Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information for

Time resolved dynamics of phonons and rotons in solid parahydrogen

Falk Königsmann and Nikolaus Schwentner
Institut für Experimentalphysik, Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, D-14195 Berlin, Germany

David T. Anderson
Department of Chemistry, University of Wyoming, Laramie, WY 82071, USA

1. Analysis of homodyne and heterodyne signal contributions

A small part of the probe beam intensity always leaks through the analyzer due to spatial inhomogeneities in the birefringence of the 3 cm long cryogenic crystal. This provides a local oscillator (*LO*) with field strength E_{LO}. The pump laser induced birefringence produces an additional electric field E_{BIR} behind the analyzer with a phase relation β with respect to E_{LO}, which depends on the time delay between pump and probe. Both contributions are superimposed in the experiment and deliver a signal field E_S whose square is proportional to the signal intensity I_S,

$$I_S = E_S^2 = \left(E_{LO} + E_{BIR}\right)^2 = E_{LO}^2 + 2E_{LO}E_{BIR}\cos\beta + E_{BIR}^2 \qquad \text{(S1)}$$

The induced birefringence originates from a difference in the index of refraction (Δn) parallel and perpendicular to the pump beam polarization, which follows from an anisotropy in the polarizability $\Delta\alpha$ in these two directions in the solid and from an alignment angle θ of the H_2 molecular axis with respect to the pump polarization. The maximum anisotropy in the polarizability of the aligned H_2 ensemble is given by $\Delta\alpha\left(\left\langle\cos^2\theta\right\rangle - \frac{1}{3}\right)$, where the anisotropy in the polarizability is weighted by the degree of alignment achieved. The difference in refractive index Δn for the probe beam is thus given by

$$\Delta n = 2\pi N\Delta\alpha\left(\left\langle\cos^2\theta\right\rangle - \tfrac{1}{3}\right) \qquad \text{(S2)}$$

where N is the number density of molecules per unit volume and α is the polarizability. Glan-Taylor polarizing prisms are used to set the relative polarizations between pump and probe to an angle of 45° for maximum sensitivity. The probe field component parallel to the pump-

polarization is delayed by Δn with respect to the perpendicular one leading to a phase lag ϕ, which scales with the interaction length l of pump and probe and inversely with wavelength λ,

$$\phi = 2\pi l \Delta n / \lambda = A\left(\left\langle \cos^2\theta \right\rangle - \tfrac{1}{3}\right) \quad \text{(S3)}$$

with

$$A = 4\pi^2 l N \Delta\alpha / \lambda \quad \text{(S4)}$$

The induced birefringence intensity I_{BIR} is related in our geometry to ϕ and the probe intensity I_0 with the analyzer parallel to the probe polarization by,

$$\frac{I_{BIR}}{(I_0 + I_{BIR})} = \sin^2\frac{\phi}{2} \quad \text{(S5)}$$

Since in the present experiments ϕ is small and $I_0 >> I_{BIR}$, we can simplify this expression to

$$I_{BIR} = \frac{I_0 \phi^2}{4}. \quad \text{(S6)}$$

Substituting this expression for I_{BIR} into eq. S1 leads to a signal intensity I_S composed of the local oscillator intensity I_{LO}, the induced birefringence intensity I_{BIR} and the cross term,

$$I_S = I_{LO} + 2\sqrt{I_{LO} I_{BIR}}\cos\beta + I_{BIR} \quad \text{(S7)}$$

The time dependence in I_{BIR} originates from the induced alignment dynamics in eq. S3 by ($\left\langle \cos^2\theta \right\rangle - \tfrac{1}{3}$). Suppose a single rotational wave packet with rotational frequency ω_R is prepared with amplitude B and it is damped exponentially with a lifetime τ:

$$\left\langle \cos^2\theta \right\rangle - \tfrac{1}{3} = B e^{-t/\tau}\sin\omega_R t \quad \text{(S8)}$$

For H_2 we can expect a rotational period of approximately 90 fs and a damping time on the order of 100 ps, in other words approximately 10^3 times the rotational period! This presents a severe challenge to the experiment. If we choose a step size in the delay line of 10 fs to fully

resolve the rotational period, then we will need to take 10^4 steps to fully map out the damping time of 100 ps. With 1s per step, a minimum of 2.8 h per scan would be necessary. In order to trust the amplitudes measured in such an experiment, would require extraordinarily high stability of both the optical system and the crystal quality for an irradiation with 10^7 pump pulses (1 kHz). Fortunately, we can reduce these demands by a sharing of tasks between the second and third terms in eq. S7.

The third term in eq. S7 is usually called the homodyne intensity I_{HOM}, such that now,

$$I_{BIR} = I_{HOM} = \frac{I_0}{4}\left(Be^{-t/\tau}\sin\omega_R t\right)^2 \qquad \text{(S9)}$$

The squaring leads to a doubling in the frequency and to a period on the order of 45 fs. With the employed time resolution (pump 166 fs and probe 130 fs) these rotationally driven oscillations will be averaged out and eq. S9 becomes,

$$I_{HOM} = \frac{I_0}{8}B^2e^{-2t/\tau} \qquad \text{(S10)}$$

Obviously I_{HOM} is better suited to read the damping time constant τ because now the signal will decrease with a time constant of $\tau/2$. We will see that in the pH_2 crystal we must deal with superimposed but different close lying ω_R rotational periods. The coherent superposition of these rotational wavepackets leads to beatings with periods of approximately 10 ps, which are fully resolved in the I_{HOM} signals. Thus, I_{HOM} should deliver these beating patterns in a clean fashion. The second term in eq. S7 is in typically called the heterodyne intensity. The $\cos\beta$ term is varying with time delay from -1 to +1 and thus we find,

$$I_{HET} = \frac{4}{8}C\sqrt{I_{LO}I_{BIR}}Be^{-t/\tau}\sin\left(\omega_R t+\phi\right) \qquad \text{(S11)}$$

The experimental time resolution of ~200 fs will dampen out the detection efficiency for the 90 fs H_2 rotational signals, but in a less severe manner than for I_{HOM} and we take this into account by a adding a damping factor C in eq. S11. The magnitude of C will also depend on the step size in the pump-probe time delay, which given the laser time resolution will now be taken in the 50 fs time range. This leads to typical stability requirements in the 0.5 h time range, which as we will show are well fulfilled. The sinusoidal term in eq. S11 indicates that from I_{HET} we can read off the rotational periods directly in real time. Therefore, a fast Fourier transform (FFT) of I_{HET} is best suited to deliver the spectrum of relevant rotational periods. Use of the full information in I_{HET} requires finally an analytical simulation including the damping time τ_i. Due to the linear dependence of I_{HET} on E_{BIR}, the signal decays directly with a time constant of τ in contrast to I_{HOM}.

The balance between I_{HET} and I_{HOM} in the observed 2D OKE signals is steered by the local oscillator intensity I_{LO}. Increasing I_{LO} strengthens the I_{HET} component in the signal and vice versa. For very weak induced signals, I_{HOM} can fall below the detection limit. In this case, the signal can be amplified to become detectible in I_{HET}. This will be important for the interpretation of the TO phonon contributions to the measured signal in the pH_2 crystals. The temporal shortness of the employed laser pulses leads to a spectral bandwidth of typically ~2 nm at 389 nm. Suppose the polarizer-analyzer combination is optimally crossed at the center wavelength of the probe beam, then dispersion in the Glan-Taylor polarizer material leads to a leakage of probe intensity on both sides of the center wavelength. This represents a spectrally dependent local oscillator field with opposite signs in the red and blue wings, respectively. The spectrally dependent I_{LO} will then add to I_{LO} caused by the strain and inhomogeneities in the

cryogenic crystal. The total local oscillator intensity therefore is minimized along the probe center wavelength and then increases to both the blue and red wavelengths reaching a maximum that then decays in the far wings because of the limited bandwidth of the probe pulse. We record with the spectrometer a large spectral range simultaneously at every delay time step and store in one measurement I_{HOM} and I_{HET} for a significant variation of I_{LO}. Thus, using the 2D OKE experimental procedure we can sort out the appropriate combinations in the final analysis of the measurements.