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# Dynamic and static effects on $^{35}\text{Cl}$ nuclear quadrupole resonance due to substitutional impurities in crystalline p-dichlorobenzene

A P Bussandri, M J Zuriaga and C Martin

Facultad de Matemática Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000-Córdoba, Argentina

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**Abstract.** The  $^{35}\text{Cl}$  nuclear quadrupole resonance (NQR) spectra of p-dichlorobenzene doped with p-bromochlorobenzene and p-dibromobenzene have been studied. The measurements were carried out as a function of the concentration up to 10% of impurities and at four temperatures in the 77 K–295 K range. The impurities diminish the integrated intensity, shift the peak of the line, and increase the linewidth. The frequency of the peak varies linearly with impurity concentration, with a slope depending upon the solute molecule and the temperature. The increment of the linewidth depends on the solute molecule, but not on the temperature. The observed changes of the  $^{35}\text{Cl}$  NQR signal are accounted for by considering the perturbation of the electric field gradient produced by elastic distortion of the lattice, and by variations in the electric charge distribution and phonon spectra.

## 1. Introduction

Nuclear quadrupole resonance (NQR) is an appropriate technique for the investigation of impurity-doped crystals by exploring the influences on the electric field gradient (EFG). Impurity-doped crystals are of special interest, since they yield valuable microscopic information on solid solutions.

The EFG in a solid depends on the configuration [1] and dynamics of the crystal [2]. The addition of a small amount of impurity with size and mass different to that of the host molecule changes the charge distribution and phonon spectra. Whenever these effects may be considered as a small perturbation, it seems reasonable to expect the NQR characteristic parameters to follow a linear relationship with the impurity concentration. In the last few years several experiments and theoretical studies have been performed on the EFG perturbation induced by impurities [3, 6]. For example,  $^{35}\text{Cl}$  NQR experiments carried out on doped chlorates and hexachlorometallates have shown that the perturbations due to substitutional impurities may be explained by invoking an elastically distorted lattice. Although Raman measurements on doped samples indicate that the lattice modes of the chlorates are affected by the difference between the masses of the host and the impurity, no definite evidence has been found for such an influence on the NQR. This effect has been assigned [4] to the presence of localized modes around the impurity; therefore in the limit of low concentration a negligible number of resonant nuclei are affected. Thus, it is not clear how sensitive the NQR is to changes in the phonon spectrum due to the presence of impurities. It is the aim of this work to shed some light on the above-mentioned points.

The present paper describes  $^{35}\text{Cl}$  NQR measurements made on p-dichlorobenzene (PDCIB) polycrystalline samples doped with p-dibromobenzene (PDBrB) and p-bromochlorobenzene (PBrClB) as functions of concentration and temperature. These compounds are isomorphic and display a large mutual solubility [8, 9].

The  $^{35}\text{Cl}$  NQR in PDCIB seems a good choice of subject if one wishes to study the impurity effect. For this system there is information available that was obtained by various techniques: Raman spectroscopy [7], x-ray diffraction [8, 9], and NQR under axial pressures in PDCIB single crystals [1]. Furthermore, in organic crystals the phonon subbands are usually coupled; therefore the observation of localized phonons will be far less common in these systems than in the ionic crystals, where the phonon subbands are usually separated and highly decoupled.

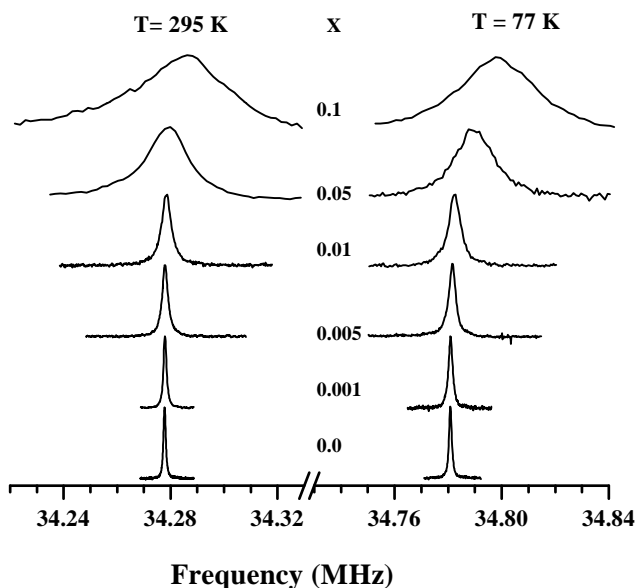
## 2. Experimental details and results

Doped polycrystalline samples with concentrations in the range  $0 \leq x \leq 0.10$  were obtained from precipitates of saturated PDCIB solutions containing the appropriate quantities of PDBrB or PBrClB.

For the 77 K measurements, the samples were immersed in liquid nitrogen. The other temperatures were measured with a thermocouple and stabilized to  $\pm 0.02$  °C. The typical error on the line peak frequency was  $\pm 80$  Hz.

The measurements were performed using an automated home-made NQR spectrometer. The conventional Hahn echo sequence was used, and the real and imaginary parts of half of the echo signal were digitized and accumulated to improve the signal-to-noise ratio (s/n). The NQR spectra were obtained by a fast-Fourier-transform (FFT) algorithm. The spectra for concentrations  $x \geq 0.03$  was reconstructed by the method of spin-echo mapping [10].

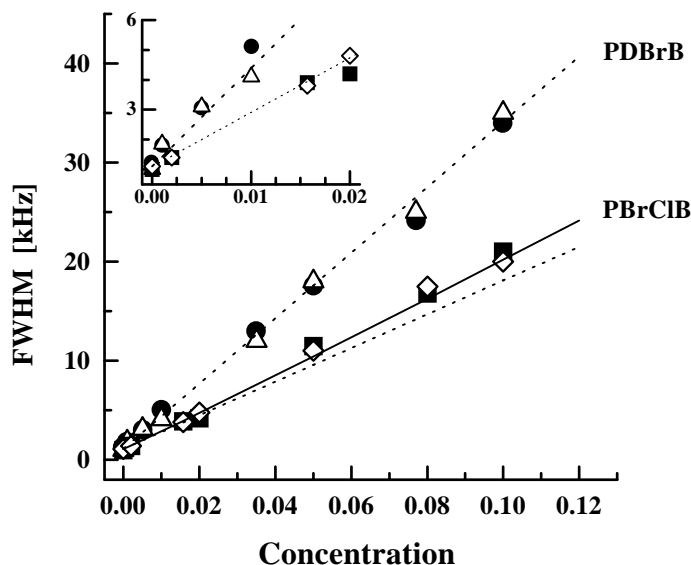
The intensity of the NQR signal exhibited a strong decrease while the impurity



**Figure 1.** The  $^{35}\text{Cl}$  NQR frequency spectra of PDCIB are depicted, at two temperatures, as functions of the concentration of PDBrB. The main features that can be seen are the frequency shift of the peak and the dramatic increase in the linewidth.

concentration was increasing. Figure 1 shows the  $^{35}\text{Cl}$  NQR spectra at 77 and 295 K for PDCIB at different PDBrB concentrations. Similar results were obtained when PBrCIB was the impurity. Impurities affected all of the  $^{35}\text{Cl}$  NQR line parameters: shape, width, and peak frequency. For pure PDCIB the lineshape is Gaussian as expected from the dipole–dipole broadening [11]. As the impurity concentration rises, the lineshape becomes progressively more Lorentzian. For concentrations larger than 0.03 an additional line appears at 70 kHz below the main line. This satellite line is due to the frequency changes undergone by those  $^{35}\text{Cl}$  nuclei that are next to the impurity molecules [12]. The analyses of these structures has been carried out in a subsequent paper [13].

The linewidth, taken as the full width at half-maximum (FWHM), which is typically 1 kHz in PDCIB, increases linearly with the concentration with a slope of  $330\text{ kHz mol}^{-1}$  (impurity PDBrB) and  $205\text{ kHz mol}^{-1}$  (impurity PBrCIB). This behaviour is shown in figure 2. The changes in lineshape and linewidth are temperature independent.

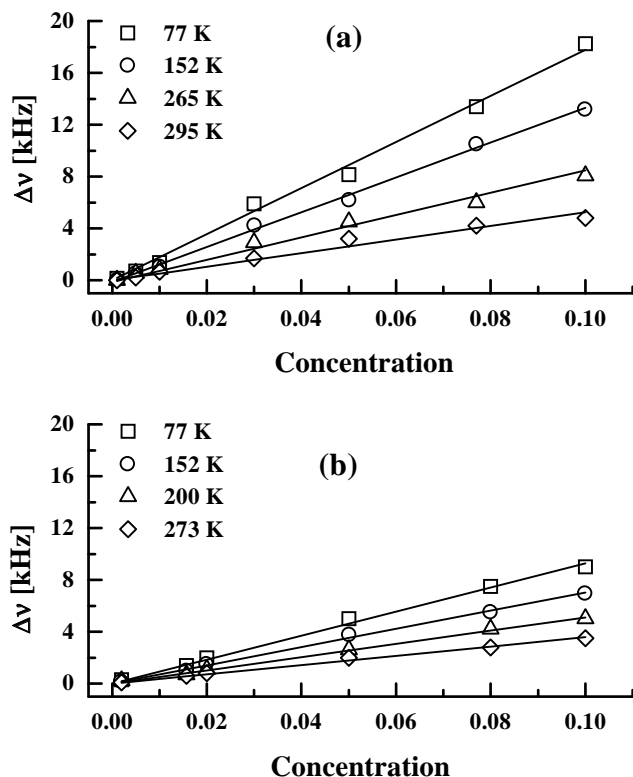


**Figure 2.** The linewidths (FWHM) of the  $^{35}\text{Cl}$  NQR spectra of PDCIB as functions of the concentrations of the impurities PDBrB and PBrCIB. The open and full symbols correspond to the values measured at 295 and 77 K respectively. A linear behaviour is clearly exhibited in both cases, and in the inset we can see that this is also true at the low end of the concentration range. The dotted lines correspond to the lattice contribution as given by equation (19). As may be seen, a good description of the data is obtained in the PDBrB case. For PBrCIB the electric dipolar contribution (equation (22)) has to be accounted for. The full line includes both contributions, providing a good description of the data.

The most interesting effect produced by the presence of the substitutional impurities is the shift  $\Delta\nu$  of the peak of the line. In figures 3(a) and 3(b) the shifts measured at four temperatures are plotted against the concentration. The resonance frequency increases linearly with the concentration with slopes depending on the temperature and impurity type.

### 3. Theory

It is well known that the NQR frequency (NQRf) generally decreases monotonically with temperature. This was explained by Bayer and Kushida [2] as due to the averaging of the



**Figure 3.** The frequency shifts of the peaks of the  $^{35}\text{Cl}$  NQR spectra are depicted as functions of the concentrations of the impurities PDBrB (a) and PBrClB (b), at four selected temperatures. As may be seen, a linear description provides a good fit of the data, in agreement with equation (13).

EFG produced by normal-mode vibrations. Assuming that the contributions to the EFG may be separated out into dynamical (intramolecular) and crystalline (intermolecular) ones, the Bayer–Kushida theory may be expressed as

$$\nu(T) = \nu_{dyn} + \nu_{cryst} = \nu_0 \left[ 1 - \frac{3\hbar}{4} \sum_{j=1}^N \frac{A_j}{\omega_j} \coth\left(\frac{\hbar\omega_j}{2k_B T}\right) \right] + \nu_{cryst} \quad (1)$$

where  $j$  runs over all of the normal modes, the  $\omega_j$  are the vibrational frequencies at the origin of the Brillouin zone, and  $A_j$  is related to the moment of inertia of the  $j$ th normal mode [14]. For the lattice modes, the  $A_j$  coincide with the reciprocals of the molecular moments of inertia.  $\nu_0$  is the NQRF in a static molecule, while  $\nu_{cryst}$  is the crystalline contribution which arises from the remaining molecules in the crystal. This equation does not consider normal-mode anharmonicities, which are responsible for the crystal thermal expansion and the decrease of the lattice frequencies. Brown [15] proposed a linear temperature dependence for the lattice frequencies:

$$\omega_j(T) = \omega_{0j}(1 - \alpha_j T). \quad (2)$$

This approach has been successfully applied to a wide range of NQR data [16].

The thermal expansion also produces a change in the crystalline contribution to the EFG. However, this change has been shown to be negligible [16] as compared with the vibrational effect. Therefore  $\nu_{cryst}$  will from now on be regarded as temperature independent.

Since we are interested in the NQR shift as a function of the concentration relative to the frequency of the pure sample, it is convenient to express equation (1) as

$$\nu(T) = \nu_0 \left[ 1 - \frac{3\hbar}{4} \sum_{j=1}^{N_{latt}} \frac{1}{I_j \omega_j^{latt}} \coth\left(\frac{\hbar \omega_j^{latt}}{2k_B T}\right) + \Theta(T, \omega^{int}) \right] + \nu_{cryst} \quad (3)$$

where  $j$  runs over those lattice modes which affect the EFG and  $I_j$  is the moment of inertia, and  $\Theta(T, \omega^{int})$  represents the contribution of the internal modes to the averaging of the EFG. On applying the high-temperature approximation [2] ( $T \geq \hbar \omega_j^{latt} / k_B \approx 80$  K) to the lattice mode terms, the following NQR results:

$$\nu(T) = \nu_0 \left[ 1 - \frac{3k_B T}{2} \sum_{j=1}^{N_{latt}} \frac{1}{I_j (\omega_j^{latt})^2} + \Theta(T, \omega^{int}) \right] + \nu_{cryst}. \quad (4)$$

The impurities may be considered as random point defects in the host lattice. If the impurities distort the lattice as a result of their size being different from that of the host, their effect may be described as an elastic distortion assuming that the crystalline contribution varies linearly with the strain [4]. Furthermore, if the impurity has a different mass, it may shift the frequencies of the lattice modes, thus changing the temperature dependence of the NQR. This artificial partition offers the possibility of correlating the NQR shift with the volume and mass differences between the impurity and host molecules. Both effects are discussed below.

The concentration dependences of some lattice modes in mixed crystals of PDCIB with PDBrB and PBrClB have been measured and analysed by Bellows and Prasad [7]. They conclude that the shifts in the lattice frequencies are mainly due to the differences between the masses of the impurities and the host molecule. At low concentrations the shifts are well fitted by the virtual-crystal model (VCA) which predicts a linear relationship between the phonon frequencies and the concentration [7]. These results and those from Brown's proposal (equation (2)) suggest linear temperature and concentration dependences of the lattice frequencies, which may be written as

$$\omega_j^{latt}(T, x) = \omega_{0j}^{latt} (1 - \alpha_j \Delta T)(1 - \beta_j x) \quad (5)$$

where  $\Delta T = T - T_0$ ,  $T_0$  being an arbitrary fixed temperature, and  $\omega_{0j}$  is the  $j$ th lattice frequency at  $T = T_0$ . On substituting  $\omega_j^{latt}(T, x)$  in equation (4), the following dynamical contribution results:

$$\nu_{dyn}(T, x) = \nu_0 \left[ 1 - \frac{3k_B T}{2} \sum_{j=1}^{N_{latt}} \frac{1}{I_j (\omega_{0j}^{latt})^2 (1 - \alpha_j \Delta T)^2 (1 - \beta_j x)^2} + \Theta(T, \omega^{int}) \right]. \quad (6)$$

As  $\alpha_j \Delta T \approx 10^{-2}$  [15] and  $x\beta_j \approx 10^{-1}$  [7], the dependence on  $T$  and  $x$  may be approximated by

$$\nu_{dyn}(T, x) = \nu_0 \left[ 1 - \frac{3k_B T}{2} \sum_{j=1}^{N_{latt}} \frac{1}{I_j (\omega_{0j}^{latt})^2} (1 + 2\alpha_j(T - T_0) + 2\beta_j x) + \Theta(T, \omega^{int}) \right]. \quad (7)$$

Assuming that  $\beta_j = \langle \beta \rangle$  and  $\alpha_j = \langle \alpha \rangle$  for all lattice modes, it is easy to see that

$$\nu_{dyn}(T, x) = \nu_0 \left[ 1 + 2\langle \alpha \rangle T_0 b_0 T - 2\langle \alpha \rangle b_0 T^2 + \Theta(T, \omega^{int}) \right] - 2\nu_0 b_0 \langle \beta \rangle T x \quad (8)$$

where

$$b_0 = \frac{3k_B}{2} \sum_{j=1}^{N_{latt}} \frac{1}{I_j (\omega_{0j}^{latt})^2}. \quad (9)$$

The first four terms in equation (8) were obtained by Brown [15], while the last term represents the overall effect of the impurities on the dynamical contribution to the EFG. Thus, the shift of the frequency with respect to that of the pure crystal is

$$\Delta v_{dyn}(T, x) = v_{dyn}(T, x) - v_{dyn}(T, 0) = -2\nu_0 b_0 \langle \beta \rangle T x. \quad (10)$$

In this way, a linear decrease in the NQRF shift with temperature, concentration, and average change of the lattice frequencies is predicted.

With respect to the crystalline contribution, as mentioned above, the strain field resulting from the inclusion of impurities gives rise to a temperature-independent shift of the NQRF [4,5]:  $\Delta v_{cryst}(x) = v_{cryst}(x) - v_{cryst}(0)$ . A detailed treatment of this perturbation to the  $^{35}\text{Cl}$  NQR in molecular alloys of PDCIB with PDBrB has been recently published [17]. In that paper it was shown that the NQRF shift  $\Delta v_{cryst}(x)$  is related to the defect-induced volume expansion by

$$\Delta v_{cryst}(x) = \frac{dv_{cryst}}{dx} x \quad (11)$$

with

$$\frac{dv_{cryst}}{dx} = -0.72 \frac{1-2\lambda}{1-\lambda} \frac{1}{\kappa} \left( \frac{dv_{cryst}}{dp_{axial}} \right) a^{-1} \frac{da}{dx} \quad (12)$$

where  $a^{-1} da/dx$  represents the lattice anisotropic expansion when PDCIB molecules are substituted for either with PDBrB molecules [8] or with PBrCIB [9] molecules,  $dv_{cryst}/dp_{axial}$  is the coefficient that relates the changes in crystalline EFG induced by strain,  $\kappa$  is the compressibility of the PDCIB [18], and  $\lambda$  is the Poisson ratio, which for molecular crystals varies from 0.25 to 0.3 [19].

Finally, the total NQRF shift,  $\Delta v(T, x) = \Delta v_{dyn}(T, x) + \Delta v_{cryst}(x)$ , produced by impurities is given by

$$\Delta v(T, x) = \left( -2\nu_0 b_0 \langle \beta \rangle T + \frac{dv_{cryst}}{dx} \right) x \quad (13)$$

and the first concentration derivative is

$$\left( \frac{\partial \Delta v}{\partial x} \right)_T = -2\nu_0 b_0 \langle \beta \rangle T + \frac{dv_{cryst}}{dx}. \quad (14)$$

This equation shows that the shift due to the strain field in the temperature range over which the measurements were made may be obtained experimentally by extrapolating to zero kelvin the temperature dependence of  $(\partial \Delta v / \partial x)_T$ . From the second derivative

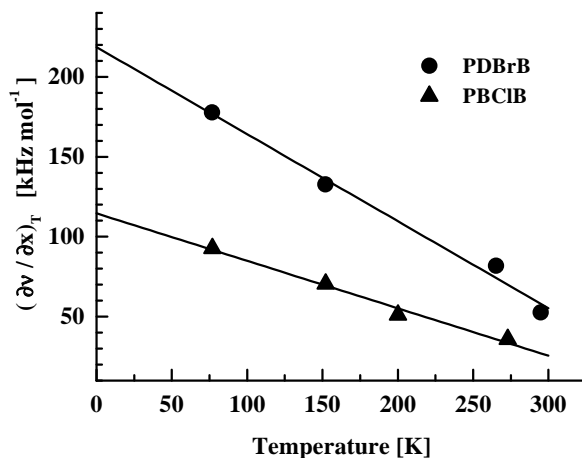
$$\partial^2 \Delta v / \partial T \partial x = -2\nu_0 b_0 \langle \beta \rangle \quad (15)$$

we may obtain an estimated value for  $\langle \beta \rangle$ .

#### 4. Analyses of experimental results

Figure 4 depicts the temperature dependence of  $(\partial \Delta v / \partial x)_T$  for both impurities—PDBrB and PBrCIB. These data clearly exhibit a linear behaviour with temperature, in agreement with equation (14). This behaviour is different for the two types of impurity. The resulting temperature dependences for  $(\partial \Delta v / \partial x)_T$  are given in table 1.

Some quantitative information on  $\langle \beta \rangle$  may be obtained by using equations (15) and (9). In PDCIB the lattice modes of interest are the molecular librations about the axis perpendicular to



**Figure 4.** The first derivative of the  $^{35}\text{Cl}$  NQR frequency with respect to the impurity concentration is depicted as a function of the temperature. The data are deduced from those shown in figure 3. The fact that the result is a straight line provides additional support for the assumptions and approximations leading to equations (13) and (14).

**Table 1.** The impurity dependence of the first and second NQRF derivatives.

Impurity	$d\nu_{\text{cryst}}/dx$ (kHz mol $^{-1}$ )	$\partial^2 \Delta\nu/\partial T \partial x$ (kHz K $^{-1}$ mol $^{-1}$ )
PDBrB	220	-0.65
PBrClB	114	-0.39

the benzene ring plane (the *y*-axis), and about the axis lying over that plane and perpendicular to the interhalogen axis (the *x*-axis). Thus, equation (9) yields [20]

$$b_0 = -\frac{3k_B}{2} \left[ \frac{1}{2I_x} \sum_x \frac{1}{(\omega_{0x}^{\text{latt}})^2} + \frac{1}{2I_y} \sum_y \frac{1}{(\omega_{0y}^{\text{latt}})^2} \right] \quad (16)$$

where the  $I_j$  are the moments of inertia and the  $\omega_{0j}^{\text{latt}}$  are librational frequencies at  $T_0 = 185$  K (equation (5)), which is the average temperature used in this work. The values of  $I_j$  and  $\omega_{0j}^{\text{latt}}$  are shown in table 2.

**Table 2.** PDCIB molecular moments of inertia and frequencies of the librations about the *x*-axis and *y*-axis.

$I$ ( $10^{-44}$ m $^2$ kg)	$\omega_x$ (cm $^{-1}$ )	$\omega_y$ (cm $^{-1}$ )
$I_x = 1.41$	60.4	30.4
$I_y = 1.26$	53.9	53.9

Substituting these values in equation (9) we obtain  $b_0 = 4.5 \times 10^{-5}$  K $^{-1}$ . The values obtained for  $\langle \beta \rangle_{\text{NQR}}$  taking  $\nu_0 = 34.8$  MHz [21] are listed in table 3. These values are compared with those predicted by the VCA as well as those obtained from Raman spectroscopy for the two most relevant lattice modes [7].

As seen—in spite of the approximations involved—there is a reasonably good agreement. Thus, we may conclude that the temperature dependence of  $\Delta\nu$  (see figure 3) is due to changes in the lattice phonon frequencies as predicted by equation (13).



**Table 3.** The concentration dependence of the lattice modes as deduced from various sources.

Impurity	$\langle\beta\rangle_{NQR}$ (mol <sup>-1</sup> )	$\langle\beta\rangle_{VCA}$ (mol <sup>-1</sup> )	$\beta_{Raman}$ (32 cm <sup>-1</sup> ) (mol <sup>-1</sup> )	$\beta_{Raman}$ (55 cm <sup>-1</sup> ) (mol <sup>-1</sup> )
PDBrB	0.21	0.25	0.44	0.28
PBrClB	0.12	0.18	0.21	—

It is important to point out that these changes are detected even at concentrations below 0.02. This improves the Raman spectroscopy results because this technique is rather inaccurate at such low concentrations [7].

The other contribution to the NQRF shifts produced by strains may be estimated from equation (12). However, it is necessary to know  $dv_{cryst}/dp_{axial}$ . Zamar [1] measured  $\partial v/\partial p_{axial}$  at 273 K for PDCIB single crystals in several crystalline directions, obtaining  $\partial v/\partial p_{axial} = -1$  kHz MPa<sup>-1</sup> in the direction of maximum volume expansion by molecular substitution. Using this value for the axial coefficient pressure, equation (12) predicts an increase of the NQRF as the impurity concentration increases. The estimated slopes are shown in table 4.

**Table 4.** Comparison of the concentration first derivative of the NQRF obtained from experiment and theory, and the relative derivative of the lattice parameter.

Impurity	$dv_{cryst}/dx$ (kHz mol <sup>-1</sup> )	$dv_{cryst}^{theory}/dx$ (kHz mol <sup>-1</sup> )	$a^{-1} da/dx$ (mol <sup>-1</sup> )
PDBrB	220	150	0.050 <sup>a</sup>
PBrClB	114	69	0.023 <sup>b</sup>

<sup>a</sup> Reference [8].

<sup>b</sup> Reference [9].

The measured values are larger than the estimated ones; however, the ratios of the values of  $dv_{cryst}/dx$  corresponding to the two types of impurity agree well with the ratio of the values of  $a^{-1} da/dx$ , providing additional support for equation (14). The discrepancy may be due to the fact that the value of  $\partial v/\partial p_{axial}$  used in the theoretical calculation (equation (12)) has two contributions [1]: one of them is the change of the crystalline EFG due to strains ( $dv_{cryst}/dp$ ), and the other is the alteration of the lattice frequencies produced by changes in the lattice force constants. However, the force constant changes caused by lattice expansion are already included in the first term of equation (13). Therefore, to estimate  $dv_{cryst}/dp$  we have taken the first derivative in equation (4) with respect to pressure:

$$\left(\frac{\partial v}{\partial p}\right)_T = \left(\frac{\partial v_{dyn}}{\partial p}\right)_T + \frac{dv_{cryst}}{dp} \quad (17)$$

with

$$\left(\frac{\partial v_{dyn}}{\partial p}\right)_T = v_0 3k_B T \sum_{j=1}^N \frac{1}{I_j \omega_j^2} \left(\frac{\partial \ln \omega_j^{latt}}{\partial p}\right) \approx 2v_0 b_0 \left(\frac{\partial \ln \omega_j^{latt}}{\partial p}\right) T \quad (18)$$

where  $\partial \ln \omega_j^{latt}/\partial p \approx 7.4 \times 10^{-4}$  MPa<sup>-1</sup> [22]. Then, the estimated value for  $(\partial v_{dyn}/\partial p)_T$  at  $T = 273$  K is 0.6 kHz MPa<sup>-1</sup>. Thus,  $dv_{cryst}/dp$  turns out to be approximately  $-1.6$  kHz MPa<sup>-1</sup>. Using this value for  $dv_{cryst}/dp$  in equation (12), the NQR frequency shifts due to strains are deduced and given in table 5.

These results show that in order to use the experimental values of the pressure coefficient to estimate the NQRF shift from the strain, it is necessary to subtract the dynamical contribution.

**Table 5.** Comparison of the concentration first derivatives of the NQRF obtained from experiment and the improved theory.

Impurity	$dv_{cryst}^{NQRF}/dx$ (kHz mol <sup>-1</sup> )	$dv_{cryst}^{theory}/dx$ (kHz mol <sup>-1</sup> )
PDBrB	220	240
PBrClB	114	110

## 5. Linewidth and lineshape

The NQR lineshape broadening has two main contributions. One of them is the lattice distortion due to a volume defect and the other is that due to the difference in electric charge distribution between the impurity and the host molecules. The latter contribution for the PDBrB case is quadrupole, and therefore the EFG decays away as  $r^{-5}$  and at low concentrations this effect is negligible. Thus, the lineshape and linewidth may be analysed just considering the distribution of the frequency shifts produced by strains. The theory of an elastically distorted lattice predicts a Lorentzian probability distribution for the NQRF shifts [12]. This is roughly confirmed by the change of the lineshape from a Gaussian towards a Lorentzian one with increasing PDBrB concentration. This model also predicts that the FWHM  $\Gamma_{stra}$  and  $\Delta v_{cryst}$  (equation (11)) are related by  $\Gamma_{stra} = 1.2|\Delta v_{cryst}|$  [4]. The experimental result for this ratio ( $\Gamma = 330x$  kHz and  $|\Delta v_{cryst}| = 220x$  kHz) is

$$\Gamma = 1.5|\Delta v_{cryst}| \quad (19)$$

in good agreement with the theoretical result. However, when the impurity is PBrClB ( $\Gamma = 205x$  kHz and  $|\Delta v_{cryst}| = 114x$  kHz) this ratio is 1.8, which is 50% higher than the theoretical result for strain broadening. This difference may be due to electric charge variations, whose leading term is dipolar for PBrClB. To estimate this contribution to the line broadening it is necessary to statistically add up the NQRF shifts produced by a random distribution of electric dipole moments.

Let us consider a chlorine nucleus located at the origin of the principal system of the EFG whose principal axis  $z$  is defined by the C–Cl bond. Supposing that all of the dipoles are oriented in the  $z$ -direction, the frequency shift due to one dipole is given by

$$\delta v_{dip} = (1 - \gamma_{\infty}) \frac{eQ}{2h} p \frac{1}{r^4} (9 \cos \theta - 15 \cos^3 \theta) = (1 - \gamma_{\infty}) \frac{eQ}{2h} p \left[ \frac{\Psi(\theta)}{r^4} \right] \quad (20)$$

where  $r$  is the chlorine–dipole distance,  $\theta$  is the angle from  $r$  to the principal axis  $z$ ,  $eQ$  is the quadrupole moment of the chlorine, and  $1 - \gamma_{\infty}$  is the Sternheimer antishielding factor.

Following the statistical method developed by Stoneham [12], the frequency distribution produced by a random distribution of electric dipoles,  $I_{dip}(v)$ , is obtained:

$$I_{dip}(v) = \frac{1}{v_0 2\pi} \int_{-\infty}^{\infty} \exp i(kv/v_0) \exp -k^{3/4} dk \quad (21)$$

with

$$v_0 = 49(1 - \gamma_{\infty}) \frac{eQ}{2h} p \frac{x^{4/3}}{V_c^{4/3}}$$

where  $x$  is the dipolar molar concentration and  $V_c$  is the volume of the unit cell. This integration has been performed numerically. The lineshape is similar to a Lorentzian with a FWHM of  $1.38v_0$ , i.e.

$$\Gamma_{dip} = 67(1 - \gamma_{\infty}) \frac{eQ}{2h} p \frac{x^{4/3}}{V_c^{4/3}}. \quad (22)$$

Taking  $\gamma_\infty \approx 50$  [23],  $eQ_{35\text{Cl}} = 7.9 \times 10^{-26} \text{ cm}^{-2}$  [23],  $p = 0.1$  Debye [24], and  $V_c = 310 \text{ \AA}^3$  [25], equation (22) gives

$$\Gamma_{dip} = 45x^{4/3} \text{ kHz.} \quad (23)$$

The line broadening caused by the elastic strain  $\Gamma_s$  is given by equation (19), and for PBrClB we obtain

$$\Gamma_{stra} = 170x \text{ kHz.} \quad (24)$$

As the frequency shift due to strain [12]  $\delta\nu_s \propto 1 - 3 \cos^2 \theta$ , it is easy to prove that  $\langle \delta\nu_{dip} \delta\nu_{stra} \rangle$ , the average over all configurations of  $\delta\nu_{dip} \delta\nu_{stra}$ , is zero. Hence,  $\delta\nu_{dip}$  and  $\delta\nu_{stra}$  can be treated as independent, and therefore the linewidth of the frequency distribution due to the two effects may be expressed as [12]

$$\Gamma = 170x + 45x^{4/3}. \quad (25)$$

Figure 2 shows the concentration dependences of the linewidth, taking into account the volume effects (dotted lines). For PBrClB the continuous line depicts equation (25). As may be seen, an excellent agreement is achieved between theory and experiment.

## 6. Conclusions

NQRF and linewidth measurements of PDBrB- and PBrClB-doped PDCIB crystals have been carried out, reported, and successfully explained for the concentration range  $0 \leq x \leq 0.1$ , and at four selected temperatures ranging from 77 K up to 295 K.

Two dominant effects, having opposite signs, contribute to the frequency shift. On increasing the concentration the lattice frequencies go down, and this effect produces a lowering of the NQRF. On the other hand, the anisotropic lattice expansion due to the molecular volume differences between the solute and the host lattice produces an increase in the NQRF. These effects have been detected at concentrations lower than 0.02, where other techniques like Raman spectroscopy fail, due to lack of sensitivity, to detect impurity modes.

The linewidth for PDBrB as an impurity is explained by invoking the lattice elastic strains due to the molecular volume differences, whereas when PBrClB is the impurity an additional effect of electric dipolar origin has to be added in order to account for the experimental results.

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