Supplementary Materials

Bond Connectivity Measured via Relaxation-Assisted Two-Dimensional Infrared Spectroscopy

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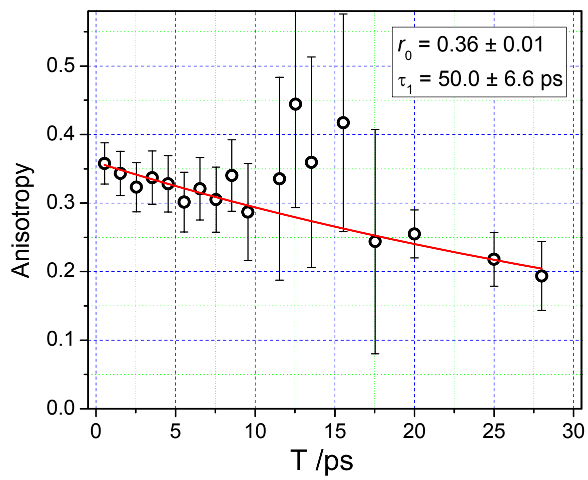

Fig. S1. Anisotropy of the CN diagonal peak as a function of waiting time *T*. The noise increase towards 18 ps is cased by a decay of the magic angle signal at 18 ps by ca. 16 times. The anisotropy was carefully measured at three delay points at 20, 25, and 28 ps by extremely long accumulation: measurements with alternating polarizations, parallel and perpendicular, were repeated 3 times for all points. The decay time, 50.0 ± 6.6 ps was obtained from the fit with an exponential decay function.

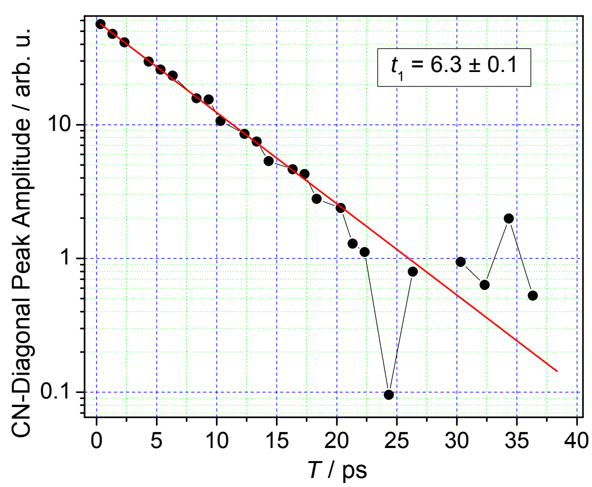

Fig. S2. Amplitude of the diagonal CN peak measured at magic angle polarization as a function of waiting time *T*. The decay time of 6.3 ± 0.1 ps was obtained from the fit with an exponential decay function.

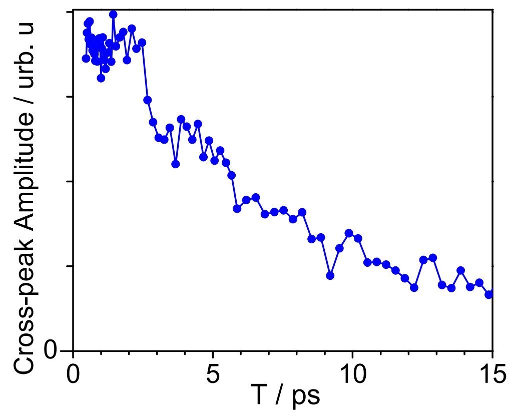

Fig. S3. Amplitude of the Am-I / 1369 cm^{-1} cross-peak as a function of time delay, *T*. A plateau is observed until ca. 2 ps delay.

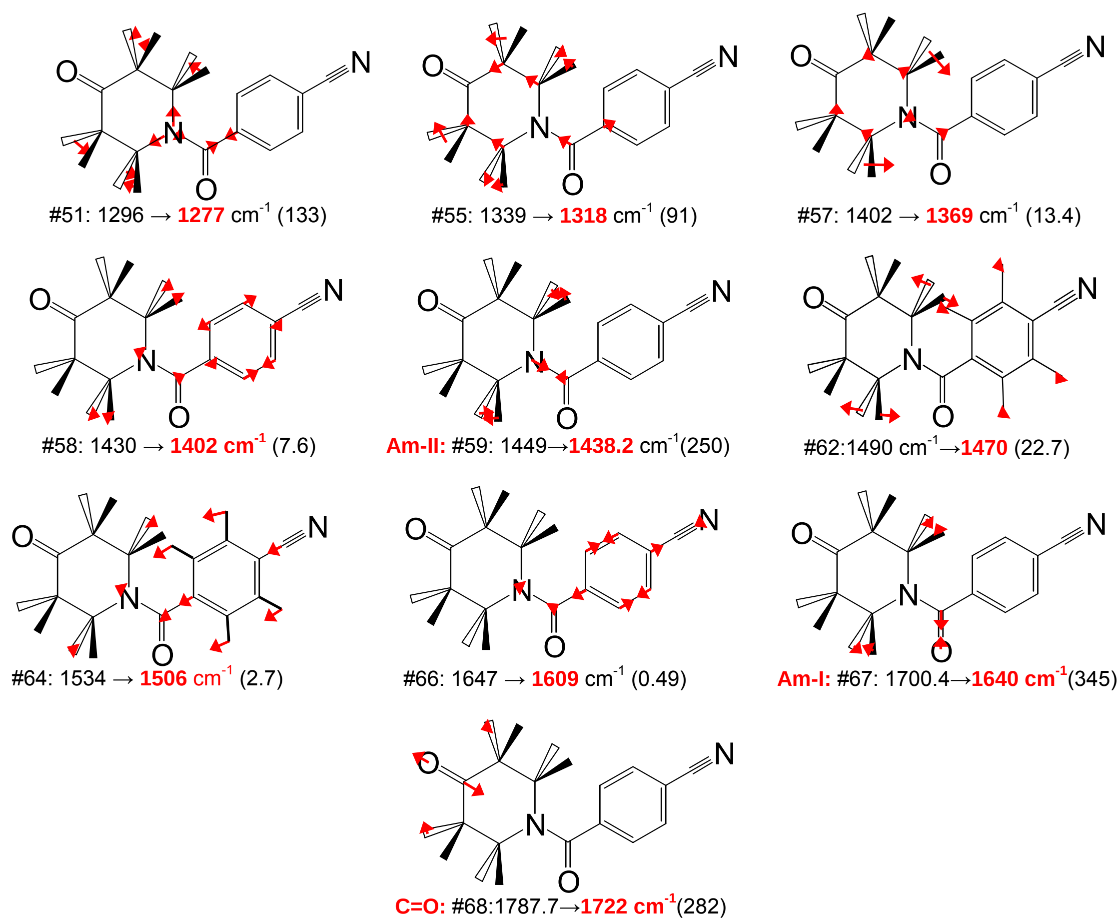

Fig. S4. Normal mode displacements of the modes of PBN in the gas phase obtained by DFT calculations with B3LYP functional and 6-311++G(d,p) basis set. The mode number, and mode assignment (in red) is given for each mode. Computed IR intensities are shown in parentheses.

Calculation of Corrections to T_{max} Values Caused by Orientational Motion

Despite rather large value of the rotational time of PBN in chloroform (τ_{or} = 50.0 ± 6.6 ps, see Fig. S1) the orientational motion slightly affects the parameters measured obtained from zzzz polarization data sets. Although this influence on both T_{max} and γ is less than 10% for all cross-peaks measured, we used the procedure outlined below for every cross peak and calculated T_{max} and γ values that are independent of orientational motion. The orientational motion contribution to the third order signal can be expresses as

$$I_{ZZZZ} = I_M (1 + 0.4 \cdot (3\overline{\cos^2(\theta)} - 1) \cdot e^{-T/\tau_{or}}) \quad (1)$$

where I_M is the orientation independent contribution (Magic angle), θ is the angle between transition dipoles of the two interacting modes, and T is the waiting time.

For the mode pairs with the known angle between transition dipoles, the I_M data sets were constructed using Eq. 1 and then fitted with two-exponential function yielding the T_{max} and γ values. For the modes in the fingerprint region the direction of the transition moments are currently unavailable. While the IR spectrum generated via DFT harmonic calculations gives a rough understanding of the mode compositions, the modeling does not provide a unique assignment. We are also confident that the anharmonic shifts in the fingerprint region will modify the modeled spectrum substantially. Therefore, the experimental data sets, I_{ZZZZ}, for such mode pairs were tested against maximum effect of orientational motion on the T_{max} value, by constructing two I_M data sets assuming θ = 0° and θ = 90°. The deviations obtained to the T_{max} and γ values were then incorporated into their error bars.