On the structure of the $^{14}$N nuclear quadrupole resonance line of hexamethylenetetramine*

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The structure of the hexamethylenetetramine $^{14}$N nuclear quadrupole resonance line has been studied in detail on a powdered sample at 77°K. An improved, frequency-stabilized spectrometer, interfaced to a digital computer, was used in resolving fine details of the experimental lineshape. The line shape could be fitted by the sum of two Gaussian lines of suitably chosen width, frequency, and amplitude.

Many studies on the hexamethylenetetramine (HMT) molecule in the solid state have been published for quite a long time, especially aiming at clarifying its structure and motions in the crystal lattice. Its nuclear quadrupole resonance (NQR) frequency has also been determined many years ago. Since then it has been again studied by many researchers.

A few of the above-mentioned works hint at a structure of the resonance line shape, which on the other hand does not appear to have been very well resolved. We believe, on the contrary, that an accurate experimental study of the line shape should be made before attempting to reproduce it from theoretical calculations. The result of such a study is shown in Fig. 1: The HMT resonance line not only appears to be structured, but even exhibits sharp asymmetry.

On the other hand a single resonance line is to be expected because the space group of the HMT crystal is cubic (T$ar{4}$ symmetry axis); therefore the asymmetry parameter $\eta$ of the electric field gradient must necessarily be zero.

The present study has been carried out at 77°K on powdered commercial samples, taken from many different manufacturers in order to be sure that no impurities, accidentally present in a single manufacturer's product, could give rise to the observed structure.

We believe that the high stability in frequency of our spectrometer was especially responsible for clearly showing out the resonance line structure. We have used a modified Robinson type spectrometer; it is controlled by a frequency stabilizer circuit (to be described in a subsequent paper) which gives the instrument a frequency stability equal to that of a quartz oscillator or frequency synthesizer, while retaining the capability of frequency sweeping with controlled amplitude and speed, and even with very high linearity. Every detail of the resonance line can therefore be examined, even some which could get lost in a conventional non-frequency-stabilized spectrometer.

Every instrumental feature which could introduce distortions of the line shape was accurately verified and conveniently set. The rf level was lowered until any further decrease gave no modification of the line shape, but only a decrease of the S/N ratio. A further test for saturation effects was made by recording the line, at the chosen rf level, with either upward or downward frequency sweeps: In both cases the line shape was exactly the same. The frequency modulation was obtained by a Varicap diode fed by a 77 Hz sinusoidal signal, whose amplitude was reduced until no further changes of the line shape could be observed. The lock-in integration time constant was less than 1 sec; it could not introduce any distortion at the chosen sweep rate (about 300 Hz/min).

Under such experimental conditions the HMT resonance line shape is that shown in Fig. 1(b). Even if $\eta = 0$, the $\pm 1$ levels of the $^{14}$N nucleus are nondegenerate

![FIG. 1. HMT NQR experimental line shape. Lines are time averaged over nine sweeps and smoothed by a digital computer.](image-url)
in the presence of the weak (about 0.6 G) Earth's magnetic field \( H_0 \); this could be believed as the origin of the observed structure. The Earth's magnetic field has been therefore compensated by a large, conveniently oriented, dc powered coil, so that the magnetic field over the sample was very nearly zero. The shape of the resonance line was then that shown in Fig. 1(a): The structure is even more apparent. Therefore the Earth's magnetic field cannot be responsible for the structure of the line, whose sensitivity to small variations of the applied magnetic field is, on the other hand, evidenced by the line shape shown in Fig. 1(c), which is obtained when the magnetic field acting on the sample is twice that of the Earth.

Under the optimum above-mentioned instrumental settings the S/N ratio of the resonance line was relatively small. Therefore each resonance line in Fig. 1 has been time averaged by a HP 2114B digital computer. In order to further increase the S/N ratio with no increase in the lock-in amplifier time constant, the time-averaged data were subjected to a smoothing process, which by no means distorted the line shape.

Therefore, if a nonzero \( \eta \) value can be excluded because of the crystal symmetry, and if all other possible reasons for the observed effects have been taken into account, we assume that the observed structure and asymmetry arise from the magnetic dipole interactions, which should be both intramolecular and intermolecular, because of the very close packing in the crystal.

We thought it useful for any future theoretical study of such effects, to reproduce the three experimental lines of Fig. 1 by a least-squares treatment, carried out on our 2114B computer. A good reproduction was found possible when using simply the derivative of the sum of two Gaussian lines as the fitting function; the linewidths between the flex points (\( \Delta_{1} \) and \( \Delta_{2} \)), the center frequencies (\( \nu_1 \) and \( \nu_2 \)), and the ratio (\( R \)) of the amplitudes of the lower- and upper-frequency lines were chosen for the best fit. The correlation coefficient was in all cases greater than 0.9986.

The results are shown in Fig. 2. Curve (a), which best reproduces line (a) in Fig. 1, has the following parameters: \( \Delta_1 = 264 \text{ Hz} \); \( \Delta_2 = 332 \text{ Hz} \); \( \nu_1 = 3407.538 \text{ kHz} \); \( \nu_2 = 3407.817 \text{ kHz} \); \( R = 1.371 \). For curve (b), which best reproduces line (b) in Fig. 1, the parameters were as follows: \( \Delta_1 = 312 \text{ Hz} \); \( \Delta_2 = 350 \text{ Hz} \); \( \nu_1 = 3407.593 \text{ kHz} \); \( \nu_2 = 3407.840 \text{ kHz} \); \( R = 1.337 \). For curve (c), which best reproduces line (c) in Fig. 1, the parameters were as follows: \( \Delta_1 = 380 \text{ Hz} \); \( \Delta_2 = 438 \text{ Hz} \); \( \nu_1 = 3407.493 \text{ kHz} \); \( \nu_2 = 3407.821 \text{ kHz} \); \( R = 1.091 \).

We have also studied the triethylenediamine molecule in order to search for similar effects. The line shape seems to be, even in this case, weakly asymmetric, but less than that of HMT. However, this result cannot be advanced with much confidence, since, even when working at the lowest rf levels achievable in our spectrometer, saturation effects were still evident.

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