Measurement of V-V vibrational relaxation rates in *ortho-para* collisions in N_2 at 77 K by double resonance stimulated Raman spectroscopy

D. Bermejo and R. Z. Martínez

Instituto de Estructura de la Materia, IEM-CSIC
Serrano, 123. 28006 – Madrid. SPAIN
Tel.:+34915616800 , E-mail: dbermejo@iem.cfmac.csic.es

We present measurements of vibration to vibration (V-V) collisional relaxation rates between the v=0 and v=1 states in the molecule of nitrogen ($^{14}N_2$) at 77K. They have been carried out using an adaptation of an experimental setup which had already been successfully used to study rotational (R-R) relaxation in acetylene [1].

The experiment was conducted on a static sample of N_2 contained in a coolable sample cell, and 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 high-power pulsed laser beams whose frequency difference is tuned to match the frequency of a single rovibrational line in 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 of N_2. For this experiment we have chosen to pump population through the J=4 line, belonging to the *ortho* nuclear spin variety.
2. After a variable delay, that for this experiment has ranged typically between 50 and 300 ns, the probe stage interrogates the rotational populations in all the rotational levels of v=1 by means of stimulated Raman spectroscopy. This is done by scanning the frequency difference of two lasers to record a high-resolution Raman spectrum of the first hot band of N_2 ($v=2 \leftarrow v=1$).

The analysis of the intensities in the hot band spectrum allows us to extract the relative populations residing in the different rotational states in v=1. Two main features stand out: First, it is observed, as expected at the sample pressure used in the experiment (100 mbar), that even for the shortest delay between pump and probe (50 ns) the rotational populations are already in Boltzmann equilibrium within each of the two spin components, that is, all the even-J components show a Boltzmann population distribution among them and so do all the odd-J components. Second, it is clearly visible 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 an 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 J=4 (an *ortho* symmetry state), rotationally inelastic collisions quickly redistribute this population among all the other *ortho* states, generating a Boltzman distribution in the *ortho* spin variety. The *para* states in v=1, however, are not accesible through relaxation from *ortho* states and can only be initially populated through vibrationally inelastic collisions of the type N_2(v=1, *ortho*) + N_2(v=0, *para*) → N_2(v=0, *ortho*)+N_2(v=1, *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 measurement of the rate of the V-V collisional relaxation process.

[1] J. L. Doménech, R. Z. Martínez, Á. Ramos, D. Bermejo, *J. Chem. Phys.* **2010**, *132*, 154303.