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Nuclear Quadrupole Resonance Investigations of Clathrate Compounds: I. The ^{35}Cl Resonance of *p*-Dichlorobenzene in Various Clathrate Systems

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Abstract. The ^{35}Cl nuclear quadrupole resonance spectra of *p*-dichlorobenzene in several clathrates are reported in the temperature range 77 K to room temperature. The information provided by this technique as to the nature of the guest-host interactions is discussed in the light of these results and it is concluded that NQR represents a useful technique in this context.

Key words: Nuclear quadrupole resonance, clathrates, *p*-dichlorobenzene, Werner complexes.

1. Introduction

One of the few spectroscopic tools which does not appear to have been so far systematically applied to the study of clathrate complexes is that of nuclear quadrupole resonance. Indeed, apart from two articles devoted to the ^{14}N spectra of molecular nitrogen in β-quinol clathrate [1, 2] there do not appear to have been any references at all to this subject.

NQR spectroscopy, however, can shed light on aspects of these complexes which are not revealed by other techniques. Thus, resonance frequency changes of a given guest molecule in different hosts reflect changes in the molecular environment, whereas the temperature dependence of the resonance frequency reflects the degree of mobility of the guest molecule within the cavity provided by the host molecule. Conversely the use of clathrates is itself a potentially useful technique in the field of nuclear quadrupole resonance spectroscopy, since a given host system can provide a more or less constant crystalline environment for the study of a series of related guest molecules. We report here the results of a preliminary study in which we have formed clathrates of *p*-dichlorobenzene with a variety of related Werner complexes of general formula: $M^{II}(\gamma\text{-picoline})_4(SCN)_2$ and with 1,2-bis(diphenylphosphinoselenoyl)ethane.

2. Experimental

The three thiocyanate complexes were prepared by a published method [3] and the selenocyanate by a straightforward adaptation of this. 1,2-Bis(diphenylphosphinoselenoyl)ethane was prepared by a published method [4] from a commercial sample of the phosphine (Alfa Chemicals). The clathrates were likewise prepared by published methods [3,4]. The NQR spectra were measured on a Decca super-regenerative spectrometer and frequencies were measured against harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802A digital thermometer and variable temperatures between 77 K and room temperature obtained using a cryostat controlled with an Artronix 5301-E temperature controller.

3. Results and Discussion

The ^{35}Cl resonance frequencies at 77 K of *p*-dichlorobenzene in the clathrates are shown in Table I, together with that of the pure compound in its three different crystalline phases.

Table I. ^{35}Cl resonance frequencies (MHz at 77 K) and temperature coefficients (kHz K^{-1} at 200 K) of *p*-dichlorobenzene clathrates

Compound	ν(MHz)	$\left(\frac{\partial \nu}{\partial T}\right)_{200\text{ K}}$ (kHz K^{-1})
Ni(γ-picoline)$_4$SCN/*p*-dichlorobenzene	35.155	−5.01
Co(γ-picoline)$_4$SCN/*p*-dichlorobenzene	35.119	−5.30
Fe(γ-picoline)$_4$SCN/*p*-dichlorobenzene	35.101	−5.44
Ni(γ-picoline)$_4$SeCN/*p*-dichlorobenzene	35.050	−5.19
1,2-bis(diphenylphosphinoselenoyl)ethane/*p*-dichlorobenzene	35.507	−3.33
α-*p*-dichlorobenzene	34.780	−2.39
β-*p*-dichlorobenzene	34.765	−2.39
γ-*p*-dichlorobenzene	35.208	−2.23

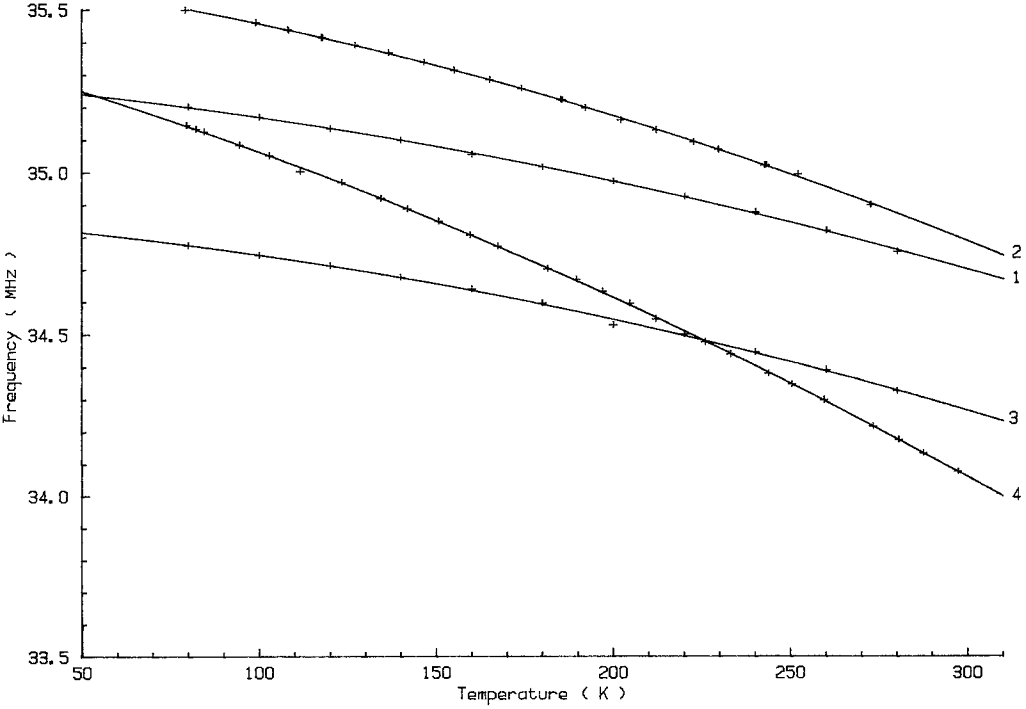

Fig. 1. Temperature dependence of the ^{35}Cl resonance frequency of crystalline *p*-dichlorobenzene and of *p*-dichlorobenzene in various clathrates: 1. *p*-dichlorobenzene, γ-phase; 2. *p*-dichlorobenzene in 1,2-bis(diphenylphosphinoselenoyl)ethane; 3. *p*-dichlorobenzene, α-phase; 4. *p*-dichlorbenzene in Ni(γ-picoline)$_4$(SCN)$_2$.

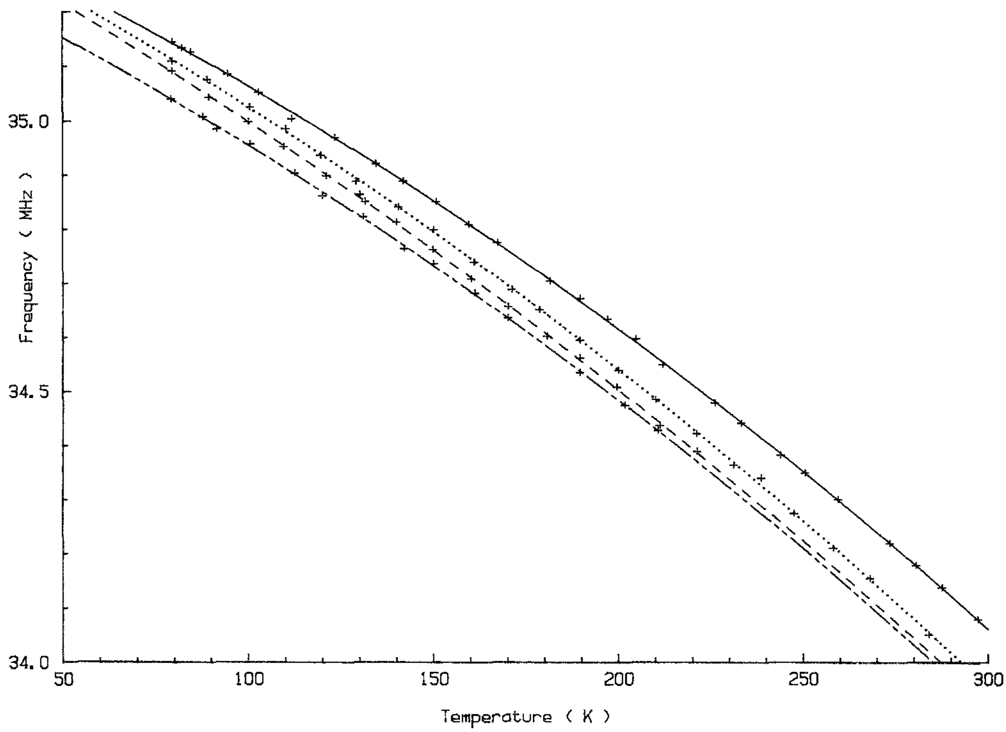

Fig. 2. Temperature dependence of the ^{35}Cl resonance of *p*-dichlorobenzene in various Werner complexes, $M^{II}(\gamma\text{-picoline})_4(XCN)_2$. ———— $M^{II} = Ni$, $X = S$; ········· $M^{II} = Co$, $X = S$; - - - - - $M^{II} = Fe$, $X = S$; -··-··- $M^{II} = Ni$, $X = Se$.

Figures 1 and 2 show the temperature dependence in the range 77 to 300 K of these resonance frequencies, again compared with those of the pure compound.

The theory of the effect of the crystal lattice on the quadrupole resonance frequency of a nucleus in a molecule forming part of that lattice has been discussed on numerous occasions [5]. Over the temperature range used here the temperature dependence is given by the Bayer–Kushida equation.

$$\nu = \nu_0 \left[1 - \frac{3\hbar}{2} \sum_i \frac{A_i}{\omega_i} \left(\frac{1}{2} + \frac{1}{\exp \frac{\hbar \omega_i}{kT} - 1} \right)\right]$$

where ν_0 is the resonance frequency inside the hypothetical static lattice, $\omega_i (= 2\pi\nu_i)$ are the various lattice frequencies and A_i is a term which may be calculated from the normal coordinate of the corresponding lattice vibration. Strictly speaking, the Bayer–Kushida equation is for the temperature dependence at constant volume; to correct at least phenomenonologically for the fact that the temperature dependencies are measured at constant pressure it is convenient to include a linear temperature dependence of the lattice frequencies [6].

$$\omega_i = \omega_i^0 (1 - g_i T)$$

As can be seen, the Bayer–Kushida equation is very unwieldy and has only been satisfactorily fitted to experiment for the most simple of cases. No attempt will be made to do this here but we will need to refer to the equation to be able to compare the results for a given molecule in different crystalline environments. Qualitatively, we may compare two different terms in this equation; the frequency difference at absolute zero and the slope of the temperature dependence at some convenient temperature. For the first we must remember that ν_0 itself is lattice-dependent so that the frequency difference at absolute zero becomes

$$\Delta\nu = \nu_{10} - \nu_{20} - \frac{3\hbar}{4}\left[\nu_{10}\sum_i \frac{A_{1i}}{\omega_{1i}^0} - \nu_{20}\sum_i \frac{A_{2i}}{\omega_{2i}^0}\right]$$

A brief consideration of the order of magnitude of the terms in this equation shows that it is only when ν_{10} and ν_{20} are identical – as in the case, for example, of a discussion of isotope effects [7] – that the terms in A/ω are important and yield a frequency difference of, at most, a few tens of kHz. In the present case, the dominant term will be $(\nu_{10} - \nu_{20})$.

The ratio of the slopes at constant pressure becomes

$$\left(\frac{\partial\nu_1}{\partial T}\right)\Big/\left(\frac{\partial\nu_2}{\partial T}\right) = \frac{\nu_{10}}{\nu_{20}}\cdot\frac{\Sigma_i\, A_{1i}\,\mathrm{cosech}^2\left(\dfrac{\hbar\omega_{1i}^0}{2k}\left(\dfrac{1}{T} - g_{1i}\right)\right)}{\Sigma_i\, A_{2i}\,\mathrm{cosech}^2\left(\dfrac{\hbar\omega_{2i}^0}{2k}\,\dfrac{1}{T} - g_{2i}\right)}\,.$$

Since the ratio ν_{10}/ν_{20} is expected to be very close to unity, any major difference in the slopes can only be due to the terms in the summation. This will usually imply that the system having the largest slope has the lowest lattice vibration frequencies or, in more qualitative terms, has a greater degree of motional liberty. This is clearly the case if we compare the slope for pure *p*-dichlorobenzene in any of its crystalline modifications and the slope for any of the clathrates reported here (Table I). The results are thus consistent with *p*-dichlorobenzene being relatively loosely held within a molecular cage in the clathrate complexes.

To compare properly the differences at absolute zero, we must be able to extrapolate reliably to that temperature and this is not possible unless measurements are made down to 4 K. Such data are available for pure *p*-dichlorobenzene but not at present for the clathrates. Qualitatively, however, we may estimate that the frequencies of the clathrates are several hundred kilohertz greater than that of γ-*p*-dichlorobenzene. Insofar as most coupling constants measured in the crystalline state are less than those measured in the gas phase, this result is again consistent with the notion that *p*-dichlorobenzene has only relatively weak interactions with the surrounding molecules in these clathrates and, thus, more closely resembles gaseous *p*-dichlorobenzene than crystalline *p*-dichlorobenzene.

If we compare the clathrates among themselves we see that whereas, as would be expected, all the Werner complexes have similar slopes, that of the 1,2-bis(diphenylphosphinoselenoyl)-ethane is intermediate between that of the Werner complexes and crystalline *p*-dichlorobenzene and we may conclude that the size of the cavity is smaller in the phosphine clathrate. Within the group of the Werner complexes the ionic radius of the central metal atom increases in the order $\mathrm{Ni^{II}} < \mathrm{Co^{II}} < \mathrm{Fe^{II}}$ and the NQR results indicate that the size of the cavity in the three thiocyanates likewise increases in that order. Finally the selenocyanate is certainly somewhat larger than the thiocyanate ion and, thus, is again reflected in the slopes for the two nickel complexes.

4. Conclusion

The results of this preliminary study indicate that useful information concerning the local environment of guest molecules in clathrates can be obtained from nuclear quadrupole resonance studies, particularly from the temperature dependence of this parameter. It suggests that measurements should be made over as wide a temperature range as possible, preferably down to 4 K. Measurements of nuclear quadrupole relaxation times as a function of temperature will provide another parameter of interest. Finally, if sufficiently large (1×10^{-3} cm^3) single crystals of the clathrate can be prepared, single crystal NQR measurements will rapidly reveal the orientation of the guest molecule within the host lattice.

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