Supplementary Information for

Interplay Between Hydrogen Bonding and Vibrational Coupling in Bulk N-methylacetamide

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Methods

**Water content in the NMA sample**

NMA is strongly hygroscopic and easily contaminated with water. The water bending mode frequency (~1635 cm$^{-1}$) lies in the spectral region of interest (1600-1700 cm$^{-1}$). To determine the actual water content in the sample, the OH-stretching mode of diluted water molecules at 3500 cm$^{-1}$ was used. FTIR spectra of two NMA samples with well-controlled water content (5 and 10% molar added) were measured and normalized to the OD of the NH-stretching mode of NMA at 3300 cm$^{-1}$ (Fig. S1). The linear fit to the data points constitutes the calibration curve from which we determined the water content in the experimental samples as 2.5 and 5% molar before and after the experimental session.

![Figure S1: Calibration curve](image)

Figure S1: Calibration curve: dependence of OD of the OH-stretching mode on water content. The stars show the data points for the molar water content of 5% and 10% added while the dots depict OD of the sample before and after the experimental session. The inset shows the NH/OH stretching region of the sample; all spectra are normalized to OD of NMA NH-stretching mode at 3300 cm$^{-1}$. 

**Linear FTIR spectra at different water concentrations**

The FTIR spectra of NMA in the Amide I region with different water content are shown in Fig. S2. The amplitude of the peak at \(\sim 1635 \text{ cm}^{-1}\) increases with increased water content so that it was identified as the bending mode\(^{55,56}\) of residual water in the NMA sample (blue line in Fig. S1). In this paper, we do not elaborate further on the water bending peak but remark that water presence might lead to slight broadening of the main Amide I peak (Fig. 1 in the main text). Also note that the increased water content decreases the peak at \(\sim 1680 \text{ cm}^{-1}\) that is assigned to a combined action of hydrogen-bonding and vibrational coupling. This suggests that the water molecules mediate NMA hydrogen bonding, in particular, in the chain structures (Fig. 2d in the main text).

![FTIR spectra of NMA samples with different water contents.](image)

Figure S2: FTIR spectra of NMA samples with different water contents.
Temperature jump

Isotropic transient pump-probe spectra calculated as \( I(\omega) = I_{||}(\omega) + 2I_{\perp}(\omega) \) (with \( I_{||}(\omega) \) and \( I_{\perp}(\omega) \) being the parallel and orthogonally polarized spectra, respectively) are shown in Fig. S3. At the early times, the spectrum is dominated by the bleaching and stimulated emission at the frequency of the \(|0>\rightarrow|1>\) transition (at \( \sim 1655 \text{ cm}^{-1} \)), and induced absorption at the frequency of \(|1>\rightarrow|2>\) transition (at \( \sim 1625 \text{ cm}^{-1} \)). At later times (> 1 ps), the spectral shape begins to deviate from that at the early times. We assign this effect to thermalization of the ground state, i.e. to the local temperature jump due to excited state relaxation. To prove this point, we calculated the difference absorption spectrum at two temperatures (Fig. S4a). As is evident from Fig. S4b, the pump-probe transient spectrum at a delay of 10 ps possesses a reasonable match with the difference between two absorption spectra of the sample measured with a temperature difference of \( \sim 3^\circ\text{C} \). Calculations based on direct conversion of the pump energy absorbed (\( \sim 2.5 \text{ \mu J} \)) into heat in the focal volume of \( \sim 10^{-7} \text{ cm}^{3} \), resulted in a temperature raise of \( \sim 5^\circ\text{C} \) which reasonably matches the pump-probe based value.

![Figure S3: Isotropic pump-probe transient spectra at different delay times (shown in legend).](image-url)
Excited state lifetime

To calculate the build-up time of the thermalization process, we analyzed the transient near the compensation point at 1644 cm\(^{-1}\) (Fig. S5, blue triangles). Fitting the transient with an exponential function yielded the rise time of 5±1 ps. Clearly, this time is very different from a much faster decay of the excited state (black and red curves). This makes us conclude that the excited state depopulation proceeds via an intermediate state, identified earlier as the NMA Amide II mode \(^{41}\). Therefore, we fit the transients at 1655 cm\(^{-1}\) (maximal bleach) and 1624 cm\(^{-1}\) (maximal induced absorption) with a three-level relaxation model \(^{41}\) where the intermediate state lifetime was fixed at 5 ps. From this fitting, the excited state lifetime was inferred as 450±100 fs. This, together with the thermalization time of 5±1 ps \(^{29}\) provides an experimental window for 2D IR spectroscopy as of ~2 ps. After this time, the 2D spectra will acquire a non-negligible contribution from the thermalization effects which not included in the theoretical model.

Figure S4: (a) FTIR absorption spectra of NMA at two representative temperatures. (b) Comparison of the isotropic transient absorption spectrum at 10 ps delay with the difference absorption spectrum.
Figure S5: Experimental transients (symbols) at a few representative wavelengths (shown in the legend), and the fits according to a three-level relaxation model (solid lines).

Two-dimensional infrared spectra

Fig. S6 and S7 show the comparison of the theoretical and experimental 2D IR spectra in the amide I region of bulk NMA at different waiting times for parallel and perpendicular polarization, respectively. The spectra were obtained as described in the methods sections at the end of the main paper. A subtle presence of a ridge, due to the couplings, is identified in the theoretical 2D IR, at a pump/probe frequency of ($\omega_1$=1655 cm$^{-1}$, $\omega_3$=1695 cm$^{-1}$) already at $t_2$=0 fs. These are not visible in the experimental 2D IR at $t_2$=0 fs, but as the waiting time is increased the 2D IR spectra acquires a more square shape, due to the growth of intensity at these off-diagonal positions.
Figure S6: Two-dimensional infrared spectra of bulk N-methylacetamide at 300 k for parallel polarization. Equidistant contour lines are drawn with 10% steps from the maximum; red colors indicate bleach, while blue colors indicate absorption.
Figure S7: Two-dimensional infrared spectra of bulk N-methylacetamide at 300 k for orthogonal polarization. Equidistant contour lines are drawn with 10% steps from the maximum; red colors indicate bleach, while blue colors indicate absorption.

Anisotropy Decay

To evaluate a possible influence of water to the Amide I anisotropy, the anisotropy decay was calculated at the three following frequencies: at the Amide I peak, at red and blue flanks of the Amide I peak (Fig. S8). The anisotropy at the red flank (i.e. closer to the water bend mode frequency) decays slower in comparison to the anisotropy at the blue flank; a similar trend is supported by the theoretical data. Therefore, the water bend does not contribute substantially into anisotropy decay. The faster dynamics at the blue side which is also evident in the theory, can be understood as follows. The anti-symmetric nature of the vibrational states at the high-energy peak (around 1680 cm⁻¹ in theory and
1690 cm\(^{-1}\) in experiment; see Figure 2 of the main text) results in transition dipoles not aligned with the hydrogen bond chain direction, which leads to a reduced suppression of the anisotropy decay due to diffusion of vibrational excitation. Furthermore, the non-hydrogen-bonded f-NMA and d-NMA species may be rotating slightly faster than the other configurations.

Figure S8: Anisotropy decays of the (a) red flank (b) center and (c) blue flank of the Amide I mode, calculated from the experimental (open symbols) and theoretical coupled (filled symbols) 2D IR spectra. The \((\omega_1,\omega_3)\) frequencies at which the anisotropy was calculated, are shown in the legends.

**Theoretical methods**

The Hamiltonian in Eq. (1) is block diagonal with a ground state block (g), an excited state block (e), and a double excited state block (f), and each block can be treated separately. The time-dependent Schrödinger equation is solved for each block, assuming that the excitations are localized on the amide I modes, and the integration is done in small time steps in which the Hamiltonian is considered constant. The time-evolution matrices, \(U(t, 0)\), are obtained for each excitation, which consequently enables the calculation of the response functions.
The population transfer defined as the probability of finding a vibration excited at time 0 to still be excited at time $t$ is determined from the equation:

$$P(t) = \sum_i \langle |U_{ii}(t, 0)|^2 \rangle,$$  \hspace{1cm} (Eq. S1)

where the brackets, $\langle \ldots \rangle$, represents the ensemble average. This is obtained by summing over the contributions from configurations generated along the MD simulation trajectory.

The linear absorption spectrum can be obtained by the Fourier transform of the response function, where $t_1 = \tau_1 - \tau_2$ is the relaxation factor that accounts for an ad hoc vibrational time $T_1$ for the single excited state. This relaxation can also be thought of as an appodization function used to slightly smoothen the spectra, without changing it significantly.

$$I(\omega) = \text{Im} \int_0^\infty dt_1 \frac{i}{\hbar} \langle \mu^g e(\tau_2) U^{ee}(\tau_2, \tau_1) \mu^e g(\tau_1) \rangle e^{-i \omega t_1} \Gamma_{LA}(t_1)$$  \hspace{1cm} (Eq. S2)

Here $\Gamma_{LA}(t_1) = e^{-t_1/T_1}$ is the exponential appodization function.

In a 2D IR experiment the three laser pulses are separated by a short time delays, namely $t_1$ is the delay between the first and second laser pulse, while $t_2$ is the delay between the second and the third pulses. The system evolves in a coherent superposition during $t_1$, since the first laser pulse brings the system to a coherent superposition between the ground state and the excited state. After the second laser pulse the system is either brought back to the ground state, to a coherent superposition between two single excited states, or to a single excited state population, where the system evolve during $t_2$. With the third laser interaction the system is brought to a coherence between the ground state and the single excited state, or to a coherence between a single excited state and a doubly excited state. The time domain signal is then obtained and Fourier transformed with respect to $t_1$ and $t_3$ giving rise to the
frequency domain signal $S(\omega_1, \omega_2, \omega_3)$. The nonlinear response functions needed to calculate a 2D IR spectra are $^{19, 32}$:

\[
S_{GB}^{(I)}(t_3, t_2, t_1) = -\left(\frac{i}{\hbar}\right)^3 \langle \mu^{ge}(\tau_1)U^{ee}(\tau_1, \tau_2)\mu^{fg}(\tau_2)U^{ee}(\tau_4, \tau_3)\mu^{fg}(\tau_3)\rangle e^{i\Gamma} (t_3, t_2, t_1)
\]

\[
S_{SE}^{(I)}(t_3, t_2, t_1) = -\left(\frac{i}{\hbar}\right)^3 \langle \mu^{ge}(\tau_1)U^{ee}(\tau_1, \tau_2)\mu^{fg}(\tau_3)\mu^{fg}(\tau_4)U^{ee}(\tau_4, \tau_2)\rangle e^{i\Gamma} (t_3, t_2, t_1)
\]

\[
S_{EA}^{(I)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \langle \mu^{ge}(\tau_1)U^{ee}(\tau_1, \tau_2)\mu^{ef}(\tau_4)\mu^{ef}(\tau_3)\mu^{fg}(\tau_4)U^{ee}(\tau_3, \tau_2)\rangle e^{i\Gamma} (t_3, t_2, t_1)
\]

\[
S_{GB}^{(II)}(t_3, t_2, t_1) = -\left(\frac{i}{\hbar}\right)^3 \langle \mu^{ge}(\tau_4)U^{ee}(\tau_4, \tau_3)\mu^{fg}(\tau_3)\mu^{fg}(\tau_2)U^{ee}(\tau_2, \tau_1)\rangle e^{i\Gamma} (t_3, t_2, t_1)
\]

\[
S_{SE}^{(II)}(t_3, t_2, t_1) = -\left(\frac{i}{\hbar}\right)^3 \langle \mu^{ge}(\tau_2)U^{ee}(\tau_2, \tau_3)\mu^{fg}(\tau_3)\mu^{fg}(\tau_4)U^{ee}(\tau_4, \tau_1)\rangle e^{i\Gamma} (t_3, t_2, t_1)
\]

\[
S_{EA}^{(II)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \langle \mu^{ge}(\tau_2)U^{ee}(\tau_2, \tau_3)\mu^{ef}(\tau_4)\mu^{ef}(\tau_3)\mu^{fg}(\tau_4)U^{ee}(\tau_3, \tau_1)\rangle e^{i\Gamma} (t_3, t_2, t_1)
\]

(Eq. S3)

where $\tau_1, \tau_2, \tau_3, \tau_4$ denote the absolute time pints, where $t_3 = \tau_4 - \tau_3, t_2 = \tau_3 - \tau_2$, and $t_2 = \tau_2 - \tau_1$.

The signal has been accounted in two detection directions, giving rise to a rephrasing and a non-rephrasing signal, represented by $I$ and $II$. To suppress noise in the spectra appodization factors $\Gamma(t_3, t_2, t_1)$ are included:

\[
\Gamma(t_3, t_2, t_1) = e^{-(t_3+t_2+t_1)/\tau_1}.
\]  

(Eq. S4)

The 2DIR spectra are given by the sum of the imaginary part of the rephrasing and non-rephrasing signals.

\[
S^{(I)}(\omega_3, t_2, \omega_1) = \int_0^\infty \int_0^\infty \left( S_{GB}^{(I)}(t_3, t_2, t_1) + S_{SE}^{(I)}(t_3, t_2, t_1) + S_{EA}^{(I)}(t_3, t_2, t_1) \right) e^{i(\omega_3 t_3 - \omega_1 t_1)} dt_3 dt_1
\]  

(Eq. S5)

\[
S^{(II)}(\omega_3, t_2, \omega_1) = \int_0^\infty \int_0^\infty \left( S_{GB}^{(II)}(t_3, t_2, t_1) + S_{SE}^{(II)}(t_3, t_2, t_1) + S_{EA}^{(II)}(t_3, t_2, t_1) \right) e^{i(\omega_3 t_3 + \omega_1 t_1)} dt_3 dt_1
\]  

(Eq. S6)
\[ I_{2\omega}(\omega_2, t_1, \omega_1) = \text{Im} \left( S^I(\omega_3, t_2, \omega_1) + S^{II}(\omega_3, t_2, \omega_1) \right) \]  

(Eq. S7)

The anisotropy is given by the normalized difference of the parallel and perpendicular polarized signals, and it is useful to study rotational dynamics.

\[ r(t) = \frac{S_{||}(t) - S_{\perp}(t)}{S_{||}(t) + 2S_{\perp}(t)} \]  

(Eq. S8)

The exact locations, where the intensities were taken from are given in the main paper. If the anisotropy is only determined by molecular reorientation it will behave as the orientational correlation function, which is given by:

\[ R(t) = \frac{1}{2} \left( 3 \cos^2 \Theta(t) - 1 \right). \]  

(Eq. S9)

Here the angle between the transition dipoles at two times separated by the delay time \( t \) is given by \( \Theta \).

**Analysis of the Dynamics**

Table S1 contains the fit parameters of the fits (Eqs. S10 and S11) of the orientational correlation function, \( R(t) \), and the population transfer, \( P(t) \). The biexponential, and the gaussian plus exponential fit parameters are defined as:

\[ R(t) = A_1 e^{-t/T_1} + A_2 e^{-t/T_2}. \]  

(Eq. S10)

\[ P(t) = A_1 e^{-t/T_1} + A_2 e^{-t^2/T_2^2}. \]  

(Eq. S11)

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Table S1: Fitting parameters for the orientational correlation function, and scaled population transfer.

The Fig. S9 presents the joint angular-radial distribution function between the CO bonds on the NMA molecules. The peak centered at $\cos(\Theta)=1$, $r=0.5$ nm represent the aligned NMA molecules in the hydrogen bonded chains. The largest deviations in the angle from the straight chain (0°) are about 60°. An isotropic distribution in the given representation would be a $\sin(\Theta)$ function giving no probability for $\cos(\Theta)=1$ and $\cos(\Theta)=-1$ and largest probability at $\cos(\Theta)=0$. 
Figure S9: The joint angular-radial distribution function for the CO configurations. \( \Theta \) stands for the angle between pairs of CO bonds, with \( \cos(\Theta)=1 \) and \( \cos(\Theta)=-1 \) representing parallel and anti-parallel bonds, respectively. The distance between the middle of the CO bond pairs, \( r \), has a value of 0.5 nm for hydrogen bonded pairs.