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^{35}Cl Nuclear Quadrupole Resonance studies of CCl_4 as a guest molecule in various clathrates.

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Nuclear Quadrupole Coupling constants measure the electric field gradient tensor at a nucleus in a molecule. The field gradients in free molecules are determined by the electronic structure, but, in the solid state, are affected by environmental factors; hence their application to the study of inclusion complexes.

Thus the resonance frequencies of a guest molecule in an inclusion complex provide information on the following points.

Site Symmetry

If a guest molecule contains more than one equivalent nucleus, e.g. CCl_4 several distinct resonances indicate that the site symmetry is less than that of the free molecule.

Example : Dianin's compound is known to form cavities having a three-fold symmetry axis. The NQR spectrum of the ^{35}Cl nucleus in CCl_4 included in Dianin's compound shows two resonances, one from the single chlorine on the three-fold axis and another more intense resonance from the three remaining nuclei.

The complex CCl_4/Fe(III)tris-(AcAc) shows similar behaviour, indicating that, here too, the cavities have three-fold symmetry.

Site multiplicity

A guest molecule showing more distinct resonances than equivalent nuclei provides clear evidence of multiple inclusion sites.

Examples :

CCl_4/Ni(exan)$_2$	(2,2'-bipyridyl)
39.561	40.061
40.260	40.352
40.627	40.708
40.763	40.890

trans $CHCl=CHCl$/Fe(III)tris-acac

34.722 34.845
35.093 35.289

Chlorobenzene/Ni(4-picoline)$_4$(SCN)$_2$

34.475 34.670

Temperature Dependence

NQR resonance frequencies show a marked temperature dependence whose principal cause is the averageing of the field-gradient tensor brought about by molecular libration. For a nucleus such as ^{35}Cl in an organochlorine molecule, where the principal field-gradient axis lies along the C-Cl bond, libration about the bond-axis has no effect on the field-gradient, while libration about an axis perpendicular to the bond decreases the field-gradient by an amount proportional to the square of the librational amplitude. For CCl_4 in a trigonally-symmetric environment there is one librational mode about the three-fold axis and a pair of degenerate modes perpendicular to it. The temperature dependence of the NQR frequency of the axial chlorine atom is thus expected to be less than that of the remaining three, whose field-gradients are affected by all three librations.

The results for the two trigonal complexes are shown below. The fade out of the resonances indicates the onset of rapid reorientation and the surmounting of the librational barrier. This is particularly clear for the "equatorial" chlorine atoms in the Dianin complex, and is consistent with the egg-shaped form of the cavity in this compound.

The Bayer-Kushida theory of the temperature-dependence of NQR frequencies has the form :

$$\nu = \nu_0 - \nu_0 \sum_i \frac{A_i}{f_i \left[\exp f_i/kT - 1 \right]}$$

where :

ν_0 = NQR frequency at 0K

$A_i = \dfrac{3h \sin^2\alpha_i}{8\pi^2 I}$

I = The molecular moment of inertia about the libration axis

α_i = The angle between the bond axis and the libration axis

$f_i = f_{0i} \; (1 - g_i \, T)$

f_{0i} = The libration frequency at 0K

g_i = A semi-empirical factor which includes the temperature dependence and anharmonicity of the librational frequency.

The temperature dependence of the NQR frequencies of ^{35}Cl in CCl_4 in the two trigonally-symmetric hosts have been fitted to this equation with the following results.

Host : Dianin's compound

ν_0^{ax} = 40.613 MHz ν_0^{eq} = 40.957 MHz

Axial libration :
f = 37.37 cm^{-1} , g = $2.047*10^{-3}$

Doubly-degenerate libration :
f = 47.04 cm^{-1} , g = $0.518*10^{-3}$

Host : Fe(III)tris-(acetylacetonate)

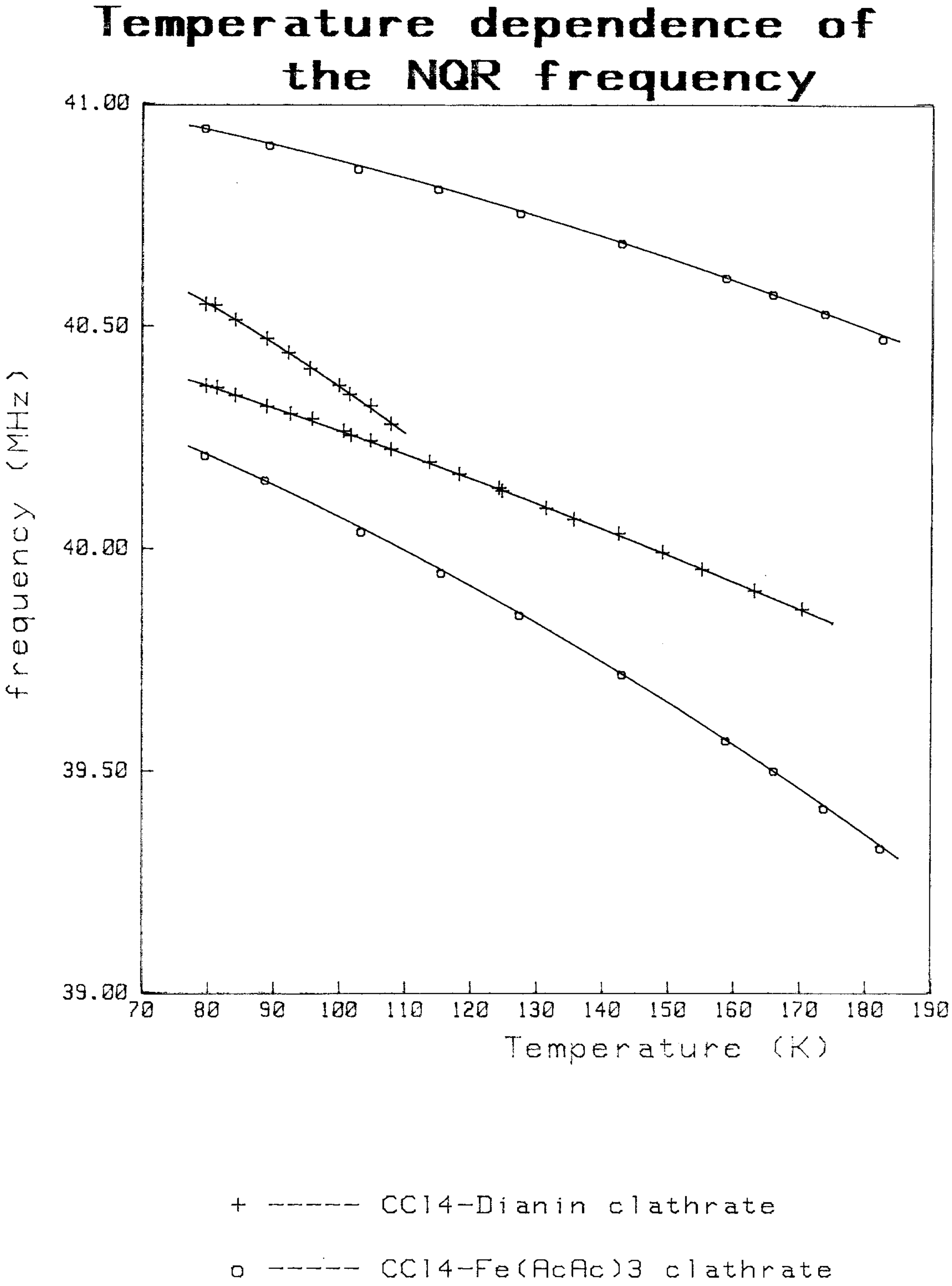
ν_0^{ax} = 41.088 MHz ν_0^{eq} = 40.529 MHz

Axial libration :
f = 43.78 cm^{-1} , g = $1.005*10^{-3}$

Doubly-degenerate libration :
f = 61.37 cm^{-1} , g = $1.070*10^{-3}$

The low librational frequency of 37 cm^{-1} and the high value of the parameter, g, is further evidence of the ease of rotation about the three-fold axis in the Dianin complex. Indeed in the sulphur analogue of Dianin's compound, where the cavities are presumably slightly bigger, the resonance from the "equatorial" chlorines has already disappeared at 77K. In contrast to this the complexes between Dianin's compound and $BrCCl_3$ or CF_3CCl_3, where the more bulky axial substituent causes a tighter fit in the cavity, the "equatorial" resonances persist to 114K and 166K respectively.

These studies are being extended to 4K and complemented by structural and spectroscopic studies.


Temperature dependence of
the NQR frequency
41.00
40.50
40.00
39.50
39.00
frequency (MHz)
70
80
90
100
110
120
130
140
150
160
170
180
190
Temperature (K)
+ ----- CCl4-Dianin clathrate
o ----- CCl4-Fe(AcAc)3 clathrate