



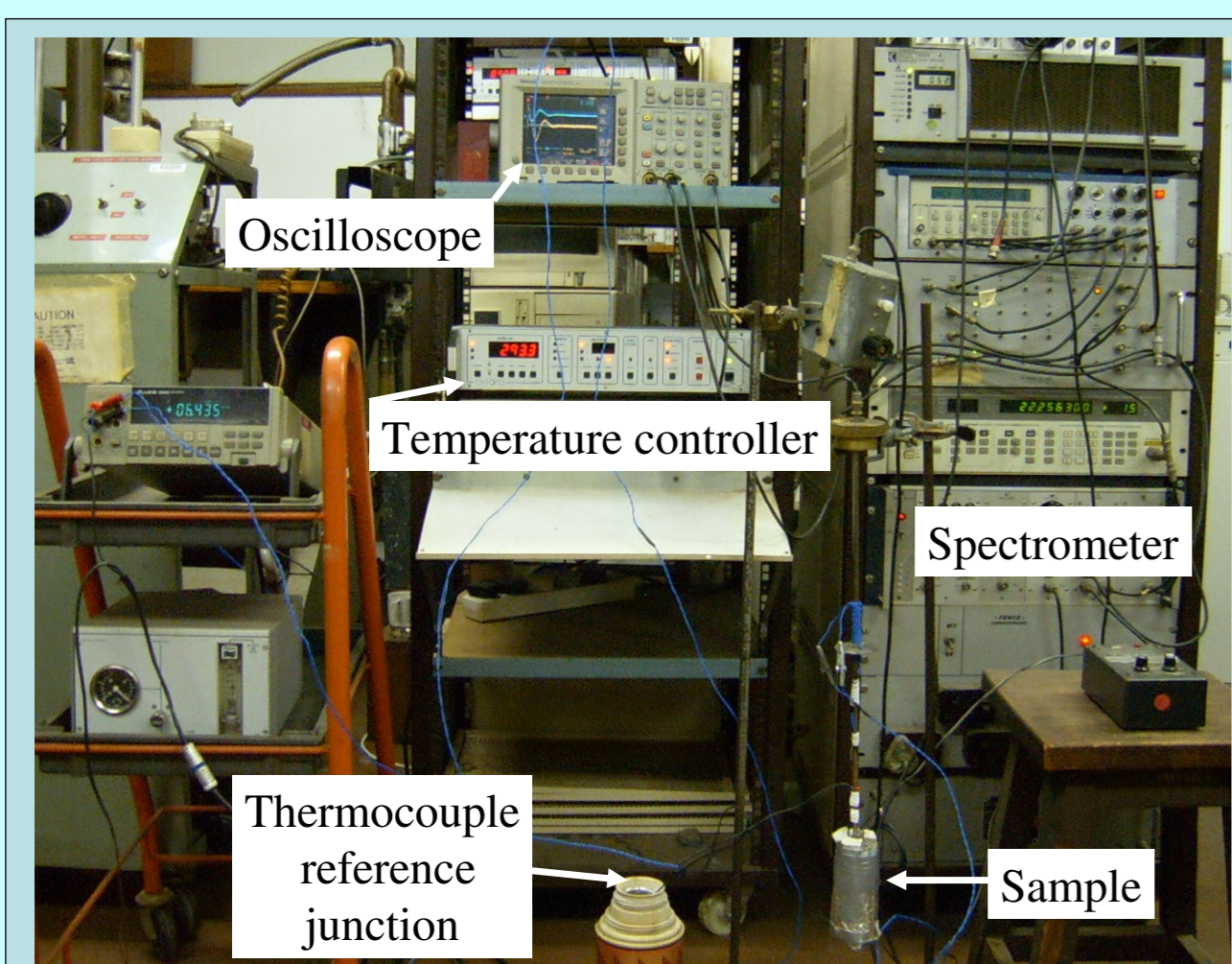
# $^{35}\text{Cl}$ spin-lattice relaxation in mercuric chloride

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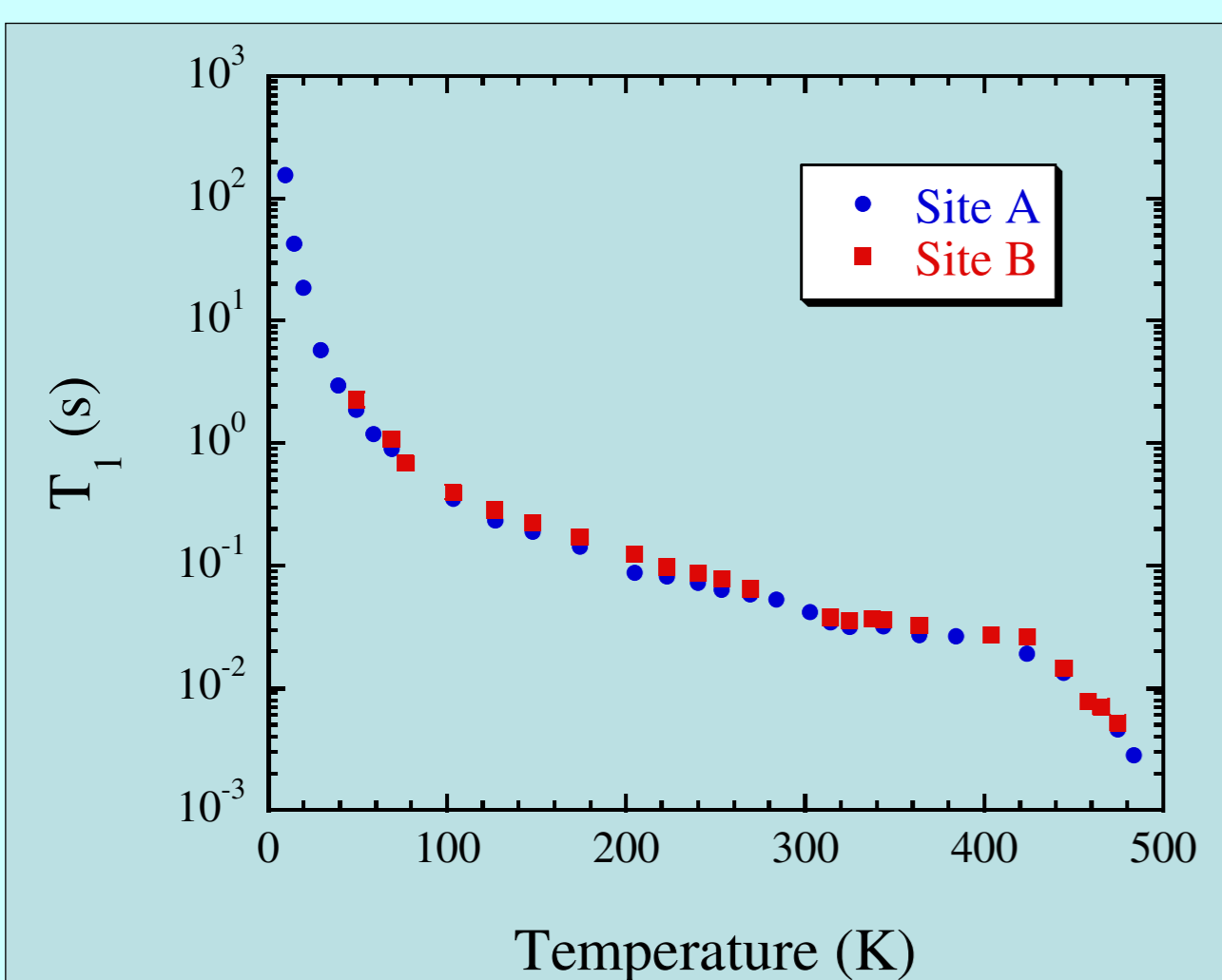
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## NQR Spectrometer



NQR spectrometer used in this investigation. It is pictured in the 'high' temperature configuration used for measurements between 300 K and 500 K. The sample is inside a copper can fitted with a heater and copper-constantan thermocouple. The entire can is placed inside a thermally insulated sleeve. Temperature control is via an Oxford ITC503 temperature controller. For temperatures below 300 K an Oxford continuous flow cryostat was used in conjunction with the temperature controller. The temperature for each  $T_1$  measurement was obtained from a previous calibration of the quadrupolar resonance frequency (presented at Euromar-2008).

## Experimental Results

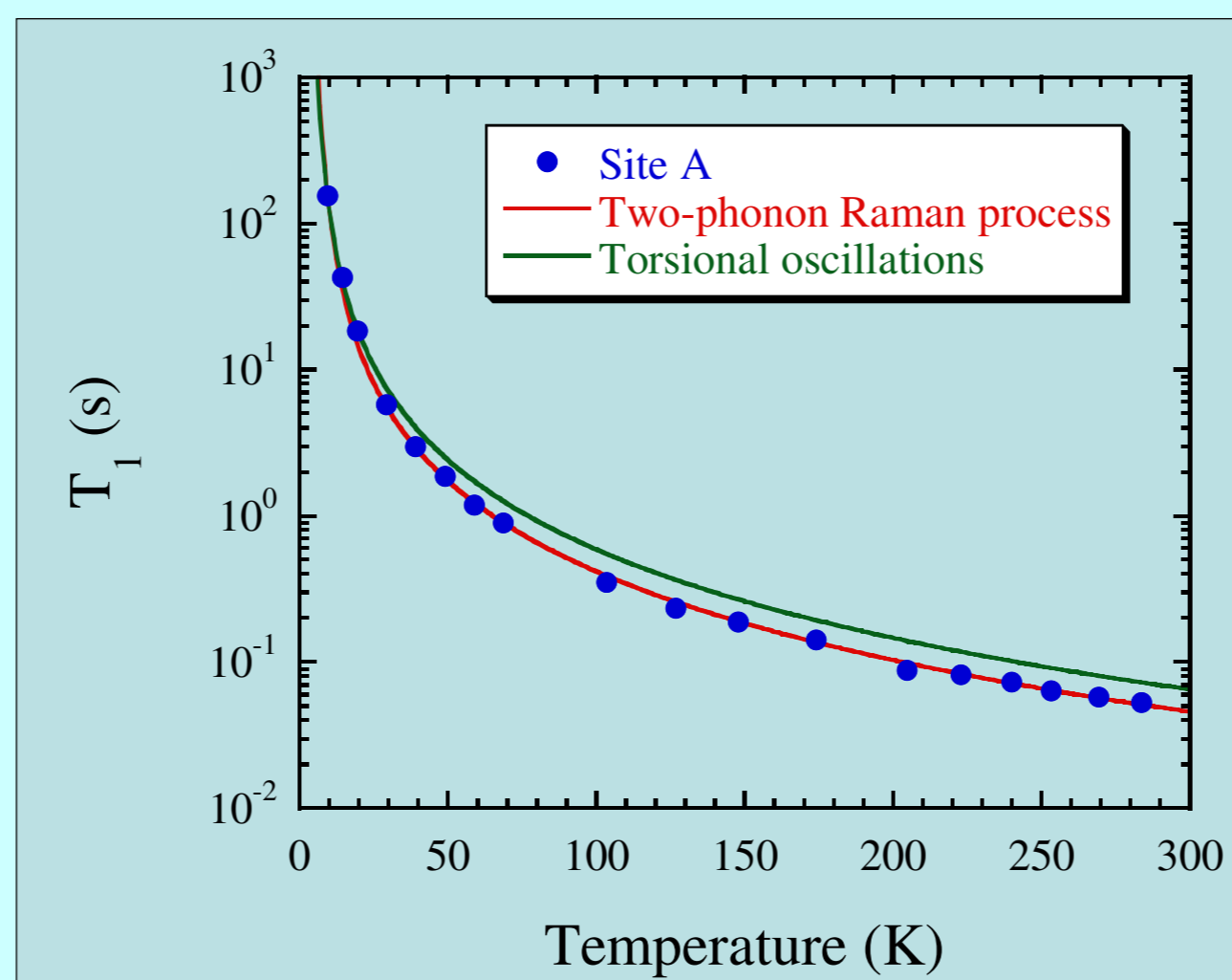


$\text{HgCl}_2$  has two inequivalent sites resulting in two distinct NQR frequencies at a particular temperature. At room temperature the resonance frequencies for two sites are 22.2489 MHz (Site A) and 22.0655 MHz (Site B). The difference in frequencies decreases as the temperature increases, and the frequencies approach one another as the temperature moves toward the melting temperature (540 K). Three distinct regions can be identified from the spin-lattice relaxation data presented for the entire temperature range studied. These are data shown in the plot above – below 100 K, between 100 K and 360 K, and above 360 K. Each of these regions is explored in detail in this presentation.

## References

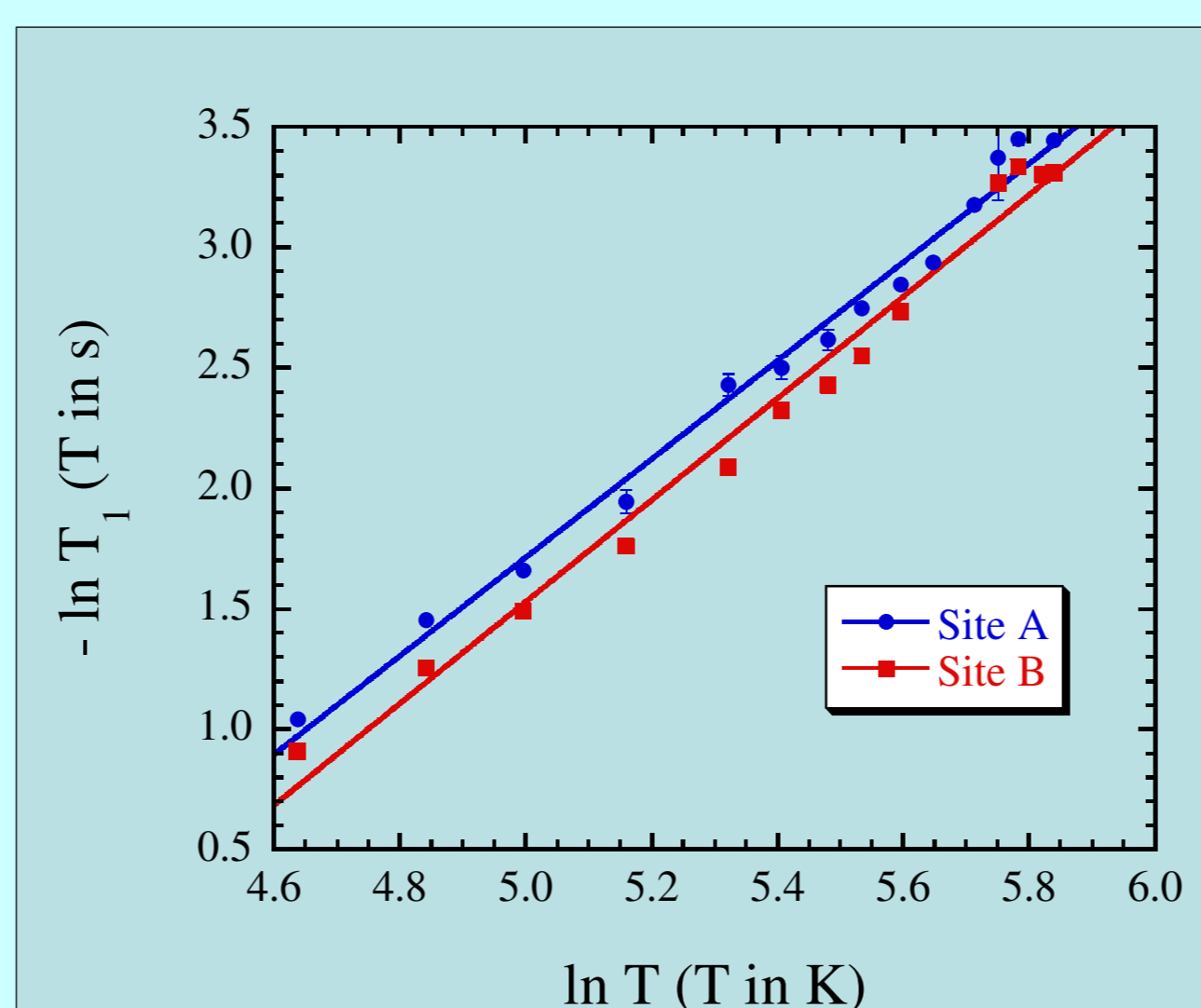
- <sup>1</sup> D. M. Adams and R. Appleby, J. Chem. Soc., Dalton Trans. **11**, 1530 (1977).
- <sup>2</sup> R. C. Zamar *et al*, Phys. Rev. B **58**, 2476 (1998)
- <sup>3</sup> J. Seliger, J. Magn. Reson. **A103**, 175 (1993)

## Low temperature region



Two models were fitted to the data at temperatures below room temperature. A two-phonon Raman model provides an excellent fit to the data in this temperature range. The Debye temperature extracted from the fit is  $47 \pm 5$  K. No value for the Debye temperature could be sourced from the literature, and there is some concern that this may be too low. Fitting the model for torsional oscillations (assuming a single mode) gives a characteristic temperature of  $31.6 \pm 0.4$  K (corresponding to a wavenumber of  $22 \text{ cm}^{-1}$ ). This does not correspond to any modes obtained by previously using Raman spectroscopy<sup>1</sup>, although there is a mode at  $18 \text{ cm}^{-1}$ . It is possible that a number of modes contribute, in which case it is the lowest wavenumber modes that dominate. It is tempting to ascribe spin-lattice relaxation in this temperature region to acoustic phonons and to offer the value for the Debye temperature extracted as realistic estimate.

## Mid-range temperature region



The temperature dependence of the vibrational modes in the temperature range 100 K to 340 K was determined using the following well-known relation:

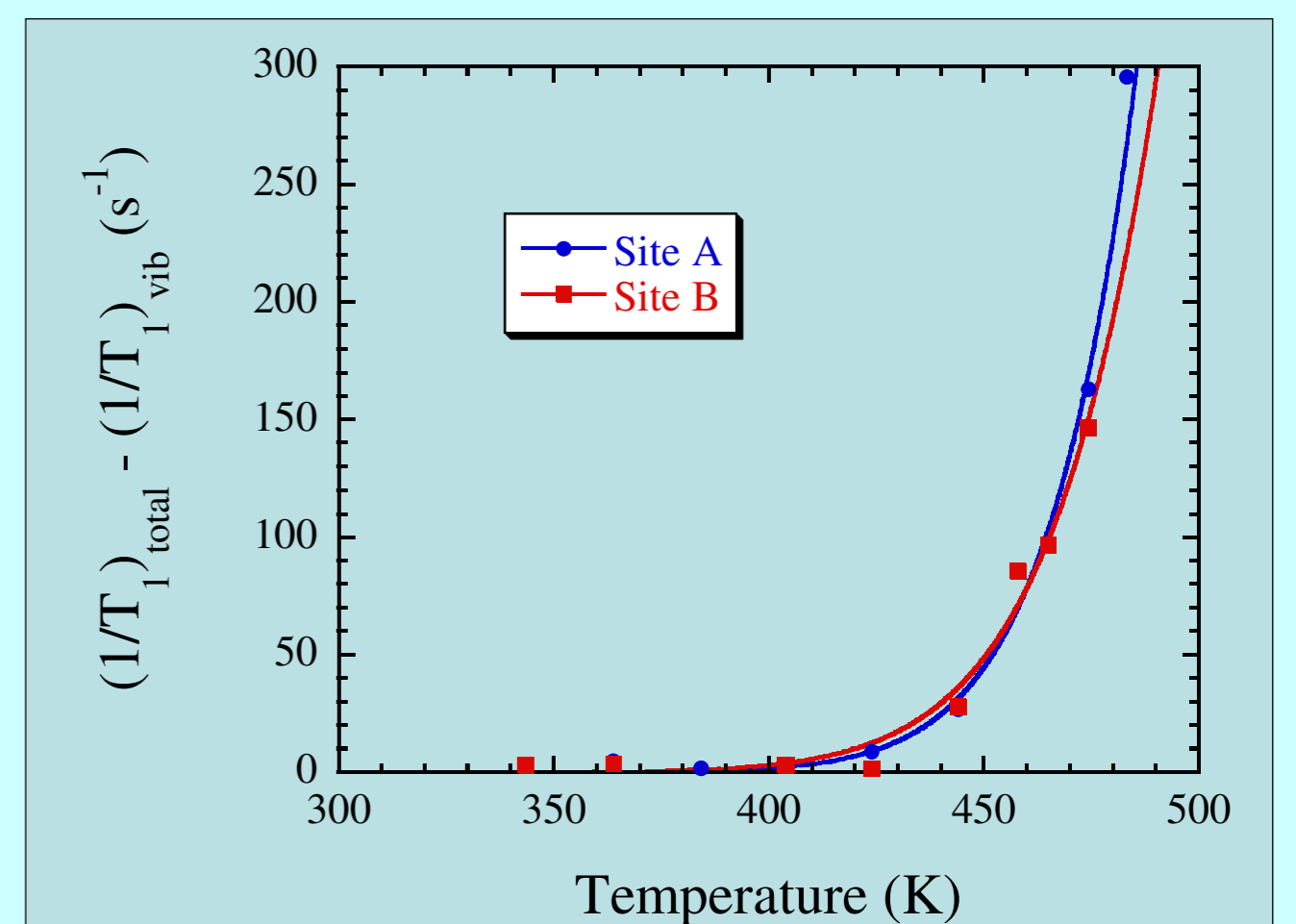
$$\frac{1}{T_1} = AT^n$$

The exponents obtained for the two sites from the plot above are as follows:

- Site A:  $n = 2.04 \pm 0.06$ ;
- Site B:  $n = 2.11 \pm 0.08$ .

A was determined by fitting over the above temperature range with  $n = 2$ , and these values were used in analysis of the high temperature data.

## High temperature region



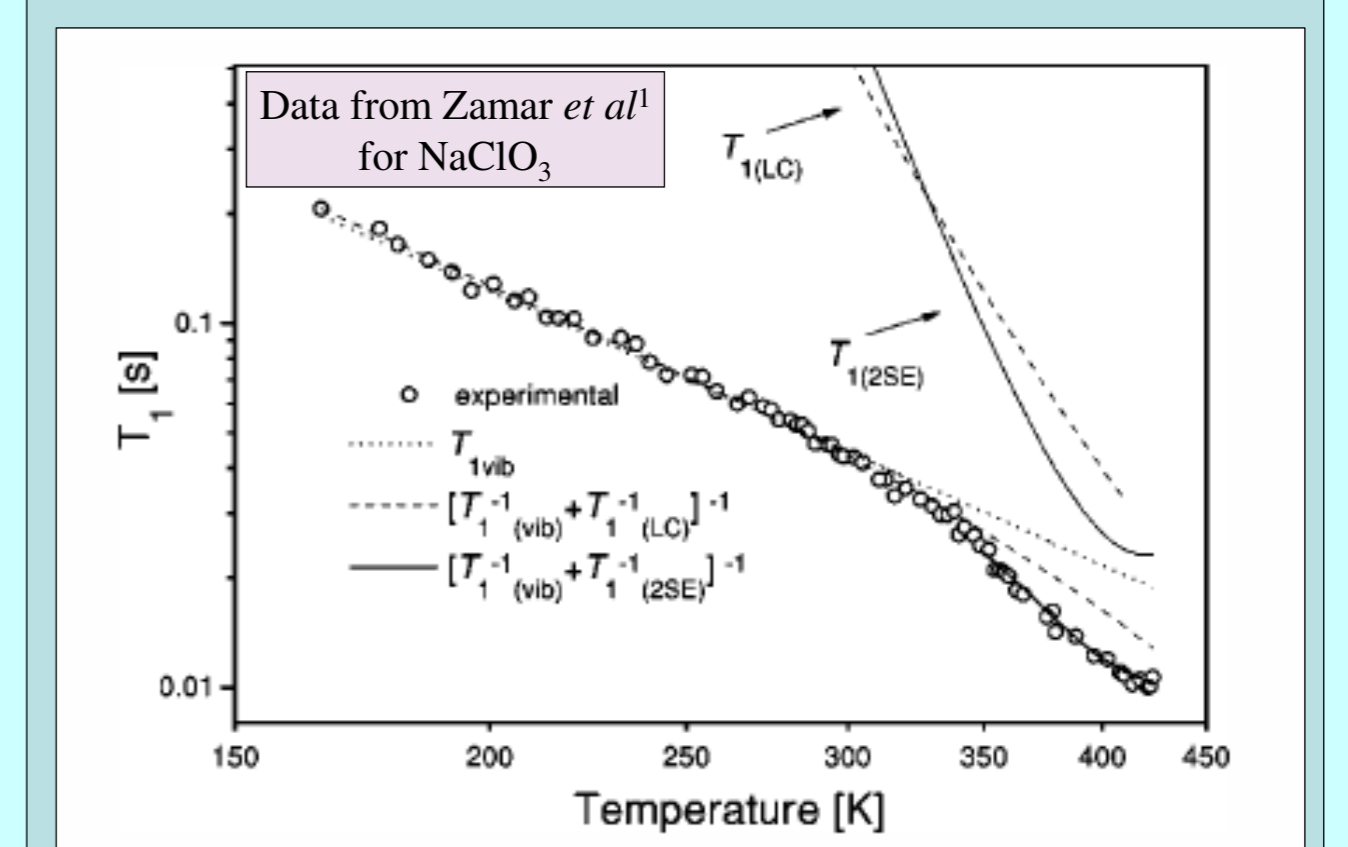
The relaxation rate attributed to the vibrational modes was subtracted from the total relaxation rate for temperatures above 340 K, and the resulting relaxation rate fitted to an Arrhenius model of the form:

$$\frac{1}{T_1} = B \exp\left[-\frac{E_A}{k_B T}\right]$$

The resulting activation energies are as follows for the two sites:

- Site A:  $E_A = 97 \pm 14 \text{ kJ.mol}^{-1}$ ;
- Site B:  $E_A = 83 \pm 10 \text{ kJ.mol}^{-1}$ .

By comparison, Zamar *et al*<sup>2</sup> obtained an activation energy of  $26.4 \pm 1 \text{ kJ.mol}^{-1}$  for  $\text{NaClO}_3$ . They also proposed that orientational disorder could account for a the large deviation from relaxation governed by vibrations. A plot of their data is shown below. There are certainly qualitative similarities between the data presented here, and their data.



Of further interest are the resonance lines obtained from Fast Fourier transforms of the quadrupolar spin-echoes shown below. Seliger<sup>3</sup> has pointed out that the resonance line will split into a doublet when conditions such as those considered by Zamar *et al* are applicable. This is exactly what is observed.

