Delayed Double Resonance Between Quadrupolar Levels: Observation of a Nuclear Spin Emission Signal in s-Triazine*

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A delayed double resonance experiment was carried out using a Robinson-type continuous-wave spectrometer. The sample chosen was s-triazine at liquid helium temperature, where the relaxation times are of the order of ten hours. Line pairings between the two Nitrogen-14 NQR sites were confirmed. Emission signals from ν_- transitions were observed after successively saturating first the ν_- line and then the ν_+ line. The results are understood in terms of a simple model of spin population dynamics.

Introduction

s-Triazine, $C_3H_3N_3$, is a simple, symmetric molecule whose nitrogen-14 NQR spectrum, in fact, consists of one pair of ν_- and ν_+ lines at temperatures higher than 198 K [1]. A second order phase transition at this temperature, however, breaks the symmetry [2], so that at lower temperatures each NQR line is split into two components, which were paired by Zussman [1].

We measured the NQR spectrum at 4.2 K and found that the relaxation times are very long, of the order of ten hours. Furthermore, the line intensities are much stronger than at 77 K, probably owing to the improved Boltzmann factor. As a result, it became possible to perform a series of time-delayed double resonance experiments which allowed us to check the pairing of the lines and which resulted in the observation of NQR emission lines.

Nitrogen-14 has a spin $I = 1$ so that when the asymmetry parameter, η, is non-zero as in s-triazine, three energy levels are present whose equilibrium populations are given by Boltzmann statistics,

$$\frac{n_i}{n_j} = \exp\left\{-\frac{E_i - E_j}{kT}\right\}.$$

Thus, three resonance lines labelled ν_+, ν_- and ν_0, may be observed. In practice, the last one is often too weak and, as in the present case, remains undetected. Therefore, when more than one site exists, unambiguous pairing of the ν_+ and ν_- lines belonging to the same three level system cannot be made and other methods must be used.

As can be easily shown, the energy level populations differ from their mean value for a three-level system by an amount proportional to $(\nu_- - 2\nu_+)$ for the E_+ level, $(\nu_+ - 2\nu_-)$ for the E_- level and $(\nu_- + \nu_+)$ for the state E_0. Because the signal intensity is proportional to the population difference it then turns out that the intensity of each ν_+, ν_-, or ν_0 line is just proportional to its particular frequency. Of course these results are only valid at thermodynamic equilibrium. This is shown schematically in Fig. 1, where the intensities of the two resonance lines, ν_+ and ν_-, reflect the corresponding differences in equilibrium populations. The bars in Fig. 1 graphically represent the populations of the energy levels at equilibrium or after saturation of transitions ν_+ or/and ν_-, as indicated. As the energy differences between quadrupolar levels are small with respect to kT and in order to accentuate the population differences in Fig. 1, a constant amount was substracted from the actual populations. In so doing variations in populations are linearly reflected by the diagrams.

Now, consider what happens when the ν_+ line in such a system is irradiated. In all that follows we shall neglect the effects of spin lattice relaxation i.e., the whole experiment must be performed in a time

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short compared with the shortest system T_1. This constraint is easily met by our experimental conditions in s-triazine at 4.2 K, where T_1's are of the order of ten hours. As a result of the ν_+ irradiation, the populations of the two levels, E_+ and E_0, tend toward a common value as the number of spins in the higher state E_+ increases at the expense of the number of spins in the ground state E_0. The bar diagram in Fig. 1.2 show the new population levels after the ν_+ line is completely saturated. Also shown in Fig. 1.2 is the reduced intensity (about 33% of original value) one would expect if one were to subsequently observe the ν_- line. An analogous experiment, where one first saturates the ν_- line and then records the ν_+ line is shown in Figure 1.3. Note that the intensity reductions described above is proof that the ν_- and ν_+ lines are "paired", i.e., they belong to the same three level system.

Either of the two experiments described above can be fruitfully extended. For example, consider the state of the system after the ν_+ line is fully saturated. The resultant spin populations are indicated in the bar diagram of Figure 1.2. Now, let us irradiate the ν_- line to complete saturation, so that the spin populations take on a new set of value depicted in the bar diagram of Figure 1.4. Note that a population inversion has been achieved for the E_+ and E_0 levels, so that an *emission* line should be observed if the ν_+ line is subsequently stimulated by a spectrometer pass. The analogous experiment, where the ν_- is saturated first and the ν_+ line next, is also possible and the expected results are shown in Figure 1.5. Note that the emission intensity in the latter experiment (Fig. 1.5) is considerably larger than expected in the former (Fig. 1.4), by about a factor of 3.

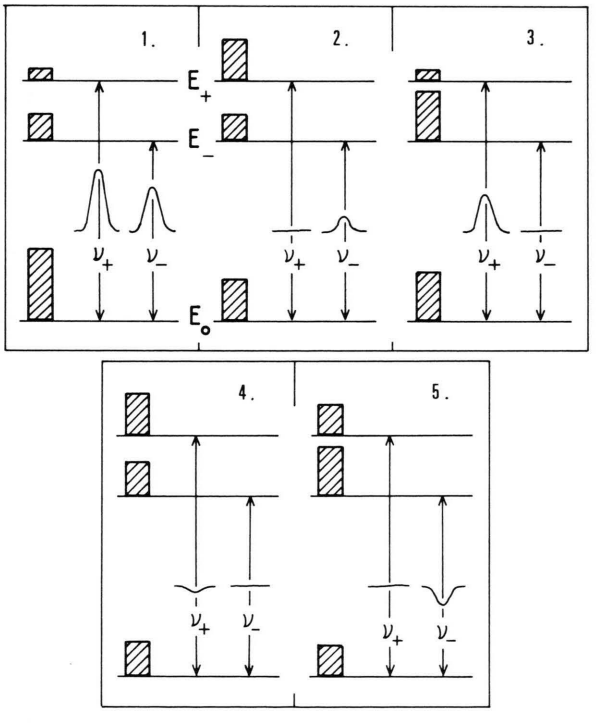

Fig. 1. Schematic representation of spin populations and signal intensities. (1) at thermodynamic equilibrium; (2) after saturating ν_+; (3) after saturating ν_-; (4) after saturation of ν_+ followed by ν_- saturation; (5) after saturation of ν_- followed by ν_- saturation.

Experimental Details

Recorder tracings of the four NQR lines of s-triazine at 4.2 K taken with the spin systems initially at thermal equilibrium are shown in Figs. 2.1 to 2.4, respectively. The ν_- lines are more intense than the ν_+ lines but their width is only half as large (about 0.5 kHz). Furthermore, they saturate almost completely after two passes. Also, we note that the low frequency wing of the ν_- lines is weaker when we sweep toward lower frequencies. This is not the case with the ν_+ lines which required sixteen passes to reach 90% saturation.

Following the procedure outlined in Fig. 1.2, we next attempted to saturate the ν_+ line at 3737 kHz, reducing its intensity to 13 mm from 95 mm after sixteen passes. Immediately after, we recorded the two ν_- lines and observed that the intensity of the line at 2852 kHz (Fig. 2.5) had significantly decreased while the line at 2814 kHz was unchanged (Fig. 2.6). Therefore, we conclude that the two lines at 3737 kHz and 2852 kHz form a pair which correspond to the same NQR site. In order to corroborate this pairing we have done the same experiment with the ν_+ line at 3660 kHz, which also took sixteen passes to saturate, reducing its intensity from 110 mm to 10 mm. This time it was the ν_- line at 2814 kHz which showed a considerable decrease in intensity (Fig. 2.7 and 2.8). The two lines at 3660 kHz and 2814 kHz were therefore confirmed to be paired and to correspond to the other crystallographic site.

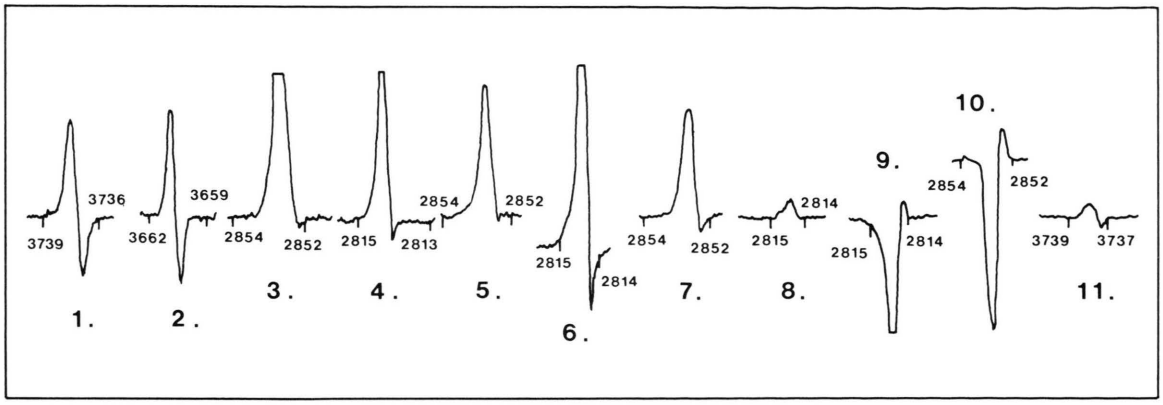

Fig. 2. Experimental traces of nitrogen-14 NQR lines for s-triazin at 4.2 K. (1) 3737 kHz ν_+ line at thermal equilibrium; (2) 3660 kHz ν_+ line at thermal equilibrium; (3) 2852 kHz ν_- line at thermal equilibrium; (4) 2814 kHz ν_- line at thermal equilibrium; (5) 2852 kHz ν_- line after saturation of 3737 kHz ν_+ line; (6) 2814 kHz ν_- line after saturation of 3737 kHz ν_+ line; (7) 2852 kHz ν_- line after saturation of 3660 kHz ν_+ line; (8) 2814 kHz ν_- line after saturation of 3660 kHz ν_+ line; (9) 2814 kHz ν_- emission line after successively saturating first 2814 kHz ν_- line then 3660 kHz ν_+ line; (10) 2852 kHz ν_- emission line after successively saturating first 2852 kHz ν_- line then 3737 kHz ν_+ line; (11) 3737 kHz ν_+ absorption line after successively saturating first 3737 kHz ν_+ line then 2852 kHz ν_- line.

The results of these pairings for s-triazine at 4.2 K are summarized below:

Site I: $\nu_+ = 3660.6$ kHz, $\nu_- = 2814.2$ kHz,

Site II: $\nu_+ = 3737.2$ kHz, $\nu_- = 2852.3$ kHz.

To observe emission signals it is next necessary to achieve a population inversion in the levels of s-triazine. Proceeding according to the method outlined in Figs. 1.3 and 1.5, we first saturated the ν_- line at 2814 kHz (site I) and then saturated the corresponding ν_+ line at 3660 kHz. A subsequent spectrometer pass over the region of the 2814 kHz transition gave an intense emission signal, shown in Figure 2.9. Similar success was achieved in observing an emission signal from the other crystallographic site (site II). Figure 2.10 shows the intense emission line observed for the ν_- transition at 2852 kHz.

Attempts to observe ν_+ emission lines, however, were unsuccessful. After following the procedure outlined in Figs. 1.2 and 1.4 for site II, a spectrometer pass over the ν_+ region resulted in a weak absorption signal (Fig. 2.11) rather than the expected emission signal. Similar attempts at frequencies corresponding to site I gave similarly negative results. These failures are most probably due to our inability to completely saturate the transitions, and to the already mentioned fact that the size of the effect for ν_+ emission is considerably smaller than for ν_- emission.

Conclusion

We have performed a series of double resonance experiments on a three-level system where the irradiations are performed serially in time. Thus only one sample coil and only one variable frequency spectrometer are necessary. The experiments are shown to be in qualitative agreement with a simple model of spin dynamics, and to provide a convincing method of pairing corresponding ν_+ and ν_- lines when other more direct pairing methods are not applicable.

The main limitation of the method is that thermal relaxation times must be much longer than the time required for the experimental procedure. In the present series of cw experiments this limitation is severe. However, one could easily envision pulsed analogues of these experiments which can be done in a small fraction of a second, resulting in a considerable increase in the applicability of the technique.

[1] A. Zussman, Phys. Letters **47 A**, 195 (1974).
[2] P. Coppens and T. M. Sabine, Mol. Cryst. **3**, 507 (1968).