The $^{35}$Cl NQR Temperature Dependence of Hexa- and Octachlorocyclophosphazene

Alexander A. Koukoulas
Pulp and Paper Research Institute of Canada, 570 St. John’s Rd., Pointe Claire, PQ, Canada H9R 3J9

M. A. Whitehead
Department of Chemistry, McGill University, Montréal, PQ, Canada, H3A 2K6

Z. Naturforsch. 47a, 305–307 (1992); received August 10, 1991

The $^{35}$Cl NQR temperature dependence in (PNC$_1$)$_3$ and (PNC$_1$)$_4$ was measured between 77 K and 293 K. The dependence in both compounds was smoothly varying. A sudden decrease in $T_2^*$ near 112 K indicated the presence of a strong broadening mechanism in (PNC$_1$)$_3$. The nature of this mechanism is interpreted in terms of the $^{35}$Cl spin-lattice relaxation.

Introduction

The nature of phosphorous-nitrogen bonding in the phosphazenes has generated a great deal of interest. In particular, the cyclophosphazenes are studied because of their unique and somewhat controversial $\pi$ bonding and molecular geometry [1]. The chlorosubstituted cyclophosphazenes (PNC$_2$)$_x$, where $x = 3$ or 4, or phosphonitrillic trimer and tetramer, as they are also known, exhibit a degree of aromaticity. The aromatic behaviour is partly responsible for the elevated $^{35}$Cl NQR frequencies observed in these compounds. This paper examines the temperature dependence of (PNC$_1$)$_3$ and (PNC$_1$)$_4$. Measurement of the inverse linewidth parameter ($T_2^*$) temperature dependence led to the identification of a previously undetected phase transition in (PNC$_1$)$_3$.

Experimental

NQR frequencies ($\nu_0$) were measured on a super-regenerative oscillator (SRO). Both Colpitts and Dean oscillators were constructed for this purpose. Overall, the Colpitts oscillator was preferred because of its increased stability and linearity. The Voltage Difference Method (VDM) was used to obtain $T_2^*$ from the SRO data [2].

Spin-lattice relaxation times ($T_1$) were measured with a Nicolet-Matec high-power, pulsed spectrometer [3]. 90° pulses of 10 $\mu$s were typical for the coil geometries used in the sample probe. Only the inversion recovery pulse sequence was used to measure $T_1$ [3]. Solvent baths were used to obtain temperatures between 77 K and 293 K. (PNC$_1$)$_3$ and (PNC$_1$)$_4$ (99%) were purchased from Aldrich. Since both compounds are highly hygroscopic, they were carefully ampouled under vacuum in glass vials (15 mm o.d.).

Results

The $^{35}$Cl NQR temperature dependence of both (PNC$_1$)$_3$ and (PNC$_1$)$_4$ exhibited a smooth monotonic decrease in frequency as a function of increasing temperature (Figs. 1 and 2). The Bayer-like temperature dependence was true for all 4 resonance lines. There was no indication of a phase transition from the $\nu_0$ vs. $T$ data. The resonance lines did not coalesce at elevated temperatures and actually diverged for the $v_3$ and $v_4$ lines in (PNC$_1$)$_3$. Least-squares analysis of the average log $\nu_0$ vs. $T^2$ gave $\alpha$ values of $-3.179 \times 10^{-7}$ K$^{-2}$ for (PNC$_1$)$_3$ and $-2.306 \times 10^{-7}$ K$^{-2}$ for (PNC$_1$)$_4$ [4]. The correlation coefficient for both fits was 0.99.

The $T_2^*$ temperature dependence in the tetramer decreased with increasing temperature, 85 $\mu$s at 77 K to 25 $\mu$s at 293 K. Between 112 K and 250 K, $T_2^*$ decreased 0.65 $\mu$s K$^{-1}$, from 198 $\mu$s to 75 $\mu$s.

In the trimer, $T_2^*$ exhibited a sharp change between 112 K and 142 K, where it decreased from 214 $\mu$s to...
The temperature dependence of the NQR frequency is often not very useful for examining higher-order phase transitions. Smooth monotonic behaviour of the $v_Q$ vs. $T$ curve, as exhibited by the chlorocyclophosphazenes, is frequently observed in the study of NQR temperature dependence. However, the absence of an obvious (i.e. first-order) phase transition in $v_Q$ vs. $T$ does not preclude the presence of higher-order phase transitions.

The abrupt increase in $T^*_2$ at 112 K for (PNCl$_2$)$_3$ indicates the presence of a strong broadening mechanism. Since the resonance frequency is smoothly changing at this temperature, the mechanism must have its origin in the lattice; any intramolecular reorientations would most likely result in a discontinuity in $v_Q$ vs. $T$. It is for this reason that the temperature dependence of the $T_1$ relaxation was measured. Although the rate of change in $T_1$ does increase near 112 K and above, the contribution of $T_1$ to the resonance linewidth is expected to be small. Nonetheless, the $T_1$ temperature dependence does indicate the presence of increased molecular motions. Other factors, such as the concentration of lattice imperfections, may be responsible for the observed broadening in (PNCl$_2$)$_3$ [5].

The VDM is valid only if the resonance signal as a function of the applied radiofrequency voltage is measured near threshold. Unfortunately, the threshold condition does not allow the $T^*_2$ measurement of closely spaced resonance lines. The $T^*_2$ for closely spaced lines represents an average of the lines. However, linewidths calculated from $T^*_2$ values agree well with those obtained from the pulsed spectrometer. For example, at 77 K (PNCl$_2$)$_3$ has 4 resonance lines: $v_1 = 28.6901$ MHz, $v_2 = 28.6045$ MHz, $v_3 = 28.3305$ MHz, and $v_4 = 28.3196$ MHz. The linewidths for each of these lines, measured with the pulsed spectrometer, were 2405 Hz, 1923 Hz, 2208 Hz, and 2830 Hz. These linewidths, under a Gaussian assumption for the lineshape, correspond to $T^*_2$ values of 220 μs, 270 μs, 240 μs, and 187 μs. In comparison, the VDM results in
only 2 $T_2^*$ values: a high frequency $T_2^*$ = 202 $\mu$s, and a low frequency $T_2^*$ = 150 $\mu$s. The correlation between the two methods is quite good and indicates that the VDM is sampling an average of the lines.

Conclusions

The $^{35}$Cl NQR frequency in (PNC$_1$)$_3$ and (PNC$_1$)$_4$ smoothly decreased as a function of increasing temperature. The temperature dependence did not suggest the presence of a phase transition between 77 K and 293 K in either compound. However, the $T_2^*$ temperature dependence in (PNC$_1$)$_3$ showed an increased broadening of the resonance linewidth beginning at 112 K. In addition, the $T_1$ values are rapidly decreasing near this temperature. The data suggests the presence of a higher-order phase transition between 112 K and 142 K.

The validity of the VDM for obtaining $T_2^*$ for closely spaced resonance lines was demonstrated.

Acknowledgements

We thank L. Levesque and R. Mentore for the painstaking $T_2^*$ measurements and NSERC for continued financial support. A. A. K. thanks PAPRICAN for its encouragement.