



# A model to describe the inhomogeneous broadening of NQR lines in chlorohalobenzenes with orientational or substitutional disorder



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## ABSTRACT

A simple model to explain the NQR lineshape in solids with orientational disorder or substitutional disorder is presented. The particular case of m-chlorobromobenzene is studied. It is based on the assumption that Bromine atoms, of m-chlorobromobenzene molecules, behave as point defects in the m-dichlorobenzene lattice that modify the crystalline Electric Field Gradient. The model is also tested successfully in solid solutions of p-dichlorobenzene-p-dibromobenzene, where Bromine atoms of p-dibromobenzene molecules are assumed to be homogeneously distributed in the p-dichlorobenzene lattice. The lineshape, of others disordered chlorohalobenzenes, are also analyzed. Also, a characterization of m-chlorobromobenzene dynamics is included. In particular, there is no evidence of molecular reorientations as it is observed in the disordered phases of o-chlorobromobenzene.

## 1. Introduction

Many organic compounds have the ability to exist in more than one crystal structure or phase having different arrangements or conformations of the molecules in the crystal lattice, an ability which is known as polymorphism. Among the polymorphs, there are those with a certain disorder in the molecular arrangement, including orientational disorder. Typical examples of this kind of disorder are p-chlorobromobenzene and p-chloroiodobenzene, which are isomorphous with p-dichlorobenzene. In these compounds the average molecule is obtained by centrosymmetric overlap of two molecules with half-weight atoms [1–3]. The disorder and isomorphism present in p-chlorohalobenzenes seems to be also present in m-chlorofluorobenzene [4] and in o-chlorohalobenzenes, (o-C<sub>6</sub>H<sub>4</sub>ClX, X = Br, F) [5], which have been recently studied using <sup>35</sup>Cl Nuclear Quadrupole Resonance (NQR). Since these crystals exhibit long-range positional order but orientational disorder, they are intermediate between crystals and true glasses. Therefore, their study is of interest, not only for its own sake, but also because it provides a useful approach to the understanding of the properties of glasses. Unlike what happens in true glasses, where lineshapes are Gaussians with a linewidth of 1 MHz, the lineshapes of m-chlorohalobenzenes and o-chlorohalobenzenes present certain structure. The question to answer is if the isomorphism with m-dichlorobenzene and o-dichlorobenzene added to orientational disorder is responsible of this kind of lineshape.

NQR allows the study of these chlorohalobenzenes by exploring the

effects of the substitution on the Electric Field Gradient (EFG) at the Chlorine nuclear site. The EFG that the nucleus feels reflects the fine details of the electronic wave functions around it (molecular orbitals). In a solid, traditionally, three contributions to EFG have to be considered: the isolated target atom (local), the space between the target atom and its nearest neighbours, and the rest of the atoms in the crystal (lattice). Intermolecular interactions change the molecular geometry (bond length, bond angles), which leads to changes in the electron density distribution, manifested by shifts of the resonance frequencies. The main contribution to the EFG comes from valence electrons of the atom considered and the EFG is given in terms of the populations of localized orbitals centred at the atom containing quadrupolar nucleus (intramolecular contribution), whereas the intermolecular interactions produce a contribution of the order or lower than 5% of the total EFG as stated by Weiss [6], Semin et al. [7] and Latosińska [8]. Particularly, Kitaigorodsky [9] concluded, base on experimental data, that the difference between the average NQR frequencies of two modifications (phases) at the same temperature does not, as a rule, exceed the 1.5% of the average frequency.

These intermolecular contributions to the EFG are well observed when p-dichlorobenzene (PDCB) is randomly substituted by p-dibromobenzene (PDBB) molecules (solid solutions) [10,11] or in other solid solutions of organic compounds [7,12]. Particularly it has been shown [10] that the resonance frequency in the solid solution of PDCB-PDBB increases linearly with concentrations up to 12%.

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It is important to point out that in chlorohalobenzenes the asymmetry parameter ( $\eta$ ) is lower than 0.15 [13]. For this reason the corrections to the quadrupolar frequency due to  $\eta$  are not considered. These corrections are lower than 0.4%.

In the present work, the local order and the dynamic of the molecules in the solid phase of m-chlorobromobenzene are characterized by NQR. As it occurs in other compounds of the chlorohalobenzenes family (p-chlorobromobenzene, o-chlorobromobenzene, o-chlorofluorobenzene and m-chlorofluorobenzene) orientational disorder is present.

A simple statistical theory is developed to explain the inhomogeneous line broadening, observed in molecular compounds with orientational disorder. The model is successfully applied to m/o-chlorobromobenzene, m/o-chlorofluorobenzene and solid solutions of p-dichlorobenzene-p-dibromobenzene with different concentration as well.

## 2. Experimental

m-chlorobromobenzene (MCBB) sample ( $C_6H_4ClBr$ ), used in the experiments, was obtained from Aldrich Chemical Co (#124036) and used without further purification.  $^{35}Cl$  NQR measurements were done using a Fourier transform pulse spectrometer with a Tecmag NMRkit II unit and a Macintosh-based real time NMR station. The sample container was a glass cylinder of length 3 cm and diameter 1 cm, closed under vacuum. NQR spectra were obtained using spin-echo Fourier transform mapping spectroscopy [14,15] with  $\pi/2 = 12 \mu s$  and  $\tau = 100 \mu s$ . The mapping frequency step used was 11.7 kHz and the scans number was 400.  $T_1$  measurements were made using the standard  $\pi/2 - \tau - \pi/2$  two-pulse sequence with  $\pi/2 = 13 \mu s$ . The temperature was controlled to within 0.1 K using a homemade cryogenic system with a Lakeshore temperature controller. The temperature range covered was between 80 and 260 K.

Doped polycrystalline samples of p-dichlorobenzene (PDCB) with concentrations of p-dibromobenzene (PDBB) in the range of 30–50% were obtained from precipitates of saturated PDCB solutions containing the appropriate quantities of PDBB. PDCB and PDBB were also obtained from Aldrich Chemical and used without further purification.

## 3. Results and discussion

### 3.1. Inhomogeneous line broadening

The nuclear quadrupole resonance frequency is proportional to the z component of the EFG ( $eq$ ) which, in the simplest approximation, is determined both by an intramolecular contribution ( $eq_{mol}$ ) and a crystalline one ( $eq_{cryst}$ ) [16]. The intramolecular contribution is mainly due to the electronic bonding, while the crystalline contribution is mainly due to short-range intermolecular interactions. In this last case, the EFG is generated by all the other molecules in the crystal, which can be treated as a distribution of charges, dipoles, distant ions or other components that surround the quadrupolar nucleus [17].

When orientational disorder is present, a wide distribution of quadrupolar frequencies appears, as it is observed in Fig. 1, where m-chlorobromobenzene (MCBB) spectrum at 80 K is shown. The spectrum presents a structure with three peaks of different areas (ratio of these areas is 3:4:1). As the number of lines is related to the number of non-equivalent nuclei in the crystal cell and the area under the NQR line is proportional to the number of resonant nuclei at that frequency, it results that no less than 8 different contributions should be considered.

For comparison, m-chlorofluorobenzene (MCFB) spectrum is included in this figure and the quadrupolar frequencies characterizing ordered m-dichlorobenzene (MDCB) are also indicated.

MDCB crystallizes in the space group  $P2_1/c$  with  $Z = 8$  and two molecules in the asymmetric unit [18]. Since each molecule has two chlorine atoms, four quadrupolar frequencies having a line width of 2 kHz were reported as shown in Table 1 [19,20]. Instead, due to disorder, spectra of MCBB and MCFB widen inhomogeneously around these frequencies.

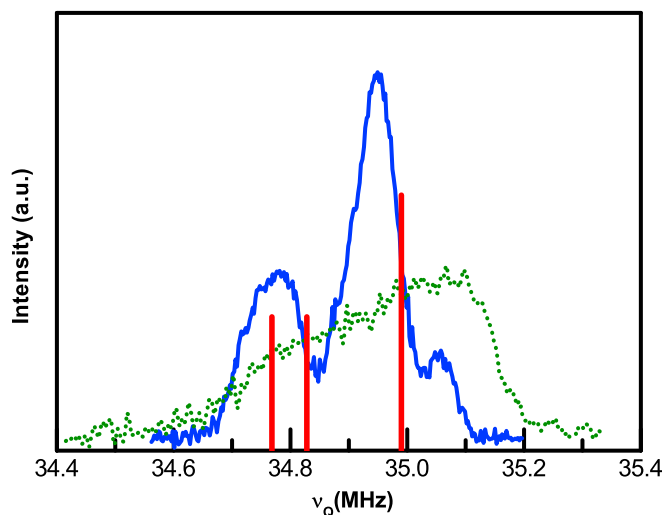


Fig. 1. NQR spectra of MCBB (blue solid line) and MCFB (green dotted line) in the disordered phase II at 80 K [4]. NQR frequencies of MDCB (red straight lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To explain these spectra, the model presented in this paper is based on the assumption that Bromine atoms, of molecules in MCBB, behave as point defects (homogeneously distributed) in the crystal lattice of MDCB that alter the crystalline contribution to the EFG.

Many branches of spectroscopy have developed theories, to explain inhomogeneous line broadening, based on “statistical method” [21–25]. Stoneham and Van Berlo assumed that the contribution of defects which causes broadening simply adds linearly, while the other authors indicate that the additivity of the physical contributions holds for the EFG tensor elements but not for its eigenvalues, i.e. the resonance frequency. However, in molecular crystals, the crystalline contribution to EFG may be considered as a small perturbation to the total EFG at the nuclear site and it seems reasonable that the NQR characteristic parameters follow a linear relationship with the substituent concentration.

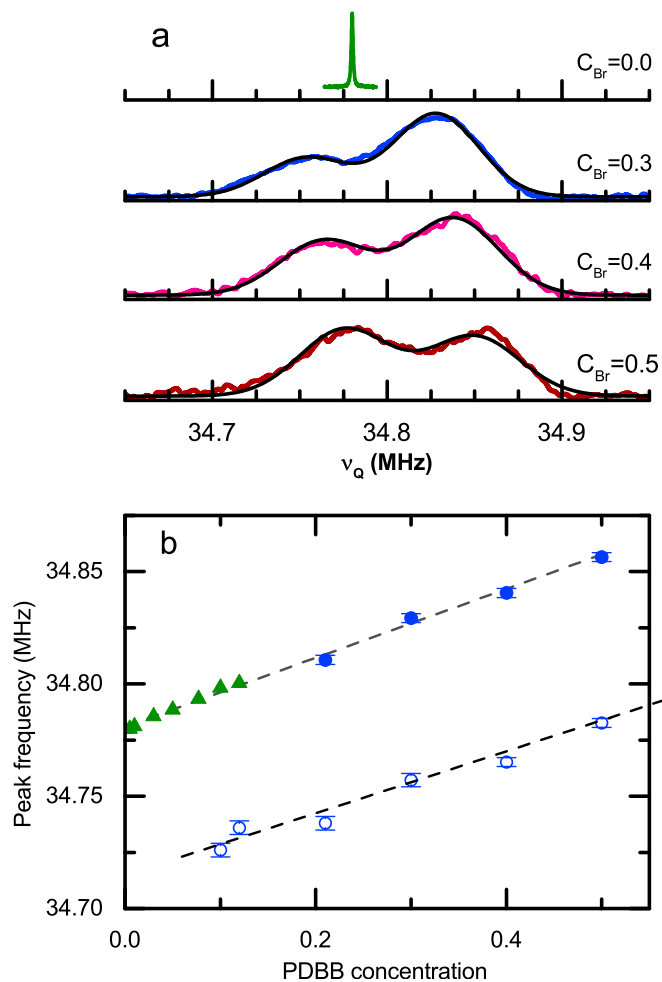
Since there is a close similarity between statistically disordered crystals and solid solutions, an equivalent assumption is also valid for solid solutions of PDCB-PDBB. In this case, it is assumed that PDBB molecules are homogeneously distributed in the crystal lattice of PDCB. Fig. 2a shows the experimental widening and splitting of the NQR line in this case for different concentrations and Fig. 2b shows the shift of the experimental frequencies of PDCB-PDBB solid solution as a function of substituent concentration. Clearly the shifts are linear with concentrations up to 50% confirming that the individual contribution of each point defect linearly overlaps, generating the crystalline contribution to the EFG [21,26]. Therefore the resonance frequency can be written as:

$$\nu_Q = \nu_{mol} + \nu_{cryst} \quad (1)$$

where  $\nu_{mol}$  is the main contribution to the frequency, due to the EFG generated by electrons in the C—Cl bond and by the molecule. Instead,  $\nu_{cryst}$  is the contribution to the frequency due to the EFG generated by all the other molecules in the crystal and it is calculated as the superposition of EFG generated by point charges. Since the C—H bonds occupy regular lattice sites, the particular charges located at these atoms do not contribute to the inhomogeneous broadening and their contribution can

Table 1  
NQR frequencies of m-dichlorobenzene.

| T [K] | $\nu_1$ [MHz] | $\nu_2$ [MHz] | $\nu_3$ [MHz] | $\nu_4$ [MHz] |
|-------|---------------|---------------|---------------|---------------|
| 77    | 34.809        | 34.875        | 35.030        | 35.030        |
| 196   | 34.724        | 34.732        | 34.503        | 34.523        |



**Fig. 2.** (a) NQR lineshape of solid solutions of PDCB-PDBB, at 77 K, at three different concentrations. Pure PDCB spectrum is included as a reference. The solid lines represent the fits with Eq. (11). (b) Shift of the frequencies of PDCB-PDBB solid solution as a function of substituent concentration. (triangle) data from Ref. [9].

be included in  $\nu_{mol}$ .

Having in mind these considerations  $\nu_{cryst} = \nu = \sum \nu_l$  where  $\nu_l$  (a random variable) is the contribution to the EFG of the  $l$ -th site in the lattice, being  $\nu_{\alpha l}$  if an element of type  $\alpha$  is present (in our case  $\alpha = Cl, Br$ ). Then, it is possible to link this problem to a random walk problem, as proposed by Cohen y Reif [26]. With these considerations in mind, the line shape is given by:

$$g(\nu) = \int \dots \int \delta\left(\nu - \sum_l \nu_l\right) \prod_l P_l(\nu_l) d\nu_l = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\nu\tau} f(\tau) d\tau \quad (2)$$

with

$$f(\tau) = \prod_l \left[ \sum_{\alpha} C_{\alpha} e^{-i\nu_{\alpha l}\tau} \right] \quad (3)$$

where  $C_{\alpha}$  is the concentration of the  $\alpha$ -th substituent ( $\sum C_{\alpha} = 1$ ). The dominant contribution to the line shape  $g(\nu)$  in the integral of Eq. (2) comes from small values of  $\tau$ , reason why it is possible to write down:

$$f(\tau) = e^{-\left(i\bar{\nu}\tau + \frac{1}{2}\sigma^2\tau^2\right)} \quad (4)$$

where:

$$\bar{\nu} = \sum_l \bar{\nu}_l = \sum_l \sum_{\alpha} C_{\alpha} \nu_{\alpha l} \quad \sigma^2 = \sum_l \left[ \sum_{\alpha} C_{\alpha} \nu_{\alpha l}^2 - \left( \sum_{\alpha} C_{\alpha} \nu_{\alpha l} \right)^2 \right] \quad (5)$$

Substitution of Eq. (4) in Eq. (2) gives a Gaussian lineshape centred at  $\bar{\nu}$  with a linewidth  $\sigma$  as it was shown in Ref. [26].

Since the EFG is proportional to  $(1/r^3)$ , charges located very close to the site under consideration give the largest contribution to the EFG. Let's assume that there is only one site ( $l = 1$ ) where the substituent contribution to the EFG is larger than those that belongs to other crystalline sites. In this situation, Eq. (4) can be written as:

$$f(\tau) = (C_{Cl} e^{-i\nu_{Cl,1}\tau} + C_{Br} e^{-i\nu_{Br,1}\tau}) \prod_{l \neq 1} [C_{Cl} e^{-i\nu_{Cl,l}\tau} + C_{Br} e^{-i\nu_{Br,l}\tau}] \quad (6)$$

where the product term can be replaced by Eq. (4) (having in mind that the product is over all the sites except the first important neighbour). Then:

$$f(\tau) \cong (C_{Cl} e^{-i\nu_{Cl,1}\tau} + C_{Br} e^{-i\nu_{Br,1}\tau}) e^{-\left(i\bar{\nu}\tau + \frac{1}{2}\sigma^2\tau^2\right)} \quad (7)$$

Resulting finally:

$$g(\nu) = \frac{1}{\sqrt{2\pi}\sigma} \left( C_{Cl} e^{-\frac{(\nu - \bar{\nu} - \nu_{Cl,1})^2}{2\sigma^2}} + C_{Br} e^{-\frac{(\nu - \bar{\nu} - \nu_{Br,1})^2}{2\sigma^2}} \right) \quad (8)$$

This means that the presence of disorder, in this special case, splits the spectrum into two contributions. In the case under consideration:

$$\bar{\nu} = \sum_{k \neq 1} \nu_{Cl,k} + C_{Br} \Delta\nu_{ClBr} \quad (9)$$

$$\sigma^2 = C_{Cl} C_{Br} \sum_{k \neq 1} (\nu_{Cl,k} - \nu_{Br,k})^2 = C_{Br} (1 - C_{Br}) \sigma_o^2 \quad (10)$$

In first term, to verify the validity of Eq. (8), lineshapes of solid solutions of PDCB-PDBB were used, with different concentrations.

PDCB in phase  $\alpha$  has a monoclinic structure [27]. At  $T = 293$  K, the first important neighbour of a chlorine atom is at  $3.8 \text{ \AA}$ , while the second neighbour is at a distance 6% greater. This implies that the contribution of second neighbours is 19% smallest and the contribution of following neighbours much smallest. So, the conditions of the proposed model are satisfied.

In order to fit data the following expression was used:

$$g(\nu) = A \left( (1 - C_{Br}) e^{-\frac{(\nu - \nu_1 - C_{Br} \Delta\nu_{ClBr})^2}{2C_{Br}(1 - C_{Br})\sigma_o^2}} + C_{Br} e^{-\frac{(\nu - \nu_2 - C_{Br} \Delta\nu_{ClBr})^2}{2C_{Br}(1 - C_{Br})\sigma_o^2}} \right) \quad (11)$$

where  $\nu_1 = \sum \nu_{Cl,k} = \nu_{Cl}$ ,  $\nu_2 = \nu_{Cl} + \nu_{Br,1} - \nu_{Cl,1}$  and  $\sigma_o^2$  are the fitting parameters with  $\nu_{Cl}$  the nuclear quadrupolar frequency of p-DCBB. In Fig. 2a it is shown the simultaneous fit, with Eq. (11), of the NQR lines corresponding to three different concentrations of solid solutions of PDCB-PDBB at 77 K. The data are well fitted with two Gaussians of amplitudes  $C_{Cl}$  and  $C_{Br}$ , with the same values of  $\Delta\nu_{ClBr}$  and  $\sigma_o^2$ . From the fit it results that:  $\sigma_o = 54 \text{ kHz}$  and  $\Delta\nu_{ClBr} = 140 \text{ kHz}$ .

After verifying the validity of Eq. (11) in solid solutions of PDCB-PDBB, it was used to reproduce the particular lineshape of MCBB. If it is assumed that MCBB has the crystal structure of MDCB but with an orientational disorder (in each site  $C_{Cl} = C_{Br} = 0.5$ ), then Eq. (11) can be applied to each NQR line in each of the four inequivalent sites of MCBB. Therefore eight Gaussians of same amplitude and width should be enough to fit the MCBB spectrum. This is clearly shown in Fig. 3a and 3b,

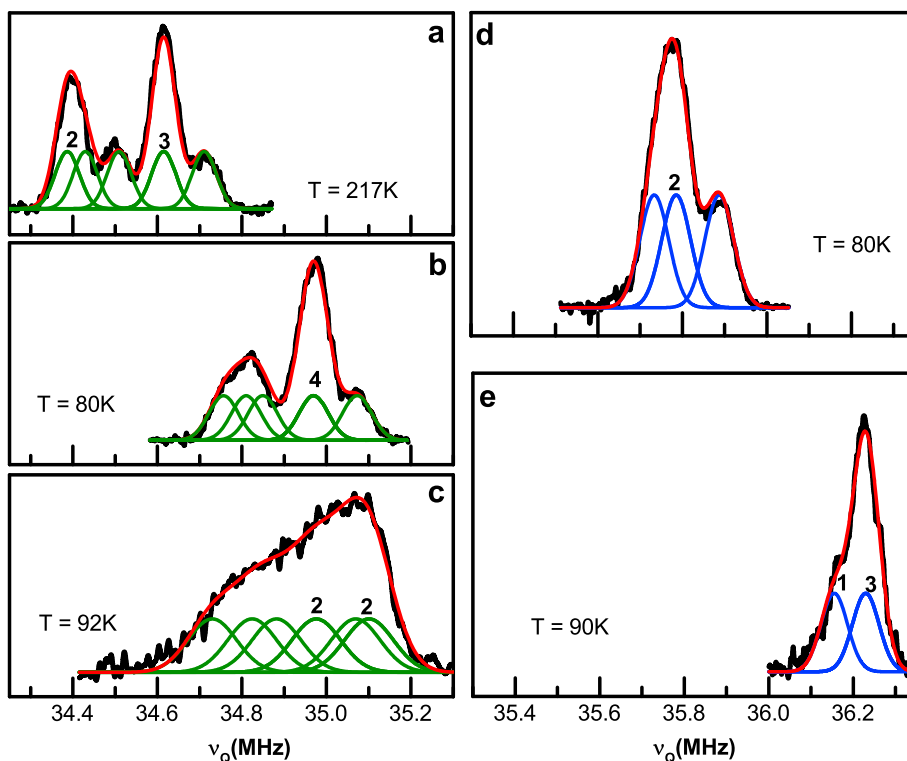


Fig. 3. NQR spectrum of: (a), (b) MCBB, (c) MCFB phase II (d) OCBB phase I and (e) OCFB phase  $\beta$ . Lines represent the fits with Eq. (11).

where  $g(\nu)$  and its fit at 80 and 217 K are shown. From the fit it results that  $\sigma_o \cong 71$  kHz.

On the other hand, since an orientational disorder was proposed in MCFB [4], the fit with Eq. (11) is also applied to the spectrum of this compound. In this case,  $\sigma_o \cong 115$  kHz (see Fig. 3c).

Recently, the disordered phases of *o*-chlorobromobenzene (OCBB) and *o*-chlorofluorobenzene (OCFB) were also associated to an orientational disorder of molecules in the *o*-dichlorobenzene lattice [5]. Therefore the model can be applied to these compounds as well.

OCBB crystallizes at high temperature in the space group  $P2_1/n$  with  $Z = 4$  and one molecule in the asymmetric unit [28]. Since the molecule has two chlorine atoms, two NQR frequencies are observed [29]. Assuming disorder, four Gaussians of same amplitude and width should be enough to fit OCBB spectrum in phase I and OCFB spectrum in phase  $\beta$ . In this last case  $\sigma_o \cong 68$  kHz (Fig. 3e) while in the former case  $\sigma_o \cong 63$  kHz (Fig. 3d).

To confirm that the EFG at each site of MCBB splits in two, due to the lattice contribution of disorder, a simulation is performed. Using the fact that the NQR frequency is proportional to the principal component of the EFG, at the chlorine site, along the Cl bond ( $V_{zz}$ ) [30] and, although no detailed calculation at the nucleus site can be performed, it is possible to obtain the main features of the inhomogeneous spectra doing a simulation of the EFG distribution with the simple model described in Ref. [5]. In order to reproduce the inhomogeneous profile of MCBB, the two molecules containing the nuclei of interest are located at the centre of a simulated cube, with a side length of approximately 170 Å, consisting of monoclinic unit cells which reproduce the  $P2_1/n$  crystalline array in MDCB and each molecule is allowed to swap the positions of the atoms of chlorine and bromine at random. For each disordered array, the inhomogeneous contribution due to the halogens was calculated at each site the chlorine atom can occupy.

About 25000 of these configurations were enough to build smooth profiles which are shown in Fig. 4a. The chlorine charge  $q_{Cl}$  was obtained using  $p = (-q)d$  and the bromine charge was set proportional to  $q_{Cl}$  ( $q_{Br} = 1.5 q_{Cl}$ ). In this way not only the EFG broadening, but also the strain broadening are being considered, as proposed by Stoneham [21].

The frequency axis has an arbitrary frequency scale since, as explained above, an absolute comparison is not possible. The area of the peaks at  $Cl_1$ ,  $Cl_2$  and  $Cl_3$  sites is twice that of one of the peaks at the  $Cl_4$  site. Therefore, the main observation to take into account is that each of the four NQR lines of MDCB is split in two Gaussian lines of same area and approximately same width, even though the splits for each site are quite different. This confirms the validity of the model proposed. The fit of the EFG distribution at each site with Eq. (11) is shown in Fig. 4a.

The difference in the splits is mainly due to the fact that intermolecular distances to first neighbours in MDCB are not equal for the non-equivalent chlorine atoms. It can be appreciated how one of the sites ( $Cl_4$  site) is the most affected by the substitution of a closer neighbour while the other sites are least affected. This is because the distance to its first neighbour is the shortest (3.46 Å).  $Cl_2$  and  $Cl_3$  sites show a similar split because, for both of them, the distance to the closer neighbour is the same (3.69 Å).

### 3.2. Nuclear quadrupole resonance frequency

The centre of gravity (average frequency) of the MCBB spectrum was chosen to follow the NQR frequency behaviour with temperature. The temperature dependence of this frequency is shown in Fig. 5. For comparison, the average frequency of the disordered phase of MCFB and the centre of gravity of the four frequencies of MDCB at two temperatures, found in the literature, are also included in this figure for the sake of comparison. Clearly there is a good agreement, meaning that the assumption, that MCBB and MCFB share a similar crystal structure that MDCB with substitutional disorder, is right.

Fig. 6 shows the temperature dependence of the central frequency of the eight Gaussian functions needed to fit the MCBB spectrum. The NQR frequency decreases monotonically with temperature due to an average effect of the molecular torsional oscillations in the EFG [31]:

$$\nu_Q(T) = \nu_o \left( 1 - \frac{3}{2} \langle \theta^2(T) \rangle \right) \quad (12)$$

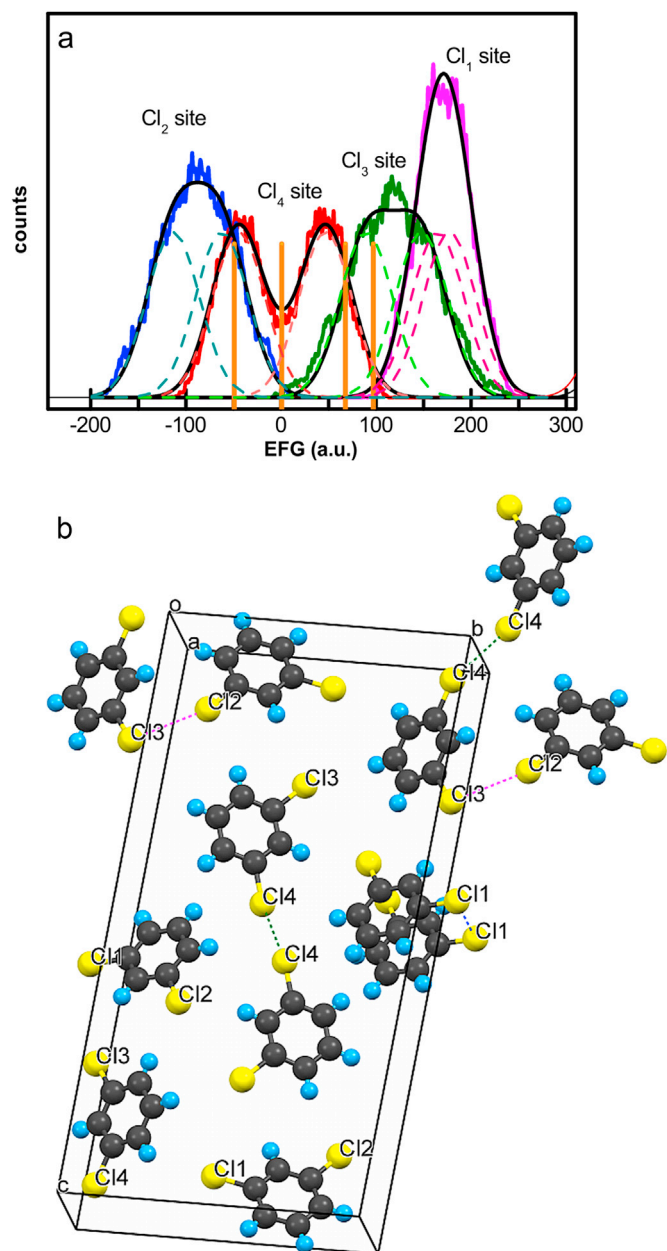


Fig. 4. (a) Distribution, due to disorder, of the intermolecular contribution to the EFG in MCBB at the four crystallographic positions of the Cl atom calculated in the crystalline structure of MDCB at 220 K. Orange straight lines: distribution obtained in MDCB. Dashed lines: fits with Eq. (11). (b) Crystalline structure of MDCB at 220 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where  $\theta$  is the angular displacement of the z-axis of EFG tensor from its equilibrium position. Experimental data are fitted using the Bayer–Kushida model [32].

$$\nu_Q(T) = \nu_o \left( 1 - \frac{3}{2} \frac{\hbar}{I\omega} \coth\left(\frac{\hbar\omega}{2kT}\right) \right) \quad (13)$$

where  $\nu_o$  is the NQR frequency in a fictitious static lattice.  $I$  is an effective moment of inertia and  $\omega_t = \omega_o(1-gT)$  is an average torsional frequency, where the anharmonic effects have been taken into account assuming a linear temperature dependence of  $\omega_t$ . The inverse of the effective moment of inertia ( $1/I$ ), calculated geometrically using the crystallographic molecular data of MDCB, is  $2.3 \times 10^{-3} \text{ (uma \AA}^2\text{)}^{-1}$ .

A least squares fit of data in Fig. 6, using Eq. (13) and the geometric

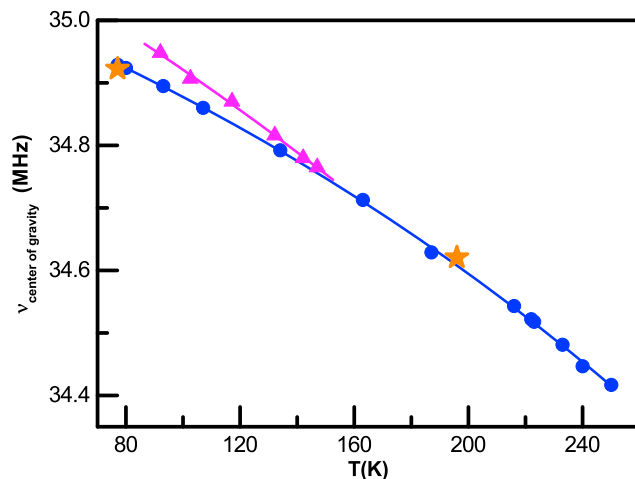


Fig. 5. Temperature dependence of the average NQR frequencies in MCBB (blue circles) compared with those of MDCB (orange star) and MCFB in the disordered phase II (pink triangle) [4]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

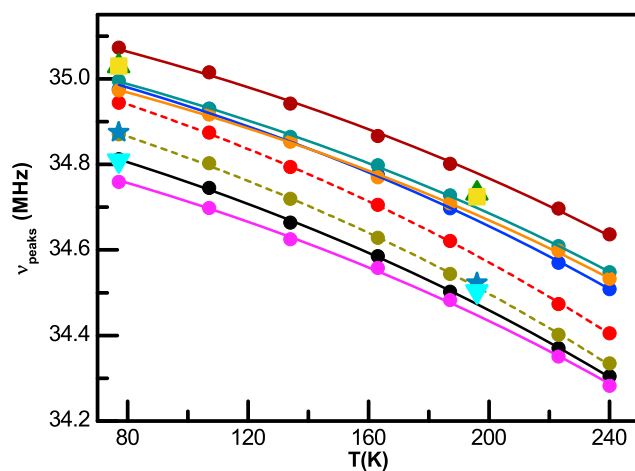


Fig. 6. Temperature dependence of the eight peaks used to fit MCBB spectrum.

moment of inertia mentioned above, gives values between 41 and 43  $\text{cm}^{-1}$  for 6 of the lines and 39  $\text{cm}^{-1}$  for the other two which have a larger slope. These values agree with the average of the lattice

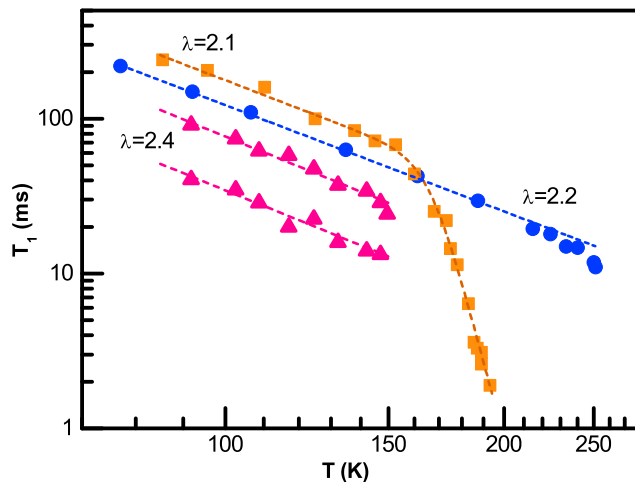


Fig. 7. Temperature dependence of  $T_1$ . MCBB (blue circle), MCFB (pink triangle) and OCBB (orange square). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

frequencies measured by Raman spectroscopy [33]. The fitted  $g$  of 0.00087 is assumed to be the same for all the lines. Clearly the two lines in MCBB with large slope (dotted lines) correspond to the splitting of the line with large slope in MDCB (blue star). Qualitatively, the distribution of the experimental central frequencies at 220 K agrees with that obtained from the simulation of the EFG (see Fig. 4a).

### 3.3. Nuclear quadrupole spin-lattice relaxation time

The temperature dependence of  $T_1$  in MCBB is shown in Fig. 7. For comparison,  $T_1(T)$  of the disordered phase of MCFB and *o*-chlorobromobenzene are also shown. As it is observed,  $T_1(T)$  has a normal behaviour due to torsional oscillations [34]:

$$\frac{1}{T_1} = AT^\lambda \quad (14)$$

A least squares fit of data with Eq. (14) gives  $\lambda = 2.2$ . Unlike what it is observed in *o*-chlorobromobenzene [5], there is no evidence of molecular reorientation.

## 4. Conclusions

A simple statistical model to explain inhomogeneous broadening of NQR lines in chlorohalobenzenes with orientational disorder is presented. It is based on the assumption that Br/F atoms of the *m*-chlorohalobenzene/*o*-chlorohalobenzene molecule behave as point defects in the *m*-dichlorobenzene/*o*-dichlorobenzene lattice that modify the crystalline EFG. The model was successfully applied in these compounds. The same model was also used to explain the lineshape of solid solutions of *p*-dichlorobenzene-*p*-dibromobenzene with different concentrations.

In the particular case of *m*-chlorobromobenzene, only one disordered phase has been found. Based on the NQR lineshape analysis, it is possible to say that this solid phase has orientational disorder. From the dynamic point of view, there is no evidence of molecular reorientation as it is observed in *o*-chlorobromobenzene.

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