# The Effect of Moisture on the N.Q.R. Relaxation of Hexamethylenetetramine at 298 K*

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With low and and high power transient methods we have found line width narrowing of the $\nu_0$ signal of HMT that contains small amounts of water at 298 K. Samples were prepared by humidifying to moistures between 0% and 28% by weight. A minimum line width was observed around HMT: 1 $H_2O$ and is likely due to reduced dipole-dipole interactions arising from a 6.4% increase in the cell dimensions. This would account for a narrowing of 140 Hz and when offset by 50 Hz from broadening due to a smaller $T_1$ yields the experimental minimum line width. The smaller $T_1$ also indicates a reduction in the $C_3$ rotation barrier of 2.2 kJ/mole. The $\nu_+$ and $\nu_-$ lines corresponding to H bonded nitrogen were found but the $\nu_0$ corresponding to the R3m structure of HMT: 6 $H_2O$ was not observed. The $\nu_0$ of dry HMT was seen with all samples. This implies that humidified HMT has a predominate $I\bar{4}3$ m crystal structure. When more than 1 $H_2O$ per HMT was present the $\nu_0$ line width was broadened in proportion. This is indicative of a non-uniform $H_2O$ distribution within the lattice.

## Introduction

In our experience, drying of nitrogen bearing polycrystalline compounds prior to N.Q.R. study has been found necessary since off-the-shelf moisture contents typically ranged between 1% and 8% by weight. While these moistures tend to have little effect on resonance frequencies they usually have a detectable effect on the inverse line width parameter, $T_2^*$.

The measurement of $T_2^*$ with a self-quenched S.R.O. [1 – 3] is a simple technique. Frequently the $T_2^*$ parameter is more sensitive to changes in the crystal lattice than the resonance signal alone. Consequently, an investigation was undertaken to determine the effect of water on the $T_2^*$ of hexamethylenetetramine, HMT, at room temperature. Line width narrowing was observed at the $^{14}N$ resonance of unhydrated nitrogen when water was present in small amounts. This was unexpected and prompted a full analysis employing pulse-FT techniques to evaluate line shape changes.

The discussions consider the available crystal and NQR data on hexahydrated HMT, HMT: 6 $H_2O$.

## Experimental

### *Spectrometers*

Low Power Transient Method: A FM self-quenched SRO was used [1] having an integrated r.f. energy of $\sim 10^{-6}$ J/pulse with a field of $\sim 4$ G/pulse. The $T_2^*$ measurements were made at threshold quench frequency [2] which ranged between 800 Hz and 1500 Hz depending on the sample and LC tank $Q$.

High Power Transient Method: This pulse-FT system, described previously [3] was used to produce a 0.66 π (90°) pulse for the line shape analysis of the FID-FT, and the spin lattice, $T_1$, relaxation times. The $T_1$'s were determined by progressive saturation. Pulse widths were 62.5 μs with an RMS power of 125 W or $\sim 10^{-2}$ J/pulse and a field of $\sim 30$ G/pulse. When performing the line shape evaluation, pulse separations were 1 to 2 orders of magnitude greater than $T_1$.

### *Samples*

Samples containing different amounts of $H_2O$ were prepared from +99.5% pure polycrystalline HMT placed inside a sealed humidity chamber. The chamber air was circulated over a saturated aqueous salt solution selected to give the desired relative humidity at 28 °C. This resulted in a specific moisture content within the HMT.

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In each case a tared amount of HMT, dried to constant weight (at 110 °C usually for 72 h), was placed in the humidity chamber for 18 h. Afterwards the sample was removed, divided in 2 weighed lots, and sealed under nitrogen at 1 atm. Using this technique the following moistures were achieved; HMT + 2.38% $H_2O$, HMT + 11.26% $H_2O$, HMT + 18.90% $H_2O$, and HMT + 27.48% $H_2O$ by weight.

### *Temperature*

Particularly in the case of the high power transient method it was necessary to immerse the tank and sample in a parafin oil bath. The bath was at room temperature and maintained at 298 K to within our measurement accuracy of 0.05 K.

### *Measurements*

$T_2^*$ measurements, on the SRO, were made 1 week, 1 month, and 24 months after the samples being sealed. The observed line width narrowing persisted with both high and low power transient methods.

## Results and Calculations

The $T_2^*$ from the SRO measurements were determined using the Voltage Difference Method [2], where

$$T_2^* = (1/n) \sum_{i>j}^{n} [\{(1/f)_i^a - (1/f)_j^a\}/\ln(V_j/V_i)]^{1/a} \qquad (1)$$

with $f$ the average of the $k^{\text{th}}$ quench frequency at a given setting, $v_k$ the average signal amplitude of the $k^{\text{th}}$ measurement, $n$ the number of sets, and $a$ the exponent dependent on the line shape (gaussian $a = 2$, lorentzian $a = 1$).

The exponent is estimated by [4]

$$a = 2 - T_2^*(G)\,[\ln 2]^{1/2}/T_1\,, \qquad (2)$$

where $T_2^*(G)$ is calculated from (1) with $a = 2$.

The conversion from and to line width is made by

$$\Delta l = 2\,[\ln 2]^{1/a}/\pi\, T_2^*(a)\,. \qquad (3)$$

The results of the $\Delta l$ and $T_1$ measurements from the high power transient method are given in Figs. 1 and 2, respectively. The $T_2^*$ from (1) of the SRO measurements are given in Figure 3. Table 1 contains the aforementioned data plus the conversions via (3).

The significance of the differences between methods in determining the line width or $T_2^*$ were tested using the standard paired $t$-test. The results from the SRO and the pulse-FT systems were found not to be significantly different.

## Discussion

In previous studies, crystals of HMT:6$H_2O$ have been prepared by slowly cooling a saturated aqueous solution of HMT to 0 °C or lower. Mak [5] determined the crystal structure of HMT · 6$H_2O$ to be R3m ($C_{3v}$), $Z_{rh} = 1$. He found that each HMT molecule occupies a cavity in the water framework

Table 1. The Line Width and Relaxation Times of the $N(0)$ Atom of HMT in the presence of $H_2O$ at 298 K. The values enclosed in brackets are the std. deviations, "$n$" is the number of measurements, and "$a$" is defined in (2).

| | | | | | |
|---|---|---|---|---|---|
| Water concentration | | | | | |
| %$H_2O$ (wt.) | 0 | 2.38 | 11.26 | 18.89 | 27.51 |
| HMT:X$H_2O$ | 0 | 0.19 | 0.99 | 1.81 | 2.69 |
| Pulse-FT | | | | | |
| $n$ | 9 | 6 | 6 | 6 | 6 |
| $\Delta l$ (Hz) | 659(8) | 631(7) | 646(6) | 644(14) | 675(34) |
| Calc. $T_2^*$ (μs) | 798(10) | 823(7) | 804(8) | 806(5) | 771(50) |
| $T_1$ (ms) | 8.6(2.9) | 3.4(1.0) | 4.0(1.4) | 3.8(1.6) | 4.0(1.1) |
| S.R.O. | | | | | |
| $a$ | 1.93 | 1.80 | 1.81 | 1.79 | 1.82 |
| $n$ | 12 | 12 | 12 | 9 | 12 |
| $T_2^*$ [$a$] (μs) | 750(40) | 776(30) | 852(55) | 820(60) | 793(15) |
| Calc. $\Delta l$ (Hz) | 702(36) | 669(25) | 610(50) | 633(46) | 656(12) |

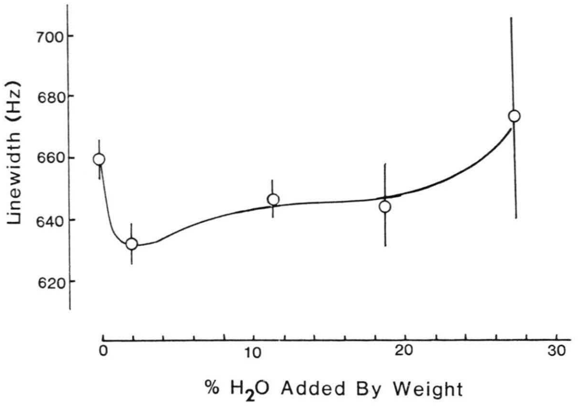

Fig. 1. The dependence of the $N(0)$ line width of polycrystalline HMT on $H_2O$ content at 298 K. The high power transient method was used.

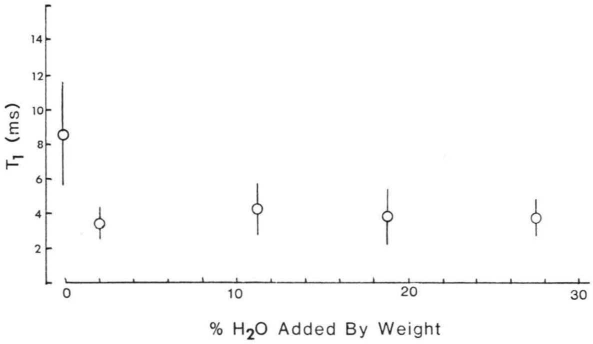

Fig. 2. The dependence of the $N(0)$ spin-lattice relaxation time of polycrystalline HMT on $H_2O$ content at 298 K. The high power transient method was used.

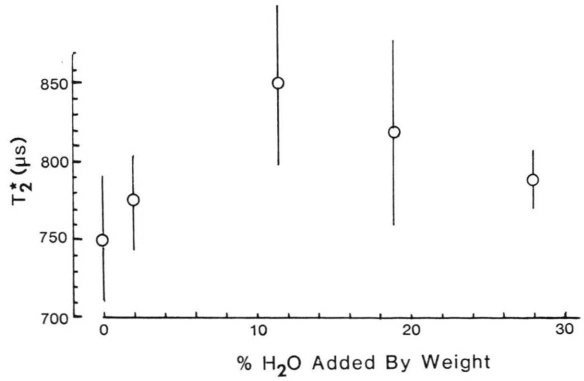

Fig. 3. The dependence of the $N(0)$ inverse line width parameter of polycrystalline HMT on $H_2O$ content at 298 K. The low power transient method was used.

of hexagonal $H_2O$ rings intra-bonded by 6 H bonds, inter-bonded by 3 H bonds, and bonded to the HMT molecules by 3 H bonds at the nitrogens. Consequently, the OH−N bonds use up 3 of the 4 available nitrogens of a molecule HMT. Two crystallographic inequivalent nitrogen sites arise. These have been labelled by Marino [6] as N(1) and N(2) corresponding to the non H bonded and the H bonded nitrogens, respectively. His NQR analysis was made at 77 K, where he observed a single resonance line at 3.573 MHz for the N(1) and two lines at 3.158 MHz 3.240 MHz for the N(2). The N(0) line, at 3.407 MHz, was not observed.

In our investigation, at 25 °C, with the low power transient method (SRO) we were unable to observe any resonances other than that of $N(0)$ in the moisture range that we studied. This is probably due to our samples being prepared by humidification and having low $H_2O$ contents where the $T_d^3$ symmetry of the lattice is expected to remain intact. As shown in Table I the average number of $H_2O$ molecules per HMT ranged from 0 to 2.96. Thus the efficiency of H bonding would be lower relative the HMT:6 $H_2O$ complex. With the high power transient method (pulse-FT) the $N(2)$ resonance signals were detected only for the HMT:2.96 $H_2O$ complex. Signals were not observed for those complexes containing less water. The observed $N(2)$ signals had a S:N that was ~2:1 after 10000 averages. This was roughly 1000 times weaker than the $N(0)$ signal with the same sample. The line widths of these signals ranged between 1000 Hz and 1500 Hz. This broadening is somewhat lower than that expected by Marino but does demonstrate a loss of environmental homogeneity at the different $N(2)$ atoms. The room temperature resonance frequencies were $\nu_+ = 3.146$ MHz and $\nu_- = 3.060$ MHz with $n = 0.042$. An extrapolation of the available 77 K data [6, 7] to room temperature using a Bayer-Kushida-Wang model fitted to pure HMT yielded $\nu_+ = 3.143$ MHz and $\nu_- = 3.064$ MHz demonstrating excellent agreement. Searching in the vicinity of 3.47 MHz to the $N(1)$ signal proved unsuccessful. This may indicate that the R3m crystal structure does not occur to a significant degree under the conditions that the samples were prepared.

The data in Table I reveal that on the average the line width decreases as the water content increases from "bone" dry until a minimum line width is reached. This minimum appears to occur around 1 molecule of $H_2O$ per HMT, after which the line width increases. We suspect that the inclusion of water into the lattice causes the cell dimension to increase. This would result in a reduction in the dipole-dipole second moment since it depends on $r^{-6}$, where $r$ is the inter atomic distance. Clearly, a small change in $r$ can have a large effect on the dipole-dipole line width. At room temperature the line width contribution from the dipole-dipole interactions in a perfect crystal has been calculated as 331 Hz [4] or about half of the total line width. Thus for a perfect crystal the maximum line width narrowing, if fully ascribed to reduced dipole-dipole interactions, would occur for $a \sim 5.5\%$ increase in the distances between the $N(0)$ atom and the 3 hydrogens in which it is nested. This 5.5% increase is probably underestimated since an increase in the crystal cell dimensions would permit greater dynamical line width broadening. The observed decrease of the $T_1$ values in samples with $H_2O$ supports this. The decrease in the $T_1$ corresponds to a line width increase of $\sim 50$ Hz [4]. If we assume that the broadening and narrowing mechanisms are competitive then the expected distance increase in the cell dimension would be closer to 6.4%. The increased dynamical motion should partially be manifested in the rotation of the HMT molecule about its 3-fold axis of symmetry. Applying the method of Alexander and Tzalmona [8], resulted in an energy barrier of 63.0 kJ/mole for HMT:1 $H_2O$ relative to 65.2 kJ/mole for dry HMT. The increased cell dimensions should also decrease the weak H bonds between the nested $N(0)$ and the nearest hydrogen atoms though this effect should be relatively small. The increase of line width when there is more than 1 molecule of $H_2O$ per HMT may indicate a wider distribution of the electric field gradients at the $N(0)$ atoms relative to dry HMT. It is suspected that this wider distribution relates to the uniformity of the $H_2O$ diffusion into the HMT poly crystals during humidification and subsequent equilibration. A full discussion would have to allow for $\Delta l$(dipolar) being less and $\Delta l$(electric) occurring in a polycrystalline system. This is being studied.

## Conclusion

In general the off-the-shelf moisture condition of some molecular crystals may yield different NQR data. Humidifying HMT to up to 1 molecule of $H_2O$ per HMT molecule resulted in both line width narrowing and broadening with the narrowing predominating at 298 K. The evidence points to decreased dipole-dipole interactions as being the main narrowing mechanism. The decrease in dipole-dipole interaction is associated with an increase in unit cell dimensions estimated to $\sim 6.4\%$. The increase in the line width observed when there is more than an average of one $H_2O$ molecule per HMT is believed to be related to the spread in the EFG at the $N(0)$ sites corresponding to the diffusion non-uniformity of $H_2O$ during humidification and equilibration.

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[1] S. Melnick, R. J. Trepanier, M. A. Whitehead, and E. P. A. Sullivan, J. Mol. Struct. **58,** 337 (1980).
[2] R. J. Trepanier and M. A. Whitehead, J. Mol. Struct. **83,** 369 (1982).
[3] R. J. Trepanier and M. A. Whitehead, J. Mol. Struct. **111,** 415 (1983).
[4] R. J. Trepanier and M. A. Whitehead, J. Chem. Soc., Faraday Trans. II, accepted for publication April 15, 1985.
[5] C. W. Mak, J. Chem. Phys. **43,** 2799 (1965).
[6] R. A. Marino, Adv. in N.Q.R. Spect. Vol. 1, 391, J. A. S. Smith ed. Heyden, London 1973.
[7] L. N. Becka and C. W. Cruickshank, Proc. Roy. Soc. A273, 435 and 455 (1963).
[8] S. Alexander and A. Tzalmona, Phys. Rev. **138,** 3A, 845 (1965).