The Temperature Dependence of the N-14 NQR Spectrum, Relaxation Times, and Line Shapes of Cyanuric Fluoride*, **

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Measurements of the N-14 NQR spectrum, relaxation times, and line shapes as functions of temperature of cyanuric fluoride are reported. This material exhibits very wide lines and thus lends itself to determining the profile of the lines from measurements of the echo heights. The material also exhibits a phase transition similar to that found in s-triazine. The phase transition occurs at 115 ± 5 K. A comparison of the results is made with those obtained previously for cyanuric chloride and s-triazine.

Introduction

This investigation is a continuation of our study of the symmetric triazine compounds. The symmetric triazine compounds are six membered ring compounds with nitrogen atoms occupying alternate ring sites and like atoms or groups bonded to each carbon in the ring. Triazines, having double bonds between nitrogen carbon pairs, are of the pyridine class and characterize the true triazines. Molecules of this type that have been studied by N-14 NQR are s-triazine [1, 2], melamine [3, 4], trichloromelamine [3] and cyanuric chloride [3, 5].

In this paper we will report our results for cyanuric fluoride, $C_3N_3F_3$. A comparison will be made of the values of the quadrupole coupling constants, the asymmetry parameters, and the σ and π electron occupation numbers for cyanuric chloride and s-triazine.

Experimental Details

A Matec NQR pulse spectrometer coupled to a Nicolet 1172 signal averager was used to acquire the data. We were able to obtain all data from observations of the amplitudes of the echoes following $90° - \tau - 180°$ pulse sequences. Pulses having widths of 20 and 40 μs with 1000 μs spacing and 3.5 sec repetition rate made up the pulse cycle. It was necessary to use between 64 and 256 repetitions in order to obtain sufficient signal to noise ratios for accurate measurements of the echo heights.

The sample temperature was controlled to within ± 0.5 K and measured with a thermocouple. The sample (volume ≈ 10 cc) was purchased from the Aldrich Chemical Company and used as supplied.

Because of the extreme width of the spectral lines, approximately 40 kHz, the width of the echo does not yield T_2^*. For this same reason neither the echo nor the free induction decay (FID) exhibit off resonance oscillations. However, a map of the echo height as a function of frequency reveals the profile of the spectrum [6]. The resonance frequencies are extracted from the map as the frequencies for which maxima occur. The line widths were measured from the map by measuring the widths of the profiles of the lines. Broadening of the spectral lines due to the convolution of the frequency spectrum of the pulse with that of the NQR spectrum was not observed to occur.

Finally, T_1 was determined from a plot of echo height as a function of sequencing time.

Results

In Table 1 are listed some of the properties of cyanuric fluoride, cyanuric chloride, and s-triazine that may have an effect on the NQR results. We have also listed a number of quantities derived

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Table 1. Quantities pertinent to the N-14 NQR analysis of cyanuric fluoride and comparative quantities for s-triazine and cyanuric chloride.

Quantity	s-Triazine	Cyanuric fluoride	Cyanuric chloride
Molecular weight	81.08	135.05	184.41
Melting point	85 ± 2 °C	− 38 ± 1 °C	147 ± 2 °C
C−X Bond length	.998 Å [7]	1.303 Å [9]	1.68 Å [8]
C−N Bond length	1.319 Å [7]	1.333 Å [9]	1.33 Å [8]
N−C−N Angle	127° [7]	127° [9]	125° [8]
C−N−C Angle	113° [7]	113° ± 1° [9]	113° (assumed)
$\overline{T_2^*}$ at 77 K	1.0 ± 0.2 ms*	28 ± 5 μs	1.5 ± 0.2 ms
$\overline{T_1}$ at 77 K	100 & 10 ± 5 s* [1]	1.0 ± 0.2 s	100 ± 40 s
$\overline{\frac{e^2qQ}{h}}$ at 77 K	4333 ± 40 kHz*	3603 ± 100 kHz	4040 ± 20 kHz
$\bar{\eta}$ at 77 K	0.40 ± 0.01*	.18 ± .03	.030 ± .005
$\overline{\nu_+^1}$ at 77 K	3710 kHz [1]	2910 ± 5 kHz	3080 ± 1 kHz
$\overline{\nu_-^1}$ at 77 K	2840 kHz [1]	2635 ± 5 kHz	3014 ± 1 kHz [5]
$\overline{\nu_+^2}$ at 77 K	3644 kHz [1]	2860 ± 5 kHz	3044 ± 1 kHz
$\overline{\nu_-^2}$ at 77 K	2805 kHz [1]	2525 ± 5 kHz	2982 ± 1 kHz [5]
$\overline{\nu_+^3}$ at 77 K		2820 ± 5 kHz	
$\overline{\nu_-^3}$ at 77 K		2465 ± 5 kHz	
$\overline{N_\sigma}$ at 77 K	1.21 ± .01*	1.29 ± .03	1.15 ± .02
$\overline{N_\pi}$ at 77 K	1.07 ± .03*	1.24 ± .03	1.14 ± .02
T_c	1.98 ± 0.1 K [1]	115 ± 5 K	

* Quantities marked with asterisks were extrapolated from the data presented in [1].

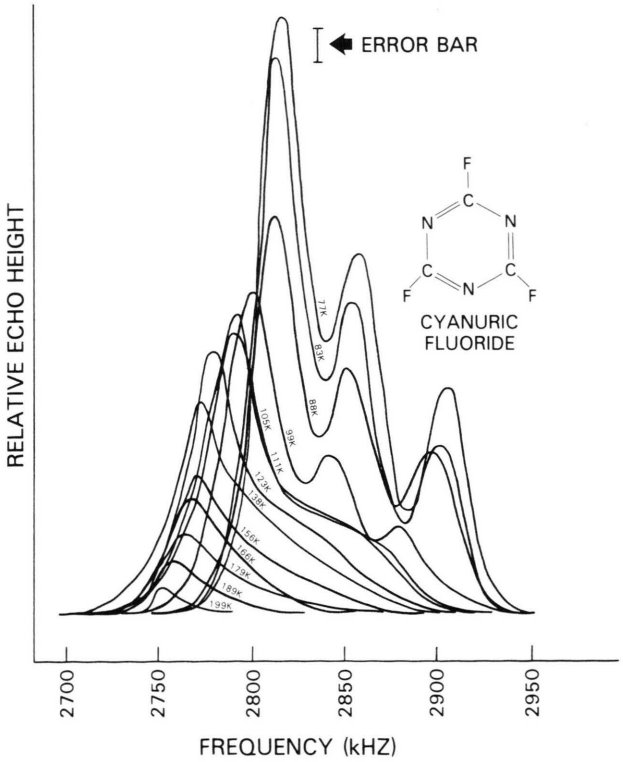

Fig. 1. A composite of the spectral profiles of the ν_+ lines of cyanuric fluoride for the temperatures indicated.

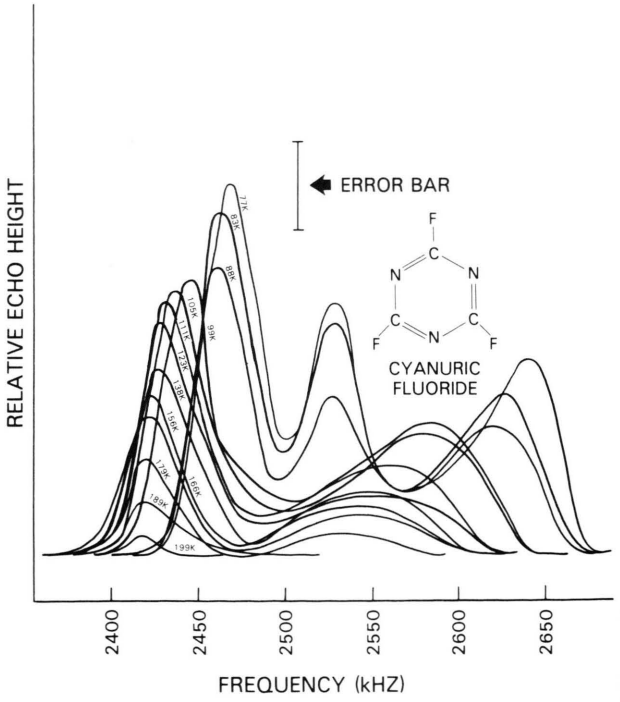

Fig. 2. A composite of the spectral profiles of the ν_- lines of cyanuric fluoride for the temperatures indicated.

from the NQR data taken at 77 K. The uncertainties indicated are the experimental uncertainties in the case of measured quantities and the range of the included values in the case of averaged calculated quantities.

The expressions used in calculating the nuclear quadrupole coupling constants, and the σ and π electron occupation numbers are listed below.

$$\frac{e^2 q Q}{h} = \frac{2}{3}(\nu_+ + \nu_-), \tag{1}$$

$$\eta = \frac{3(\nu_+ - \nu_-)}{(\nu_+ + \nu_-)}, \tag{2}$$

$$N_\sigma = 2 - \left(\frac{1}{1 - \mathrm{Cot}^2 \gamma}\right)\frac{4\nu_-}{3C_\mathrm{p}}, \tag{3}$$

$$N_\pi = N_\sigma - \frac{4}{3}\frac{(\nu_+ - \nu_-)}{C_\mathrm{p}}. \tag{4}$$

Here γ is half of the angle (C–N–C). C_p is the coupling constant generated for a single 2p electron and is taken to be 8.4 MHz for our calculations. N_σ and N_π are the electron occupation numbers for the σ and π orbitals, respectively.

Figures 1 and 2 are composite graphs of the spectra of ν_+ and ν_- resonances of cyanuric fluoride taken at several temperatures. Figures 3 and 4 are graphs of the resonant frequencies as a function of temperature.

Discussion

The most evident conclusions to be drawn from our results for cyanuric fluoride are: 1) a definite change in the profiles of the resonant lines occurs as the temperature is increased from 77 K to 200 K, and 2) a phase transition occurs near 115 K.

The cyanuric fluoride spectrum is unique among the triazine spectra in that we find three ν_+ and ν_- lines at 77 K instead of the expected two. Between 115 K and 180 K only two lines are apparent although a second very broad ν_- line is evident and

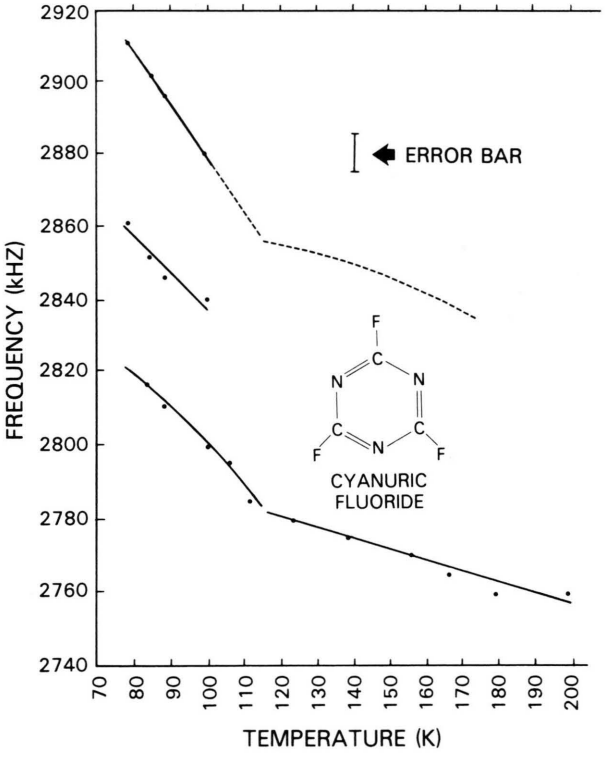

Fig. 3. Plots of the resonant frequencies as a function of temperature for the ν_+ lines of cyanuric fluoride.

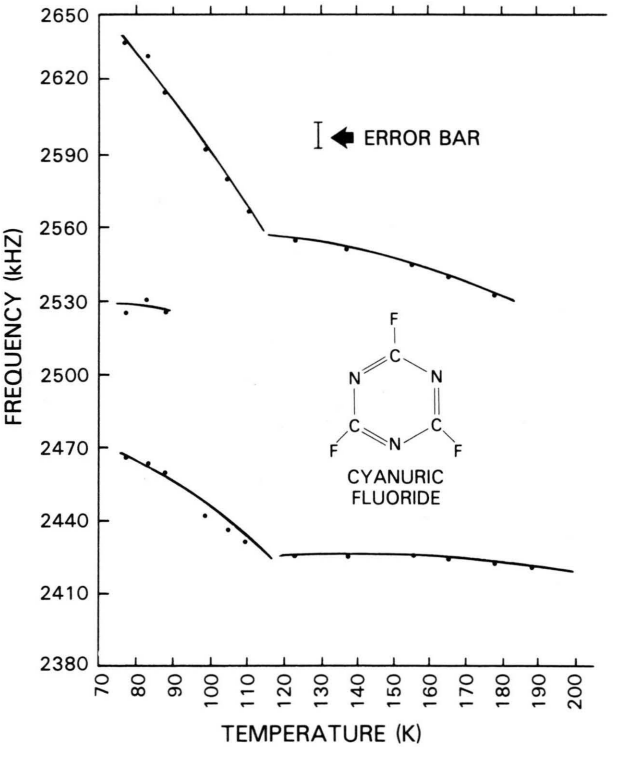

Fig. 4. Plots of the resonant frequencies as a function of temperature for the ν_- lines of cyanuric fluoride.

the semblance of a second broad ν_+ line can be conjectured. At temperatures above 180 K only two lines are found. The coalescing of the six spectral lines into pairs of lines and the discontinuity in slope of the ν vs. T curves indicates a phase transition similar to that observed in s-triazine [1]. Therefore the phase transition can be attributed to a continuous angular deformation of the whole crystal.

Comparing the relaxation times for cyanuric fluoride with those for s-triazine we conclude that the force constants for the fluoride must be smaller than for s-triazine. The calculations of Durig and Nogarayan [10] confirm this observation.

We also observe from Table 1 that the average asymmetry parameter η increases with decreasing C–X bond lengths. The large differences between the η's for the compounds in Table 1 is in sharp contrast to the rather small differences reported by Shempp and Bray [11] for the corresponding pyridines. It appears that the presence of hydrogen near the nitrogen sites has considerable effect on the magnitudde of η in these compounds.

Our results for the σ and π electron densities for the triazines are consistent with the results for the pyridines [11]. The changes produced in these quantities, when the off ring atoms adjacent to the nitrogen atom are changed from hydrogen to fluorine to chlorine in the pyridines, are comparable to those produced in the triazines for the same changes in substituents.

Conclusions

Solid cynuric fluoride at 77 K exhibits an N-14 NQR spectrum indicative of three unequivalent nitrogen sites. At 115 K the spectrum reveals that the solid has undergone a phase transition and that the nitrogen atoms more nearly experience the same environment above this temperature. The transition temperature extrapolated from the σ vs. T graphs is 115 ± 5 K.

The σ and π electron occupation numbers for the triazines follow the same pattern as for the pyridines with the same substituents in the 2 position of the ring. Compared to the other compounds the fluoride compounds show relatively larger occupation numbers.

Finally, cyanuric fluoride exhibits much smaller T_2^*'s and T_1's than s-triazine and cyanuric chloride.

[1] A Zussman and M. Oron, J. Chem. Phys. **66,** 743 (1973).
[2] M. Oron, A. Zussman, and E. Rapaport, J. Chem. Phys. **68,** 794 (1978).
[3] C. Stutz and D. Early, J. Mole. Struct. **111,** 31 (1983).
[4] A. Peneau, L. Guibe, and C. Stutz, Noveau J. Chimie **9,** 427 (1985).
[5] A. Péneau, B. Manallah, and L. Guibé, presented at 8th NQR Symposium, Darmstadt, Germany 1985, 5275, Nr. 12.
[6] E. Fukushima and S. Roeder, Experimental Pulse NMR. A Nuts and Bolts Approach, Addison Wesley, Reading (Mass.) 1981, p. 51.
[7] P. J. Wheatly, Acta Crystallogr. **8,** 224 (1955).
[8] Y. Akimoto, Bull. Chem. Soc. Japan **28,** 1 (1955).
[9] S. H. Bauer, K. Katada, and K. Kimura, Structural Chemistry and Molecular Biology (A. Rich and W. Davidson, eds.). W. H. Freeman and Co., San Francisco 1968, p. 653.
[10] J. R. Durig and G. Nogarayan, Acta Physica Polonica **35,** 867 (1969).
[11] E. Schempp and P. J. Bray, J. Chem. Phys. **49,** 3450 (1968).