Supplementary Information

Two-dimensional infrared spectroscopy from the gas to liquid phase: Density dependent *J*-scrambling, vibrational relaxation, and the onset of liquid character

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2DIR spectra and CLS decays of N_2O in SF_6 at ρ^* = 0.86:

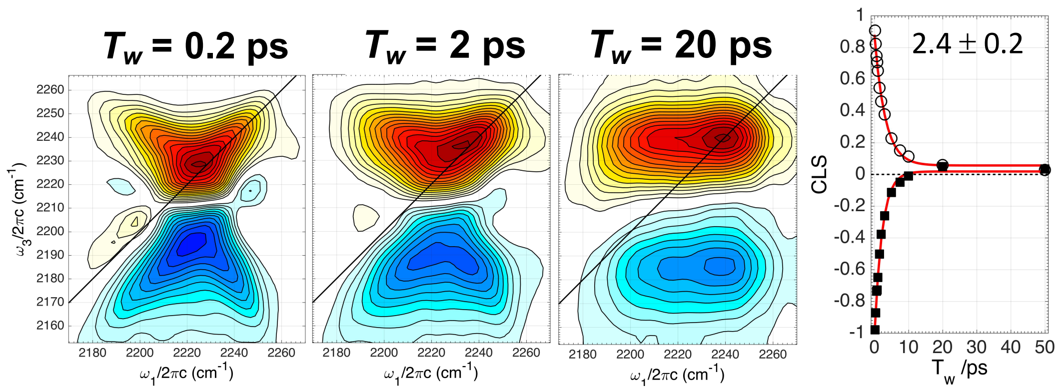

Figure S1. 2DIR spectra and corresponding CLS decays of N_2O ν_3 in SF_6 at ρ^* = 0.86. Red contours denote positive-going GSB-SE signals and blue contours denote negative-going ESA signals.

Hard sphere collision time determination:

The mean free time for a single N_2O molecule is calculated using a hard sphere model at the given state point density of SF_6 and the mean speed is based on a Maxwell-Boltzmann speed distribution for an ideal gas. The collision frequency, ν_{coll}, is given by:

$$\nu_{\mathrm{coll}} = N_{\mathrm{A}} \rho_{\mathrm{SF_6}} \pi \left(r_{\mathrm{SF_6}} + r_{\mathrm{N_2O}}\right)^2 \sqrt{\frac{8RT}{\pi \mu_{\mathrm{N_2O}}}} \qquad \text{(Eq. S8)}$$

where N_{A} is the Avogadro constant (6.022×10^{23} mol^{-1}), $\rho_{\mathrm{SF_6}}$ is the respective density of SF_6[1], $r_{\mathrm{SF_6}} = 2.326 \times 10^{-10}$ m^2 and $r_{\mathrm{N_2O}} = 1.94 \times 10^{-10}$ m^3 are the radii of SF_6 and N_2O, respectively, R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), T is the temperature of the solution, and $\mu_{\mathrm{N_2O}} = 0.03382$ kg mol^{-1} is the reduced mass of N_2O. The mean free time between collisions is then calculated as the inverse of the collision frequency:

$$\tau_{\mathrm{coll}} = \frac{1}{\nu_{\mathrm{coll}}} \qquad \text{(Eq. S9)}$$

FTIR spectra of N_2O in liquid SF_6 (ρ^* = 1.87):

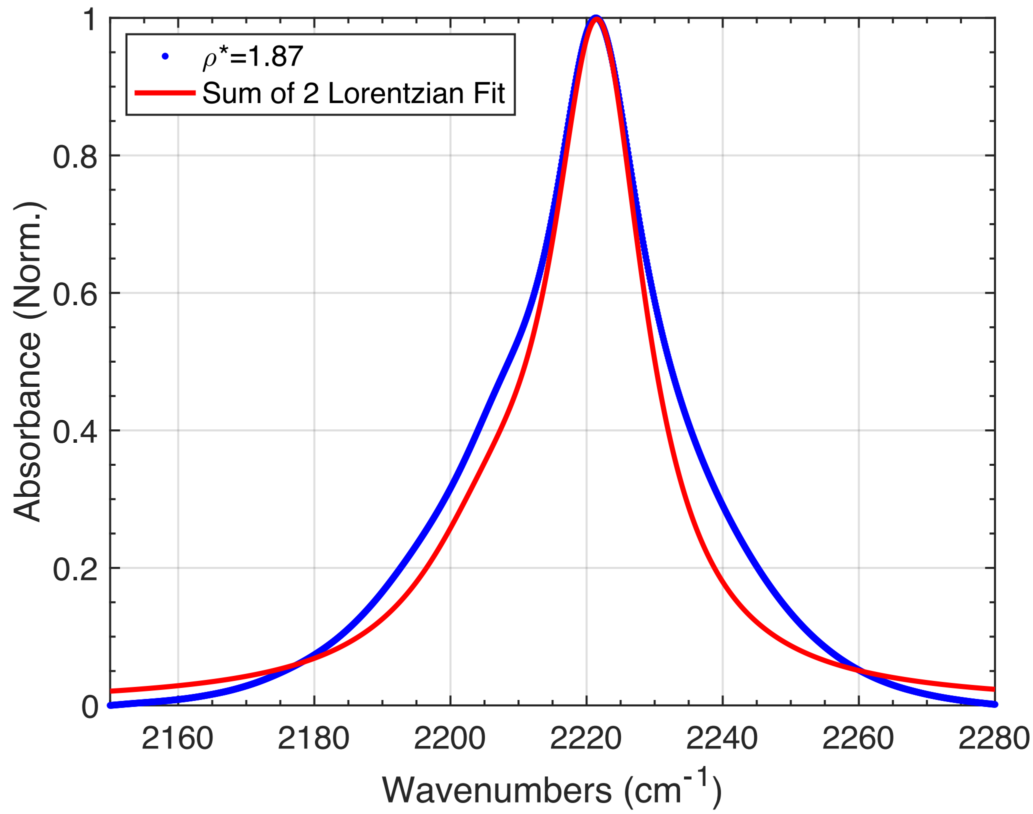

Figure S2. Observed (blue) FTIR spectrum of the ν_3 asymmetric stretch mode of N_2O in ρ^* = 1.87 (liquid) SF_6 (20°C, 22 atm, 0.92T_c, 0.60P_c). A sum of 2 Lorentzian fit (red) is overlaid with peaks centered at 2221 cm^{-1}, the observed ν_3 peak maximum, and 2209 cm^{-1}, the frequency of the red-shifted N_2O bending (ν_2) hot band absorption ($\nu_2 \rightarrow \nu_2 + \nu_3$) to demonstrate the dominant Lorentzian character of this absorption feature.

Magic angle, one-color, pump-probe responses of the ν_3 $v = 1$ excited state of N_2O in SF_6:

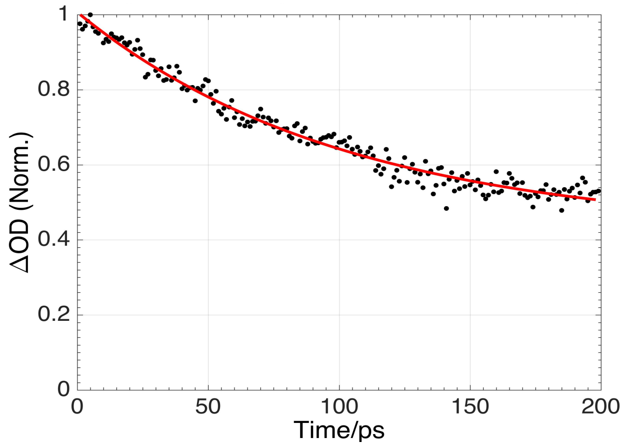

Figure S3. Magic angle pump-probe spectrum of N_2O ν_3 in SF_6 at $\rho^* = 0.16$.

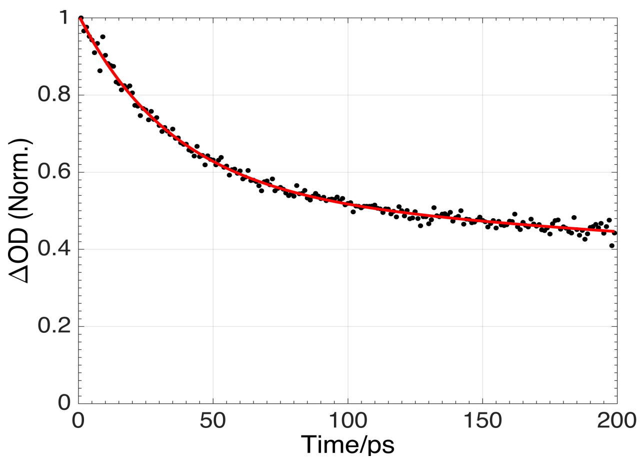

Figure S4. Magic angle pump-probe spectrum of N_2O ν_3 in SF_6 at $\rho^* = 0.30$.

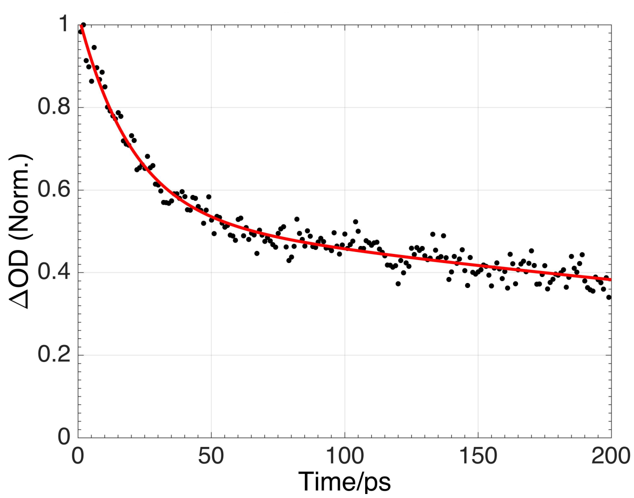

Figure S5. Magic angle pump-probe spectrum of N_2O ν_3 in SF_6 at $\rho^* = 0.86$.

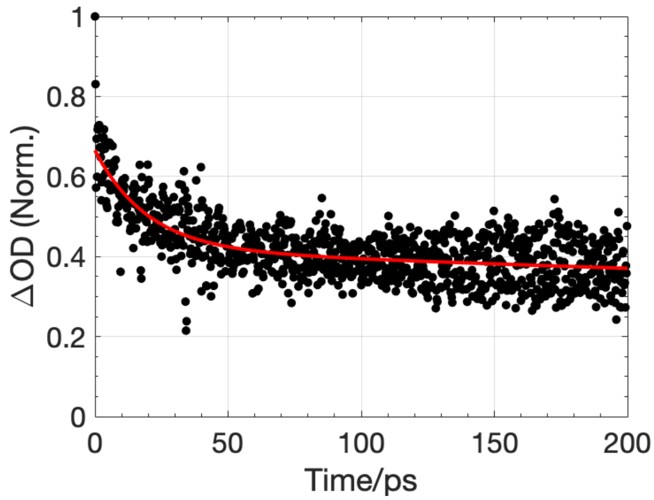

Figure S6. Magic angle pump-probe spectrum of N_2O ν_3 in SF_6 at $\rho^* = 0.99$.

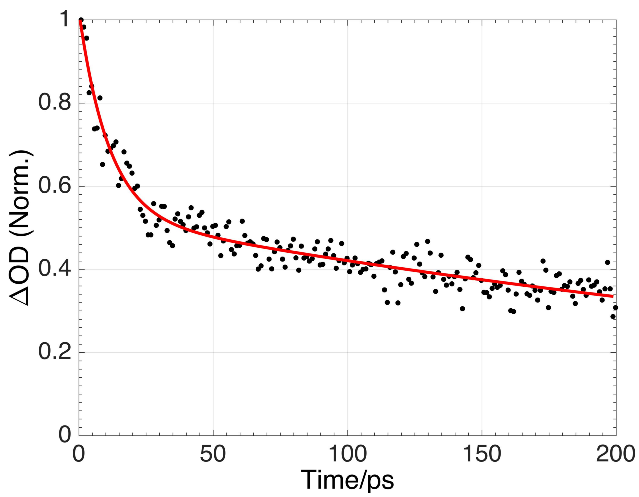

Figure S7. Magic angle pump-probe spectrum of N_2O ν_3 in SF_6 at ρ^* 1.36.

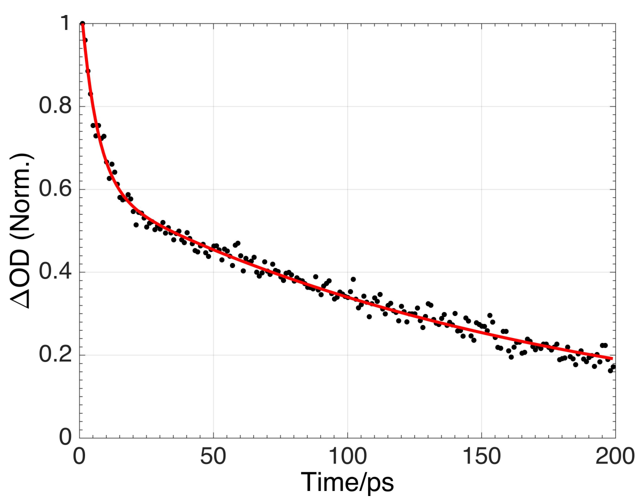

Figure S8. Magic angle pump-probe spectrum of N_2O ν_3 in SF_6 at ρ^* 1.87.

Rate equations for this one-color N_2O ν_3 pump-probe response in SF_6 corresponding to mechanism:

The differential rate equations for the N_2O ν_3 pump-probe responses in SF_6 are given by:

$$\frac{dN_{001}}{dt} = -\frac{N_{001}(t)}{T_1} \quad \text{(Eq. S1)}$$

$$\frac{dN_{100}}{dt} = \frac{N_{001}(t)}{T_1} - \frac{N_{100}(t)}{T_2} \quad \text{(Eq. S2)}$$

$$\frac{dN_{000}}{dt} = \frac{N_{100}(t)}{T_2} \quad \text{(Eq. S3)}$$

The time-dependent populations within this model are given by:

$$N_{001}(t) \propto e^{-t/T_1} \quad \text{(Eq. S4)}$$

$$N_{100}(t) \propto \frac{T_2}{T_2 - T_1} e^{-t/T_2} - \frac{T_2}{T_2 - T_1} e^{-t/T_1} \quad \text{(Eq. S5)}$$

$$N_{000}(t) \propto 1 - \frac{T_2}{T_2 - T_1} e^{-t/T_2} + \frac{T_1}{T_2 - T_1} e^{-t/T_1} \quad \text{(Eq. S6)}$$

The corresponding normalized pump-probe signal at delay time t is correspondingly given by:

$$\Delta OD(t) = C_1 e^{-k_1 t} - C_2\left(\frac{k_1}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t}\right) \quad \text{(Eq. S7)}$$

where C_1 and C_2 are proportional to the $(00^0 0) \rightarrow (00^0 1)$ and $(10^0 0) \rightarrow (10^0 1)$ absorption cross sections respectively, and k_1 and k_2 are the inverse lifetimes of the ν_3 and ν_1 N_2O states, respectively. The fit parameters, i.e., the coefficients and lifetimes, are given for all densities in Table 2.

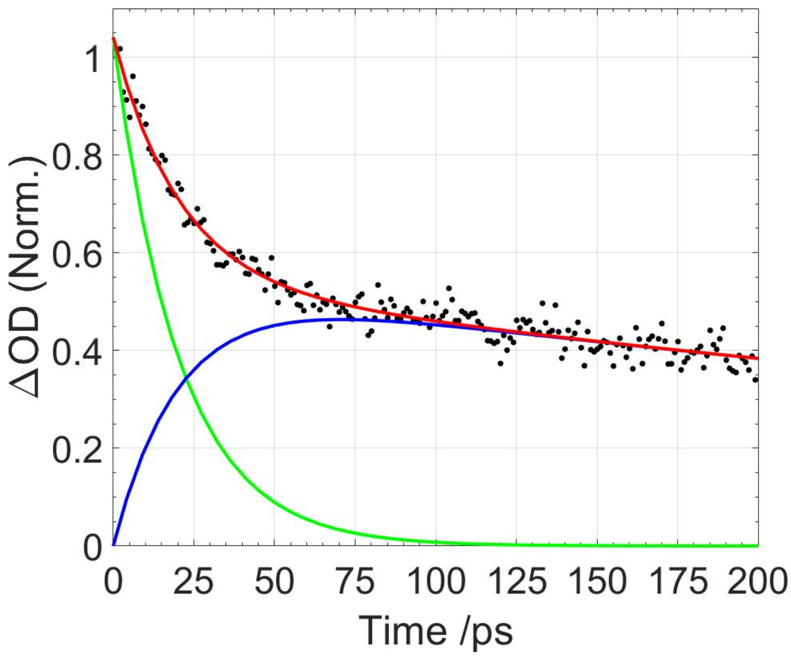

Figure S9. Representative best-fit to the ν_3 resonant pump-probe response in $\rho^* = 0.86$ SF_6 and the component kinetics for the ν_3 vibrational energy relaxation and the subsequent ν_1 population build up

References:

1. NIST Chemistry WebBook. 2001 ed.; National Institute of Standards and Technology: Gaithersburg MD.
2. Jameson, C. J.; Jameson, A. K., Effective collision cross sections for SF6 from nuclear magnetic relaxation. *The Journal of Chemical Physics* **1988,** *88* (12), 7448-7452.
3. Yardley, J. T., *Introduction to Molecular Energy Transfer*. Academic Press: New York, 1980.