d). Interestingly, in a spectrum (not shown) measured with a waiting time of 10 ps, the relative ellipticity was measured to be 0.69, comparable to that measured at 303 K with a waiting time of 25 ps.

It is clear from the data that the hydrogen bonding interactions between RDC and heptanediol lead to an inhomogeneously broadened lineshape, arising from fluctuations of the H-bonding network that are slow in relation to the waiting time of the experiments at 2 ps. Increasing the waiting time to 25 ps allows spectral diffusion, which manifests itself as a reduction in the ellipticity of the 2D-IR lineshape. The rate of this process increases as the temperature of the system increases due to more rapid fluctuations of the H-bonded network. A detailed measurement of ellipticity versus waiting time can be employed to provide a direct measurement of the frequency correlation function $C(\tau)$ for this system.

Conclusions

It has been shown that 2D-IR spectroscopy can be used to provide a measurement of the timescale for fluctuations of the solvent bath around a solute species. The ellipticity of the lineshape measured for an inhomogeneously broadened system reduces as a function of the waiting time due to spectral diffusion. For a hydrogen-bonded system such as RDC in heptanediol, the rate of this evolution has been observed to increase with increased temperature.

Acknowledgements

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