

Partial disorder and molecular motion of 4-chlorobiphenyl studied by ^{35}Cl NQR and Raman spectroscopy

J. Schneider, A. Wolfenson, C. Schürer, and A. Brunetti

FaMAF, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, Ciudad Universitaria, 5000 Córdoba, Argentina

L. A. de O. Nunes

Instituto de Física de São Carlos, Universidade de São Paulo, Av. Dr. Carlos Botelho 1465, Caixa Postal 369, CEP13560-970, São Carlos, São Paulo, Brazil

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Pulsed ^{35}Cl nuclear quadrupole resonance (NQR) and Raman spectroscopy studies were performed to get information about the structural and dynamic thermal behavior of the 4-chlorobiphenyl. NQR measurements of the line shape and the spin-lattice relaxation time (T_1) were obtained in the temperature range 80–320 K. An inhomogeneously broadened NQR line shape was observed, suggesting a disordered structure in all the scanned temperature range. The disorder may be of conformational type, tentatively associated with a random distribution of dihedral angle values of the molecules in the crystal. Anomalously short T_1 values, nearly temperature independent, were measured for temperatures lower than 200 K. For higher temperatures, a dynamical mechanism enhances the spin-lattice relaxation. The T_1 values follow an Arrhenius type law, with an activation energy of 26 ± 1 K J/mol. The effects of this dynamical process are observed in the temperature behavior of the NQR frequencies between 150 and 200 K. Raman measurements between 4.5 and 300 K show an anomalous temperature behavior in the 80 cm^{-1} frequency zone. The thermally activated process could be assigned to hidden rotations of phenyl rings between close equilibrium dihedral angle values.

I. INTRODUCTION

Biphenyl compounds show interesting structural and dynamical features. Members of this family, with similar morphology, exhibit quite different thermal behavior among them. Biphenyl shows a phase transition sequence from a crystalline ordered phase to a bidimensional incommensurate phase (IC), at 40 K, and to a one-dimensional IC at 17 K.^{1,2} A conformational parameter of the molecule, the dihedral angle φ between the benzene rings, is incommensurately modulated in these two low temperature phases. The IC's transitions arise from the competition between intramolecular forces (ortho-hydrogen steric repulsion, conjugation of π electrons) and intermolecular forces among neighbor molecules.² In the gas phase, the measured value of the dihedral angle is $\varphi=42^\circ$.³ The effects of relatively intense intermolecular interactions in the solid phase are made evident by the planar molecular conformation of biphenyl ($\varphi=0$) in the higher temperature phase.

In recent years another biphenyl substituent showing an IC phase, 4,4'-dichlorobiphenyl sulphone, has been identified by ^{35}Cl nuclear quadrupole resonance (NQR).^{4,5} In spite of the very different morphology and crystal structure of this compound relative to biphenyl, the nature of the incommensuration is assumed to be the same as the one in the biphenyl case. Several experimental studies⁶ have confirmed that the IC parameter is the dihedral angle.

With the present work we begin the study of some simple chlorinated substituents of biphenyl in order to analyze the effects of these substitutions on the periodicity of the crystalline phase. One of the most simple substituents, the 4-chlorobiphenyl (abbreviated here as CB), was studied by ^{35}Cl NQR and Raman spectroscopy. The ^{35}Cl NQR spec-

trum, the spin-lattice relaxation time T_1 , and Raman frequencies were measured as a function of the temperature.

II. EXPERIMENT

The specimen of CB used in the NQR study was obtained from Pfalz and Bauer and subjected to recrystallization and purification by zone-melting method. This process was performed very slowly, avoiding the generation of intense strains into the crystalline sample. The obtained colorless semitranslucent sample was sealed in a glass cylinder of 2 cm length and 0.8 cm diameter.

Measurements of NQR from ^{35}Cl frequency and T_1 as a function of temperature were performed between 80 and 320 K. The spectrometer, based in the pulse method, has been described elsewhere.⁷ Sampling frequency of the nuclear signal between 200 KHz and 20 MHz was used. NQR spectra were obtained from the fast Fourier transform (FFT) of the digitized echo after a 90° - τ E - 180° pulse sequence with a 90° pulse length between 20 and 25 μs . The characteristic value of τ_E was 200 μs . The measurements were performed using the transmitter maximum peak power of 150 W. The instrumental width of the spectrometer response is approximately 12 KHz with a pulse length of 25 μs . Measurements of T_1 were made on the echo by the standard pulse sequence (90° - τ - 90° - τ_E - 180°), with separation times τ varying from 0.1 ms to $5T_1$. Each T_1 value determination was performed with a minimum of 30 τ values and a maximum of 50 values. The NQR spectrometer temperature control provides temperature stability better than 0.1 K during all the experiment. The sample thermal stabilization time before any NQR mea-

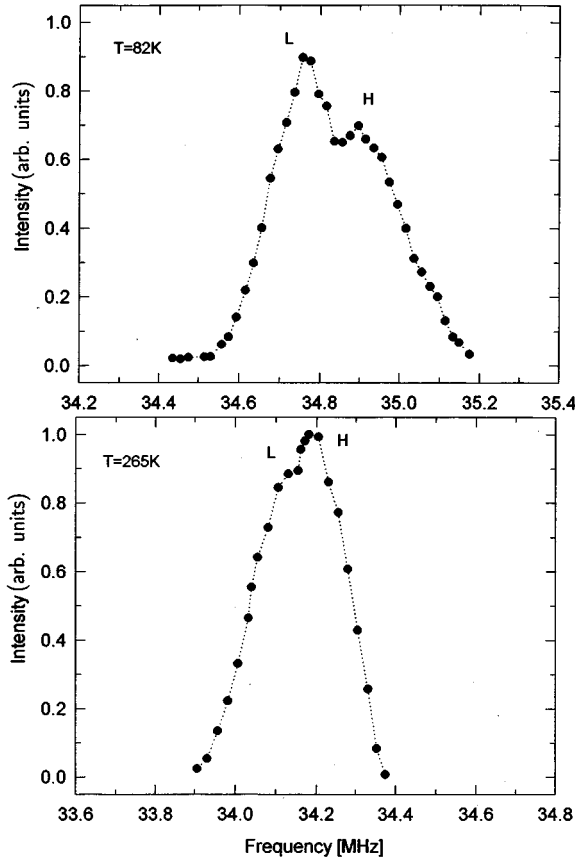


FIG. 1. The inhomogeneously broadened NQR line shape of 4-chlorobiphenyl at 82 and 265 K. The high and low frequency peaks are labeled as *L* and *H*, respectively.

surement was, for each temperature, approximately 6 h.

Raman measurements for powder CB samples were carried out by using the 488 nm line of an Ar-ion laser as an exciting source. A Spex double monochromator equipped with single-photon counting and a homemade data acquisition system was used for the detection of the scattered radiation. The temperature of the sample was controlled by a helium flux cryostat. The spectral resolution of the measurements was of 1 cm^{-1} .

III. EXPERIMENTAL RESULTS

A. ^{35}Cl NQR spectrum

Figure 1 shows the NQR spectrum at 82 K. This spectrum was obtained from the recording of echo amplitude as a function of the irradiation frequency. It can be observed that the spectrum is inhomogeneously broadened, with a half height width of about 240 KHz. There are two well-defined maxima in this electric field gradient (EFG) distribution, labeled as *H* and *L* in the figure. The temperature evolution of the CB NQR spectra was measured from liquid nitrogen temperature to 320 K.

As a preliminary approach to the description of the temperature behavior of this broad NQR spectrum, two sets of parameters have been chosen: the width of the EFG distribution and the NQR frequencies of the two peaks.

The linewidth Δ was obtained from the numerically calculated second moment of the measured EFG distribution:

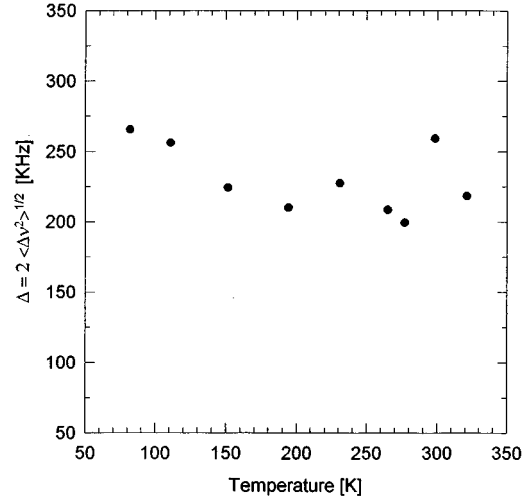


FIG. 2. Linewidth of the NQR spectrum of 4-chlorobiphenyl as a function of temperature. The linewidth value Δ is defined from the second moment of the spectrum $\langle \Delta \nu^2 \rangle$ as $\Delta = 2\langle \Delta \nu^2 \rangle^{1/2}$.

$$\Delta \equiv 2\sqrt{\langle \Delta \nu^2 \rangle}, \quad (1)$$

where the second moment is defined as

$$\Delta \nu^{(2)} \equiv \frac{\int_{-\infty}^{\infty} g(\nu)(\nu - \bar{\nu})^2 d\nu}{\int_{-\infty}^{\infty} g(\nu) d\nu}. \quad (2)$$

$g(\nu)$ is the spectrum amplitude at frequency ν , and $\bar{\nu}$ is the mean value of the frequency distribution:

$$\bar{\nu} \equiv \frac{\int_{-\infty}^{\infty} g(\nu) \nu d\nu}{\int_{-\infty}^{\infty} g(\nu) d\nu}.$$

Figure 2 shows that the linewidth is nearly temperature independent above 150 K. A small decrease in the linewidth values can be observed from 80 to 150 K. The spectral broadening may be due to structural disorder in the solid. The magnitude of the spread in the EFG values suggests that disorder could be attributed to small distortions in the molecular conformation. A glasslike disorder affecting molecular positions or orientations could cause a spread of the EFG of the order of MHz,⁸ greater than the observed one in this compound. The most significant internal molecular parameter that could be perturbed in a relatively easy way is the dihedral angle. Then, the spectral width could be associated to a distribution of dihedral angles into the sample. In Sec. IV, a more quantitative approach to the angle distribution will be proposed.

On the other hand, the temperature evolution of the NQR frequency of the two observed maxima, ν_H and ν_L , is shown in Fig. 3. The inset shows the difference between the frequency of the maxima, revealing changes of behavior in the dynamical processes that rule the temperature dependence of the effective EFG. There are three well-defined temperature ranges.

(i) Low temperatures ($80 \text{ K} < T < 160 \text{ K}$): the frequency difference between the peaks takes a nearly constant value of 120 KHz, suggesting that the temperature dependence on both peaks is determined by the same dynamical processes.

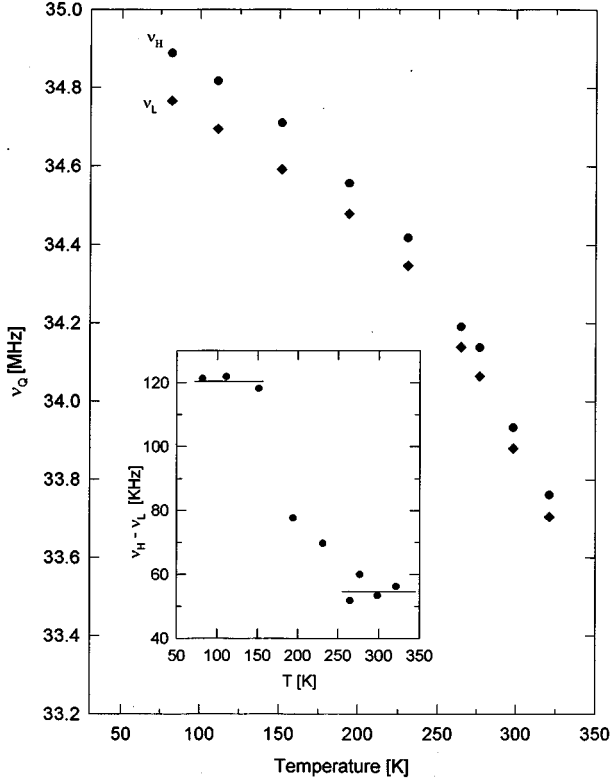


FIG. 3. Temperature dependence of frequencies ν_H and ν_L of the two maxima of the NQR spectrum. The inset shows the difference $\nu_H - \nu_L$ as a function of temperature. There are two temperature ranges ($T < 160$ K and $T > 250$ K) where the difference takes a nearly constant value.

(ii) High temperatures ($250 < T < 340$ K): the frequency difference takes values around 55 KHz, indicating a dynamical change with respect to the low temperature regime.

(iii) Intermediate temperatures ($160 < T < 250$): changes in the molecular motions involved in the effective EFG averaging are showed by a decrease in the frequency difference, leading to the high temperature dynamical regime above 250 K.

In order to roughly characterize the dynamics of the dominant processes at low and high temperatures ranges, a fitting using the Bayer-Kushida expression⁹ of the NQR frequencies was performed assuming only one oscillation mode:

$$\nu(T) = \nu_0 - \frac{3}{4} \frac{\hbar \nu_0}{I \omega} \coth \left[\frac{\hbar \omega}{2k_B T} \right], \quad (3)$$

where $\omega = \omega_0(1 - \alpha T)$ is the frequency of the mode, I is a quantity with units of moment of inertia, and ν_0 is the limiting static value of the NQR frequency. By taking into account that the temperature dependence on both peaks is the same in each temperature range, the fittings were performed using the measured frequencies ν_L and the data resulting of the subtraction $\nu_H - \Delta$, with $\Delta = 55$ KHz or $\Delta = 120$ KHz in the high and low temperature range, respectively. The least square fit of (3) to the two data sets yielded the parameters shown in Table I. The obtained torsional frequencies are 100 and 75 cm^{-1} in the low and high temperature ranges, respec-

TABLE I. Fitting parameters of the Bayer-Kushida expression (3) in the low and high temperature ranges.

Range	ω° [cm^{-1}]	[a.m.u. \AA^2]	ν_0 [MHz]	$\alpha \times 10^4$ [K^{-1}]
$80 < T < 160$	100	2100	34.95	4
$250 < T < 340$	75	1900	35.76	4

tively. This fact reveals that low frequency mode contributions to the EFG averaging become more important in the high temperature range.

B. Spin-lattice relaxation time (T_1)

The spin-lattice relaxation time was measured saturating the frequencies corresponding to peaks H and L . Figure 4 shows the inverse of T_1 values associated to each peak, namely T_1^H and T_1^L , as a function of the temperature. Two temperature regions with different T_1 behavior can be observed. At temperatures lower than 220 K T_1 , anomalously short values (one order of magnitude) are shown relative to the observed ones in other molecular crystals. Furthermore, T_1 values in CB exhibit a weak temperature dependence. At temperatures above 220 K, T_1 values of both peaks begin to show the same behavior and a substantial drop of the values can be observed. In order to compare the temperature dependence on T_1 in CB, for temperatures lower than 220 K, with the behavior observed in ordered molecular crystals, a fitting of the experimental data to the standard expression corresponding to the torsional oscillations model⁹

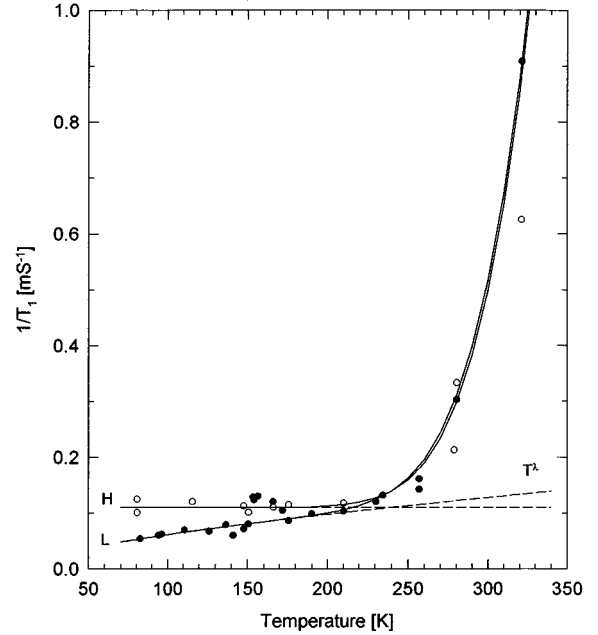


FIG. 4. Temperature dependence of the inverse of the spin-lattice relaxation time measured at frequencies ν_H and ν_L on the NQR spectrum. Broken lines represent the fitting of expressions of the type T^λ to the $1/T_1$ values of each peak in the low temperature region. The whole temperature range can be adequately fitted by adding a thermally activated term (Arrhenius type) to the T^λ dependence. These fittings are represented by the solid lines.

TABLE II. Fitting parameters of expression (4) for T_1 values from peak H and L at temperatures lower than 220 K.

Peak	A [$\text{ms}^{-1} \text{K}^\lambda$]	λ
H	0.11 ± 0.01	0
L	$(2.8 \pm 0.4) \times 10^{-3}$	0.67 ± 0.03

$$\frac{1}{T_1} = AT^\lambda \quad (4)$$

was performed. Usual values of λ in ordered molecular crystals are slightly above 2. The parameters resulting from the fittings are shown in Table II. The values obtained for exponent λ are anomalously small. For T_1^H , the exponent is indistinguishable from zero, giving a constant value of 9 ± 1 ms for the relaxation time in all the temperature range. For peak L , the exponent λ is greater than zero, but its value is very small with respect to the measured one in ordered crystals. The fittings for T_1^H and T_1^L are plotted in Fig. 4.

For temperatures above 220 K, a very efficient relaxation mechanism dominates the temperature behavior of the T_1 of both peaks. The effect of this dynamic process on the relaxation times suggests a thermally activated molecular reorientation, at slow rate with respect to the time scale associated to the NQR frequencies. The contribution to the relaxation can be written as⁹

$$\left[\frac{1}{T_1} \right]_{\text{reor}} = B e^{-E/RT}, \quad (5)$$

where E is the activation energy of the reorientation. The fitting of the expression (4), with the corresponding parameters of Table II, was subtracted to T_1 values of each peak in all the temperature range (80–320 K). The resulting values were used in the fitting with expression (5). Table III shows the parameters obtained, and the curve is plotted in Fig. 4. The activation energy resulting from the fitting is 26 ± 1 K J/mol. This high energy value suggests the reorientation of a heavy molecular group. Therefore this process could be tentatively assigned to molecular reorientation of the phenyl rings among different dihedral angles equilibrium positions.

C. Raman spectroscopy

Preliminary Raman spectra of CB were recorded in the range $50\text{--}1700 \text{ cm}^{-1}$ at 4.8 K and room temperature. Changes only in the low frequency spectral lines were observed, therefore detailed measurements were carried out in the range $30\text{--}220 \text{ cm}^{-1}$. Figure 5 shows three typical Raman spectra obtained at different temperatures. A multiple Lorentzian fit was performed on the measured spectra. The tem-

TABLE III. Fitting parameters of the expression (5) with all the data points.

B [ms^{-1}]	E [K J/mol]
12000 ± 5000	26 ± 1

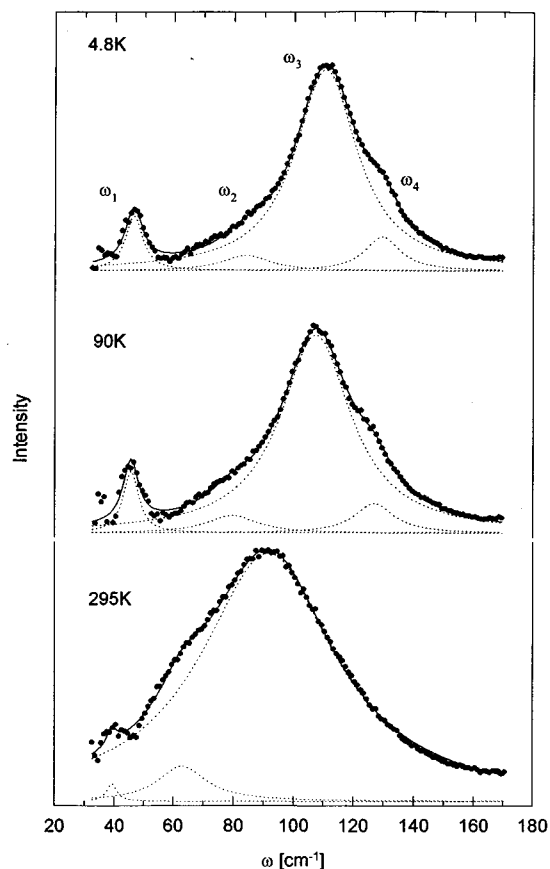


FIG. 5. Some typical low frequency Raman spectra of a powder sample of 4-chlorobiphenyl taken at different temperatures. These spectra can be fitted by the sum of Lorentzian functions, with central frequencies labeled as ω_i .

perature dependence of the frequencies of the fitted Lorentzian is shown in Fig. 6. As it can be seen, the temperature behavior of the frequencies is approximately linear in all the temperature range. The line labeled as ω_2 shows a notorious change at about 150 K and the line ω_4 becomes unobservable above 200 K. Least square fittings were performed on all the well-resolved lines, in the linear behavior temperature regions. The resulting parameters are summarized in Table IV, indicating the fittings temperature range.

IV. DISCUSSION

The observed T_1 values and thermal behavior at temperatures lower than 220 K show the existence of very efficient relaxation mechanisms notoriously different from the present in ordered molecular crystals. This weak temperature dependence of T_1 values is characteristic in disordered solids where the relaxation is dominated by low frequency oscillation modes. At temperatures above 220 K, the reorientation of the phenyl rings becomes the more efficient mechanism of relaxation. The effects of this slow-rate process are also observed in the temperature dependence of the NQR frequencies. The dynamic parameter ω_0 obtained from the fitting of Bayer-Kushida expression (3) is sensitive to the reorientation process, showing a high temperature value of 75 cm^{-1} , 25% smaller than the low temperature value of 100 cm^{-1} .

On the other hand, the parameters obtained for ω_2 Raman

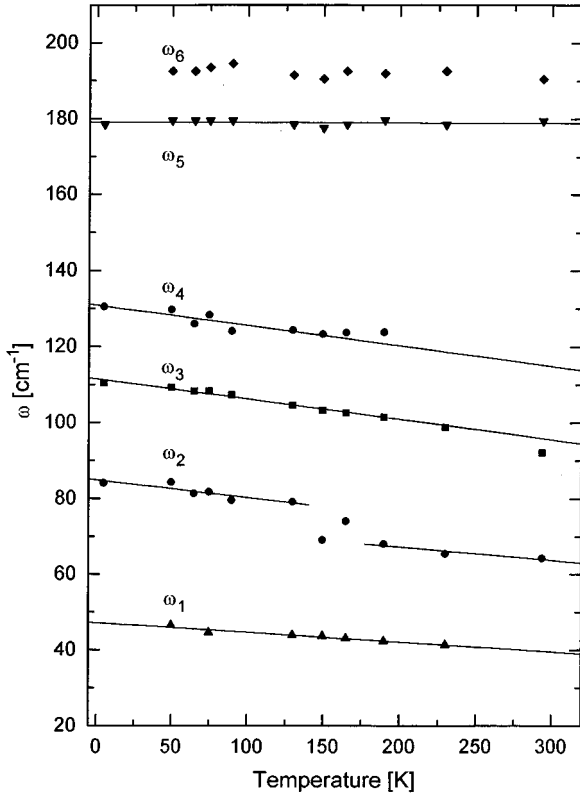


FIG. 6. Temperature dependence of the fitted Lorentzian functions to the measured Raman spectra. Linear least square fittings were performed on all the well-resolved peaks.

line, the only detected line that shows changes of temperature behavior, are $\omega_0 = 74 \text{ cm}^{-1}$ and $\omega_0 = 85 \text{ cm}^{-1}$ at high and low temperatures, respectively. These values show a reasonable agreement with the ones obtained from the NQR data, especially at low temperatures. Therefore, it could be reasonable to think that the EFG average at ^{35}Cl sites is mainly determined by molecular motions associated to ω_2 Raman line. These motions are coupled in some way with the reorientation of phenyls rings.

According to the anomalous low temperature behavior of T_1 , the inhomogeneous broadening observed in the CB NQR spectra could be related to a certain degree of structural disorder. As it was indicated in Sec. III A, the disorder could be associated to a spread in the values of dihedral angle of CB molecules. Following a method proposed by Ref. 10, the NQR spectrum profile can be calculated from a given distri-

TABLE IV. Thermal parameters of the more intense low frequency Raman lines of CB: $\omega = \omega_0 (1 - \alpha T)$. The numeration of lines is according to Fig. 6.

Raman line	$\omega_0 [\text{cm}^{-1}]$	$\alpha \times 10^4 [\text{K}^{-1}]$
ω_1	47.2 ± 0.4	5.3 ± 0.4
ω_2 (4–130 K)	85 ± 1	6 ± 1
(190–275 K)	74 ± 3	4 ± 1
ω_3 (4–190 K)	111.5 ± 0.3	4.8 ± 0.3
ω_4	131 ± 1	4 ± 1
ω_5	179.0 ± 0.4	0.0 ± 0.2

bution function of the disorder parameter. The NQR frequency of a chlorine atom from a molecule with a dihedral angle φ can be expanded in a power series of a molecular distortion field $u(\varphi)$. This distortion field is a function of the departures of the geometrical parameter φ relative to a most probable molecular conformation φ_0 .

Assuming small distortions and retaining here only the first order term, the NQR frequency can be written as¹⁰

$$\nu \approx \nu_0 + a_1 u(\varphi). \quad (6)$$

The distortion field $u(\varphi)$ can be characterized by the distribution function $f(u)$. The spectral density resulting from such distribution of u values is given by

$$\rho(\nu) = \frac{f(u)}{\left| \frac{d\nu}{du} \right|} \quad (7)$$

and using the relation (6)

$$\rho(\nu) = \frac{f(\nu)}{|a_1|}. \quad (8)$$

The NQR spectrum can be obtained by means of the convolution of the spectral density with the homogeneous line shape $L_H(\nu)$ (usually a Lorentzian function):

$$F(\nu) = \int_{-\infty}^{\infty} L_H(\nu - \nu') \rho(\nu') d\nu'. \quad (9)$$

The presence of two maxima, ν_H and ν_L , in the NQR spectrum suggests two most probable values of the distortion field $u(\varphi)$. Therefore, there must be two maxima in the distribution function $f(u)$. The distribution function can be decomposed as the sum of two distribution functions, associated to peaks H and L :

$$f(\nu) = f_L(\nu) + f_H(\nu). \quad (10)$$

The most simple distribution function to be proposed for $f_H(\nu)$ and $f_L(\nu)$ is the Gaussian. Nevertheless, Fig. 1 shows that the low frequency profile of the spectrum is not exactly Gaussian-like. Therefore, as the simplest approximation compatible with the observed NQR spectral features, the distribution functions could be proposed in the following way.

(i) Peak H : a single Gaussian distribution function

$$f_H(\nu) = \frac{A}{\sigma_A \sqrt{2\pi}} \exp\left[-\frac{(\nu - \nu_1)^2}{2\sigma_A^2 a_1^2}\right]. \quad (11)$$

(ii) Peak L : an asymmetric distribution function obtained by the superposition of two single Gaussian functions

$$f_L(\nu) = \sum_{i=2,3} \frac{B_i}{\sigma_i \sqrt{2\pi}} \exp\left[-\frac{(\nu - \nu_i)^2}{2\sigma_{B_i}^2 a_1^2}\right]. \quad (12)$$

Figure 7 shows the calculated spectrum from expression (10) using the proposed $f(\nu)$, a Lorentzian homogeneous line shape $L_H(\nu)$ of 1 KHz width and fitting the amplitudes, heights, and widths of the three Gaussian functions. These results show a good agreement with the measured NQR

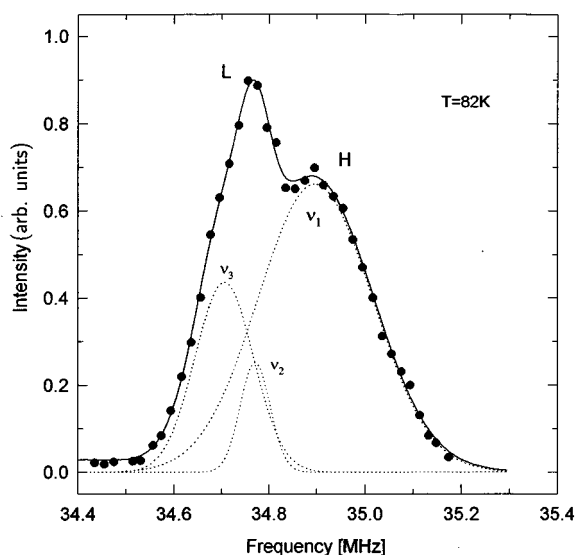


FIG. 7. Fitting of the inhomogeneously broadened NQR spectrum by assuming a random distribution of electric field gradient values with two most probable values associated to the peaks *L* and *H*. The probability distribution equation is the composition of a symmetric Gaussian distribution (centered at ν_1) and an asymmetric one, represented by two Gaussian functions (centered at ν_2 and ν_3).

spectrum. All the recorded spectra were well fitted following this procedure. Figure 8 shows the temperature evolution of frequencies ν_1 , ν_2 , and ν_3 obtained from these fittings; the inset of this figure shows the frequency differences $\nu_1 - \nu_3$ and $\nu_2 - \nu_3$. As can be seen, the difference $\nu_2 - \nu_3$ is nearly

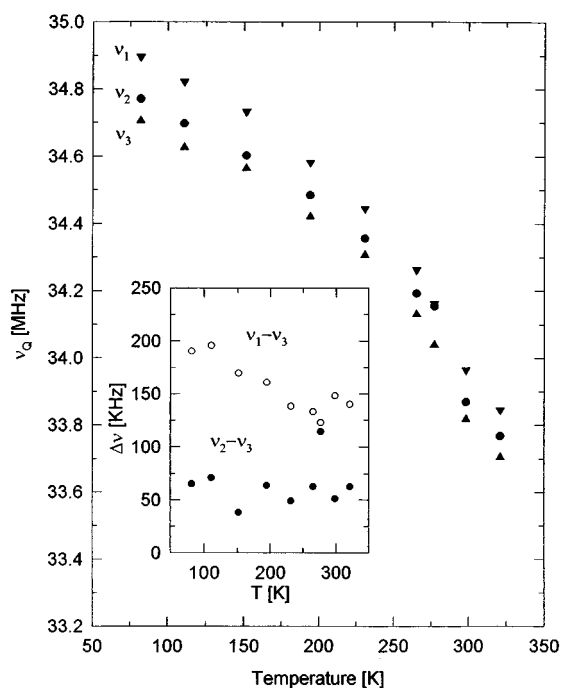


FIG. 8. Temperature dependence of the central frequencies of Gaussian functions used in the fittings to the measured NQR spectra. The inset shows the frequency differences taken ν_3 as a reference.

constant in all temperature ranges indicating that both Gaussians have the same temperature dependence. This result is consistent with the assumption that these two functions are associated with a unique frequency distribution $f_L(\nu)$ in (12).

Despite the fact that the crystal structure of CB is not yet resolved, it is interesting to examine the crystallographic data of a very close halogens substituent: the 4-bromobiphenyl (BB).¹¹ The solid phase of this compound at 152 K shows an ordered crystalline structure (orthorhombic, $Pna2_1$) with eight molecules in the unit cell. The dihedral angle for the molecules in the crystal can assume two possible values: 20.4° or 17.8° . These angles are very compressed with respect to the observed value of about 40° in the free molecule of biphenyl,³ suggesting important intermolecular effects on the crystalline molecular conformation of BB. The possible effect of the substitution of a bromine atom by chlorine, with a lower atomic radius, could be only a reduction in the intermolecular distances and consequently a more dense crystal packing in solid CB. This situation could result in an enhancement in the intermolecular interactions in CB and a more perturbed molecular conformation. These facts are compatible with the experimentally observed two-peaked NQR spectra in CB. The enhanced intermolecular interactions could be responsible of the conformational disorder revealed by a broad EFG distribution. The proposed thermally activated molecular reorientation of CB molecule between different equilibrium configurations of φ could be compatible with the reported two close equilibrium dihedral angles in BB molecules.¹¹

V. CONCLUSIONS

The 4-chlorobiphenyl presents a structurally disordered phase in all the scanned temperature range. This fact is made evident by the broad NQR spectrum and the anomalous temperature behavior of the spin-lattice relaxation time. The nature of the disorder could be attributed to a distribution of inter-ring dihedral angles of the molecule along the sample. This conformational disordered structure may be originated by the competition between the intermolecular and intramolecular forces that determine the internal molecular conformation. Similar effects of loss of periodicity have been observed in other compounds of the same family, such as biphenyl and 4-4' dichlorobiphenylsulphone. A thermally activated dynamical process, tentatively associated to reorientations of phenyl rings, was observed for temperatures above 220 K. This dynamical change has been detected by NQR and Raman measurements. The same dynamical parameters for this process were obtained from NQR and Raman data.

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