Supporting Information:
State-to-state Rate Coefficients for NH$_3$-NH$_3$
Collisions from Pump-Probe Chirped-Pulse Experiments

Christian P. Endres,*† Paola Caselli,† and Stephan Schlemmer‡

†Max-Planck-Institut für extraterrestrische Physik, Garching, Germany
‡I. Physikalisches Institut der Universität zu Köln, Köln, Germany

E-mail: cendres@mpg.de

Contents

1 Chirped-Pulse Fourier Transform Spectrometer S-2
2 Measurements S-2
3 Global Fit S-4
References S-4
1 Chirped-Pulse Fourier Transform Spectrometer

The spectrometer at the Center for Astrochemical Studies at MPE is based on the chirped-pulse technique coupled with a K-band waveguide. It uses a 5 GHz, 2-channel arbitrary waveform generator (Keysight M8190A) as a source to generate probe (chirp) and pump pulses. Its I/Q signals are upconverted in an I/Q mixer (Marki Microwave MLIQ-1845L) by the power splitted output (Marki Microwave PD-0140) of a phase-locked 70 GHz signal generator (Keysight PSG E8257D). A 4 W solid-state amplifier (Microsemi C1826-36-T964) with internal high-speed pulser, whose output is protected by a circulator (DiTom D3C1826K), amplifies the signal before it is fed into one end of a 1.5 m long K-band waveguide. The other end is connected to a low noise amplifier (B&Z BZR-P0226500-351032-182525), whose input is protected by a pin diode switch (Kratos F9022). A second I/Q mixer downconverts the signal. Both outputs are again amplified (MiniCircuit ZX60-V62+) and connected via filters (Mini-Circuits SHP-100A+; 0.1-3.0 GHz) to the inputs of a 2-channel digitizer (Acqiris M9310A). The arbitrary waveform generator, digitizer and signal generator are all locked to a rubidium reference (SRS FS725), whose 1 PPS signal is used to trigger the pulse sequence. The sample marker outputs of the arbitrary waveform generator trigger the acquisition in the digitizer as well as a delay generator which controls the protection switch and the amplifier pulsar. Two pressure ports are mounted close to both ends of the waveguide. Capacitance gauges (Pfeiffer CMR 365, 0.1 hPa F.S.) are connected to both of them followed by needle valves that control the flow of the molecular sample through the waveguide towards the turbo molecular pump to guarantee a constant pressure in the waveguide.

2 Measurements

Measurements have been conducted at pressures ranging from 4 to 30 µbar by adjusting a slow stable flow in the order of 10^{-5} mbar l/s of the ammonia sample (Air Liquide N38, 99.98%) through the waveguide. The pressure was continuously read during the experiment.
Table S1: Experimental conditions covered by the measurements used in the global fit.

| Parameter                        | Range         |
|----------------------------------|---------------|
| Pressure                         | 4-30 µbar     |
| Sweep direction (chirp)           | up / down     |
| Field strength $E$                | 200 V/m, 400 V/m |
| Max. pump pulse length $\tau_\pi$| 50 µs         |
| Pumped inversion doublets         | $J = 1 - 6, K = 1$ |

Its gradient between both ends was typically 1 µbar, and its stability about 0.5 µbar.

In contrast to previous, similar experiments (Oka$^{52}$), a rather low power has been selected for the pump pulses, in order to limit radiative excitation of transitions that are close in frequency to the frequency of the pump (off-resonant excitation). Measurements have been performed using power levels of 12.25 µW and 24.5 µW (combined AWG output) which, according to instrument specifications correspond to electric field strengths inside the waveguide of $E \approx 200$ V/m and $E \approx 400$ V/m, respectively. These values are in good agreement with the $E \approx 390$ V/m and $E \approx 430$ V/m derived from the effective $\pi$-pulse lengths $\tau_{pi} = 600$ ns and $\tau_{pi} = 380$ ns experimentally observed for the (3,1) - and (2,1) - transitions ($P_{out}^{AWG} = 24.5$ µW). The pump pulse length has been increased up to $\tau_\pi$ and in more than half of the measurements up to 50 µs. Damped Rabi oscillations are observed in the latter measurements.

200 ns long and 5 GHz-broad chirped pulses have been applied that covered both the pumped $(J, K)$ transition, as well as the $(J \pm 1, K)$ transitions. The frequency of the signal generator was 22.0 GHz or 20.5 GHz and was located in the center of the band. Each pump-probe experiment was repeated, changing the direction of the frequency sweep from upwards to downwards. The combined output power of the AWG signals (both channels) have been set to 2.45 mW, which corresponds to $E \approx 4000$ V/m in the waveguide following the instrument specifications. Under these conditions, inversion doublets with $J=1-6$ and $K=1-3$ have been studied (pumped), but of those only measurements altering $K=1$ are presented in this work.
3 Global Fit

The temporal evolution of the systems studied in this work has been simulated numerically. The simulations are based on optical Bloch equations$^{33}$ in which the phenomenological rates $T_{1}^{-1}$ are replaced by a set of rate equations (master equation). The global fit uses one common set of parameters to calculate the temporal evolution of each system and to fit the experimental data.

In total, 29 parameters are included in the global fit:

- for each inversion doublet addressed by the pump pulse ($J=1-6$) the Rabi frequency (6) and a coherence loss rate (6) is included

- for each inversion doublet the rate coefficient for parity-changing collisions within the doublet (6) is included

- for each collision induced transition with ($\Delta J = 1$), one rate coefficient for parity-changing (5) and one rate coefficient for parity-conserving (5) collisions are included.

- one pressure-independent coherence loss rate (1) is included

Rate coefficients involving the inversion doublets (7, 1) are not included in the fit, because this inversion transition has not been observed. Therefore, rate coefficients determined in the fit for higher $J$ are not presented in Tab. 2 of the letter.

References

(S1) Brown, G. G.; Dian, B. C.; Douglass, K. O.; Geyer, S. M.; Shipman, S. T.; Pate, B. H. A broadband Fourier transform microwave spectrometer based on chirped pulse excitation. *Review of Scientific Instruments* **2008**, *79*, 053103.

(S2) Oka, T. Microwave Studies of Collision-Induced Transitions between Rotational Levels. IV. Steady-State Measurements in NH$_3$. *J. Chem. Phys.* **1968**, *48*, 4919–4928.
(S3) Grabow, J.-U. *Handbook of High-resolution Spectroscopy*; John Wiley & Sons, Ltd, 2011; pp 724–800.