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$_2$O in SF$_6$ at $\rho^* = 0.86$:

![2DIR spectra and CLS decays](image)

**Figure S1.** 2DIR spectra and corresponding CLS decays of N$_2$O $\nu_3$ in SF$_6$ at $\rho^* = 0.86$. 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 N₂O molecule is calculated using a hard sphere model at the given state point density of SF₆ and the mean speed is based on a Maxwell-Boltzmann speed distribution for an ideal gas. The collision frequency, \( \nu_{\text{coll}} \), is given by:

\[
\nu_{\text{coll}} = N_A \rho_{SF_6} \pi (r_{SF_6} + r_{N_2O})^2 \frac{8RT}{\pi \mu_{N_2O}}
\]  
(Eq. S8)

where \( N_A \) is the Avogadro constant \((6.022 \times 10^{23} \text{ mol}^{-1})\), \( \rho_{SF_6} \) is the respective density of SF₆⁻¹, \( r_{SF_6} = 2.326 \times 10^{-10} \text{ m}^2 \) and \( r_{N_2O} = 1.94 \times 10^{-10} \text{ m}^3 \) are the radii of SF₆ and N₂O, respectively, \( R \) is the universal gas constant \((8.3145 \text{ J mol}^{-1} \text{ K}^{-1})\), \( T \) is the temperature of the solution, and \( \mu_{N_2O} = 0.03382 \text{ kg mol}^{-1} \) is the reduced mass of N₂O. The mean free time between collisions is then calculated as the inverse of the collision frequency:

\[
\tau_{\text{coll}} = \frac{1}{\nu_{\text{coll}}}
\]  
(Eq. S9)
FTIR spectra of N\(_2\)O in liquid SF\(_6\) (\(\rho^* = 1.87\)):

**Figure S2.** Observed (blue) FTIR spectrum of the \(\nu_3\) asymmetric stretch mode of N\(_2\)O in \(\rho^* = 1.87\) (liquid) SF\(_6\) (20\(^\circ\)C, 22 atm, 0.92\(T_c\), 0.60\(P_c\)). A sum of 2 Lorentzian fit (red) is overlaid with peaks centered at 2221 cm\(^{-1}\), the observed \(\nu_3\) peak maximum, and 2209 cm\(^{-1}\), the frequency of the red-shifted N\(_2\)O bending (\(\nu_2\)) 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 $\nu_3$ $\nu = 1$ excited state of N$_2$O in SF$_6$:

Figure S3. Magic angle pump-probe spectrum of N$_2$O $\nu_3$ in SF$_6$ at $\rho^* = 0.16$.

Figure S4. Magic angle pump-probe spectrum of N$_2$O $\nu_3$ in SF$_6$ at $\rho^* = 0.30$.

Figure S5. Magic angle pump-probe spectrum of N$_2$O $\nu_3$ in SF$_6$ at $\rho^* = 0.86$. 
Figure S6. Magic angle pump-probe spectrum of N$_2$O $\nu_3$ in SF$_6$ at $\rho^*$ = 0.99.

Figure S7. Magic angle pump-probe spectrum of N$_2$O $\nu_3$ in SF$_6$ at $\rho^*$ 1.36.

Figure S8. Magic angle pump-probe spectrum of N$_2$O $\nu_3$ in SF$_6$ at $\rho^*$ 1.87.
Rate equations for this one-color N₂O ν₃ pump-probe response in SF₆ corresponding to mechanism:

The differential rate equations for the N₂O ν₃ pump-probe responses in SF₆ 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 (00^00) \(\rightarrow\) (00^01) and (10^00) \(\rightarrow\) (10^01) absorption cross sections respectively, and \(k_1\) and \(k_2\) are the inverse lifetimes of the ν₃ and ν₁ N₂O 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 $\nu_3$ resonant pump-probe response in $\rho^* = 0.86$ SF$_6$ and the component kinetics for the $\nu_3$ vibrational energy relaxation and the subsequent $\nu_1$ population build up
References:

1. NIST Chemistry WebBook. 2001 ed.; National Institute of Standards and Technology: Gaithersburg MD.