How-to calculate intensities of rovibronic cold-beam spectra for molecules with nuclear spin symmetry

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1 Introduction

Molecules with two or more nuclei equivalent with respect to its symmetry operations show spin-statistics in the population of their rotational energy levels. In the simulation of rovibronic spectra the populations of the ground state levels are needed for the calculation of transition intensities.

For molecules in cold beams, produced by the helium droplet pick-up technique or by supersonic co-expansion of the molecules in seed gas at high pressures, the nuclear spin states are often far from thermodynamical equilibrium. That is, whereas one observes rotational temperatures of 0.38 K for molecules embedded in a helium droplet, the nuclear spins don't relax on the typical time-scales of these experiments.

Usually molecules are at or above room-temperature before they get picked up by a helium droplet beam or co-expanded in a supersonic expansion. This will be assumed in the following.

At room temperature the different nuclear spin states are in thermodynamic equilibrium and rotational states show nuclear spin statistical weights according to their symmetry. Consider, for example, a molecule belonging to the symmetry group C_{2v} having two identical fermionic nuclei under that symmetry and a b_2 ground electronic state. It's rotational states with K_a even will have different nuclear spin statistical weights than rotational states with K_a odd, giving rise to relative populations of 3:1 for even:odd. If such an molecule is cooled to low temperatures without relaxation of nuclear spin this ratio will remain constant, that is, even at low temperatures the population in all states with K_a even will be three times the population in all states with K_a odd.

2 Calculation of ground state populations

To account for the scenario described above one has to retreat to a two-step calculation of rotational state populations. Initially one calculates the energies of all rotational levels in the vibronic ground state, up to a certain maximum. Then one has to separate these levels into two individual stacks, one for all rotational levels corresponding to one nuclear spin symmetry and the second one corresponding to the other nuclear spin symmetry. In the example given above these stacks would corresponds to states with K_a even vs. K_a odd.

For each of these stacks the relative population of states within the stacks is calculated by a Boltzmann distribution and taking degeneracies (for example the $2J+1$-M degeneracy of asymmetric rotor states in field-free space) into account. The ratio between the two stacks has to be fixed at the high-temperature value, though. That is, all states in one (or both) of the two stacks have to be normalized according to the nuclear spin statistical weights of the states they are compromised off. This can be achieved by setting the population of the lowest level in each stack to some arbitrary value, calculating the populations of the remaining states (up to some maximum value for J for popualtion os states are practically zero) within that stack relative to the lowest state, summing up all these population numbers, and finally multiplying all (including the lowest state) populations within that stack by the nuclear spin statistical weight factor of the states in this stack divided by the sum of the populations calculated above. Following this procedure for both stacks the relative overall populations of the two stacks will reflect the nuclear spin statistical weights, and the population of nuclear spin states at high temperatures. For the example given above that means that the overall population of all states with K_a even must be 3 and the overall population of all states with K_a odd must be 1.

Following this procedure the line intensities can be calculated from the obtained ground state populations and rotational line strength factors.

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