Measurement of V-V vibrational relaxation rates in \textit{ortho-para} collisions in N$_2$ by double resonance stimulated Raman spectroscopy

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We present measurements of vibration (V-V) collisional relaxation rates between the v=0 and v=1 states in the molecule of nitrogen (N$_2$) at 77, 150, 225, and 300K.

The experimental setup is based on a sequential pump-probe scheme with variable delay in which both the pump and the probe stages make use of the stimulated Raman effect:

1. The pump stage uses two pulsed laser beams whose frequency difference is tuned to match the frequency of a single rotational line of the Q-branch of the Raman spectrum of the N$_2$ fundamental. In this way, the process of stimulated Raman pumping promotes population to a specific rotational level of the v=1 excited state.

2. After a variable delay, between 50 ns and 1.5 $\mu$s (depending on the pressure and temperature), the probe stage interrogates the populations in all the rotational levels of v=1 by means of stimulated Raman spectroscopy. This is done by recording a Raman spectrum of the Q-branch of the first hot band of N$_2$ (v=2 $\rightarrow$ v=1).

The analysis of the intensities of the rotational lines in the hot band spectrum allows us to extract the relative populations residing in the different rotational levels in v=1. Two main features stand out. First, it is observed that the rotational populations are already in Boltzmann equilibrium within each of the two spin components even for the lower time and pressure conditions. Second, it is observed that the ratio of populations between the ortho and para varieties changes as the delay increases, with nearly all the population residing in the ortho components at short delays and the relative populations converging towards a 2:1 ortho-para ratio at long delays.

The observations above can be easily explained in terms of collisional relaxation: since all the population arriving in v=1 is initially placed in a single rotational level (an ortho symmetry one), rotationally inelastic collisions quickly redistribute this population among all the other ortho states, generating a Boltzmann distribution in the ortho spin variety. The para states in v=1, however, are not accessible through relaxation from ortho states and, initially, can only be populated through vibrationally inelastic collisions of the type:

\[ N(v=1, \text{ortho}) + N(v=0, \text{para}) \rightarrow N(v=0, \text{ortho}) + N(v=1, \text{para}). \]

Thus, the rate of growth of the para/ortho population ratio in v=1 provides, when fitted to the integrated equation governing the process, a specific measurement of the rate of the V-V collisional relaxation process.

Since only the relative populations of the ortho and para species are needed for the data analysis, the experiment is self-normalized and impervious to the effects of any other mechanisms that contribute to signal loss in v=1 as long as they do not show rotational dependence. Thus, processes like V-T relaxation (removing population from v=1) or molecular diffusion (removing molecules from the focal region) do not affect the results of the analysis, even if they contribute to a decrease in the total amount of population in v=1.

The effect of inelastic collisions between two vibrationally excited molecules (in v=1), promoting one of them to v=2 and the other to v=0, has been neglected in the present model. This approach is based on the observation that the intensity of the second hot band (v=3 $\rightarrow$ v=2) is only about 3% of that of the first hot band (v=2 $\rightarrow$ v=1). Some authors have also reported detectable but small amounts of population in v=2 and higher states in a similar experiment run at a much higher densities.