Anharmonic Librations and the Temperature Dependence of NQR Frequencies *

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The temperature dependence of NQR frequencies of nuclei in molecules undergoing quasi-harmonic rotational oscillations is calculated. Following the model proposed by Bayer, the instantaneous orientation of the electric field gradient principal axes is assumed to change from its average orientation as a result of rotational oscillations, while the EFG magnitude remains constant. The eigenstates and energy eigenvalues of a rotator in a potential of the form $V(\theta) = V_2 \theta^2 - V_4 \theta^4$ are calculated by standard perturbation methods, followed by the evaluation of statistical averages of square angular amplitudes. For molecular crystals with more than one molecule in a unit cell the angular displacements are expressed in terms of normal coordinates, and the same procedure is followed. The final expression for the change in the NQR frequency consists of two terms, the first one being related to the harmonic part of the potential and the second one to the quartic term. At the absolute zero it yields a nonzero contribution to $\langle \theta^2 \rangle$, and for high temperatures it reproduces the nonlinear character of $v_Q(T)$ observed experimentally. The model has been tested with measurements on solid Cl_2 performed by Nakamura and Chihara, combined with libration mode frequencies measured in Raman spectroscopy by Cahill and Leroi and analysed according to our anharmonic libration picture. The fitting of our equation to experimental data supports Cahill and Leroi's hypothesis about the existence of an undetected libration mode in Cl_2 Raman spectra of frequency near $60\ cm^{-1}$.

Key words: NQR, Bayer's Model, Anharmonic Vibrations.

Introduction

Nuclear quadrupole resonance (NQR) frequencies are temperature dependent because molecular overall and internal vibrations bring about time modulation of the energy of interaction between the quadrupole moment of the resonant nucleus (nuclear spin $I \geq 1$) and the electric field gradient (EFG). In the principal axes system the EFG tensor has the cartesian components V_{XX}, V_{YY} and V_{ZZ}, and the nuclear quadrupole Hamiltonian can be written as [1]

$$H_Q = \frac{e^2 Q q}{4 I (2I-1)} [3 I_Z^2 - I^2 + (\eta/2)(I_+^2 + I_-^2)], \quad (1)$$

where $e Q$ is the nuclear quadrupole moment, $e q = V_{ZZ}$ and the asymmetry parameter is defined as $\eta = (V_{XX} - V_{YY})/V_{ZZ}$, for $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$. As the

molecule containing the nucleus undergoes rotational oscillations, sometimes referred as librations, the EFG becomes time dependent both in the magnitudes of the principal components and the orientation of the principal axes. These oscillations occur at frequencies much higher than the NQR frequencies, hence the NQR Hamiltonian can be kept in the static form of (1), with the parameters $e q$ and η replaced by their time-averaged values. For the common case of a spin 3/2 nucleus in an electric field of small asymmetry, the NQR frequency is

$$v_Q = e^2 Q q / 2 h. \quad (2)$$

As the molecule experiences very fast rotational oscillations about two orthogonal axes perpendicular to the EFG symmetry axis, v_Q can be expressed as [2]

$$v_Q = v_0 [1 - (3/2)\langle \theta_X^2 \rangle - (3/2)\langle \theta_Y^2 \rangle], \quad (3)$$

where $v_0 = (e^2 Q q_0 / 2h)$ is the resonant frequency which would be observed in a stationary molecule and θ_X, θ_Y are very small angular displacements with respect to the equilibrium orientations of the X, Y axes.

It follows that v_Q is temperature dependent through the mean square libration amplitudes. NQR frequencies thus provide information about both the electrostatic charge distribution in the vicinity of the resonant nucleus and the lattice dynamics.

Bayer [3] presented a simple theory to translate (3) into a temperature dependence based on the following assumptions: (a) the EFG is averaged only by the librational motion of rigid molecules; (b) each molecule oscillates independently of its neighbors about three axes which coincide with the EFG principal axes; (c) librations are purely harmonic; (d) the magnitude $e q_0$ is not affected by the motion, hence $\eta = 0$. It follows from the statistical mechanics of quantum harmonic oscillators that the mean square angular amplitudes are

$$\langle \theta_k^2 \rangle = (\hbar/2 I_k \omega_k) \coth(\hbar \omega_k/2kT). \tag{4}$$

The NQR frequency can, according to Bayer, be written in the form

$$v_Q(T) = v_0 \left[1 - \left(\frac{3\hbar}{4} \right) \sum_k \frac{\coth(\hbar \omega_k/2kT)}{I_k \omega_k} \right], \tag{5}$$

where $k \equiv X, Y, I_k$ are the corresponding molecular moments of inertia and ω_k are the librational angular frequencies. The validity of Bayer's equation can be tested by fitting it to experimental NQR frequency data over a wide range of temperature. If the tensor of inertia is known from molecular geometry, then the "static molecule" frequency v_0 and ω_k could in principle be calculated as best fit parameters, but this procedure does not yield reliable results. In fact, (5) fits very well to experimental points in the low temperature region, but it predicts an asymptotic linear dependence for higher ($kT > \hbar \omega_k$) temperatures, while the measured frequencies follows a parabolic curve. Also the ω_k values are strongly dependent upon the selected temperature range width, and they seldom coincide with those measured by vibrational (Raman) spectroscopy.

Without modifying Bayer's fundamental assumption (5) about motional averaging of the nuclear quadrupole Hamiltonian, several authors made attempts to improve his simple model in order to obtain a better agreement with experiment. Kushida [4] included the coupling of molecules within a unit cell, so that angular displacements become linear combinations of normal coordinates, and (5) is modified to admit contributions from all compatible normal

modes. Kushida, Benedek and Bloembergen [5] assumed that librations are not purely harmonic and their frequencies are temperature dependent due to thermal expansion. They derived phenomenological equations relating ω_k to the volume which, combined with the equation of state, led to a pressure and temperature dependence of v_Q. Brown [6] introduced into Bayer's equation an empirical linear relationship $\omega_k = \omega_{k0} (1 - g T)$ which is observed in Raman spectra taken in the high temperature region and is imputed to lattice vibration anharmonicity and thermal expansion. This Bayer-Brown equation yields good fittings to most of NQR frequency versus temperature data, but this is chiefly due to the role of a new parameter cleverly located; since it is not related to a physical model, no specific information about lattice dynamics arises from its value, which is also dependent on the temperature range. In another approach, intended to introduce nonlinear vibration effects, Brookeman, McEnnan and Scott [7] extended (3) by adding terms up to the sixth power in θ, obtained from the cosine function power series expansion.

Nakamura and Chihara (N & C) [8] measured ^{35}Cl and ^{37}Cl NQR frequencies in solid chlorine from 21 K to a few degrees below the melting point. The data were analysed by use of Bayer's equation assuming a single doubly degenerate librational frequency. After calculating v_0 from $v_Q(T)$ for $T < 60$ K, (5) was solved for ω_k at each temperature, showing that it changes from 90 cm^{-1} to 74 cm^{-1} in a nonlinear way. Later, Cahill and Leroi (C & L) [9] measured the libration mode frequencies of solid Cl_2 by Raman spectroscopy in a wide temperature range. The plot of their ω_k versus T data suggests a plateau at low temperatures and a linear decrease of ω_k in the higher temperature range.

We have demonstrated in [10] that those features can be explained by a model of quasi-harmonic librations under potentials of the form $V(\theta) = V_2 \theta^2 - V_4 \theta^4$. That leads to equations fitting quite well to experimental data. The decrease of the libration mode frequencies with temperature increase is connected to the V_4 coefficient. In the present work the same rotational potential well is employed to evaluate the mean square angular amplitudes of (3) and to get an improved version of Bayer's formula, applicable in simple molecular crystals.

Theory

1. Single Oscillator

Let us assume a molecule containing a resonant nucleus at a site of axially symmetric EFG. The Z principal axis of the EFG coincides with one of the principal axes of the tensor of inertia, and let the directions X, Y be determined by the molecule structure. Let θ be the angular displacement away from equilibrium about the X or Y axis, and the restoring potential be given by

$$V(\theta) = (1/2)\, I\, \omega_0^2\, \theta^2 - \lambda\, \theta^4, \qquad (6)$$

where I is the molecular moment of inertia about the oscillation axis, $I\omega_0^2$ is the harmonic force constant, and the quartic term for the maximum libration amplitude is small enough to allow the use of perturbation methods for the evaluation of $\langle \theta^2 \rangle$. Following the procedure described in [10], we write the energy levels for the anharmonic rotator

$$E_n = \hbar \omega_0 (n+1/2) - \hbar\, \Omega (n+1/2)^2 - \hbar\Omega/4,$$
$$(n = 0, 1, \ldots), \qquad (7)$$

where

$$\Omega = (3\hbar/2I^2 \omega_0^2)\, \lambda. \qquad (8)$$

The corresponding eigenstates are

$$|\psi_n\rangle = |n\rangle - (\lambda/\hbar\omega_0) \sum_{m \neq n} |m\rangle \frac{\langle m|\theta^4|n\rangle}{n-m}, \qquad (9)$$

and the expectation value of the square angular amplitude for a molecule in the level E_n is

$$\theta_n^2 = \langle \psi_n|\theta^2|\psi_n\rangle = \langle n|\theta^2|n\rangle$$
$$- (2\lambda/\hbar\omega_0) \sum_{m \neq n} \frac{\langle n|\theta^2|m\rangle \langle m|\theta^4|n\rangle}{n-m}. \qquad (10)$$

The evaluation of the matrix elements is not difficult, although laborious, and can be carried out through sequential application of θ written in terms of creation and annihilation operators, a^+ and a,

$$\theta = (\hbar/2I\omega_0)^{1/2}\, (a^+ + a), \qquad (11)$$

resulting in

$$\theta_n^2 = \frac{\hbar}{I\omega_0}(n+1/2) + \frac{2\hbar\Omega}{I\omega_0^2}(n+1/2)^2 + \frac{\hbar\Omega}{2I\omega_0^2} \qquad (12)$$

after use of (8). The partition function

$$Z = \sum_n e^{-E_n/kT} = e^{\varepsilon/4} \sum_n e^{-x(n+1/2)}\, e^{\varepsilon(n+1/2)^2}. \qquad (13)$$

where $x = \hbar\omega_0/kT$ and $\varepsilon = \hbar\Omega/kT \ll x$, does not converge unless $\varepsilon = 0$, but if we assume that only the first few lowest levels have significant populations, so that $\exp(\varepsilon n^2) \approx 1 + \varepsilon n^2$, the sum can be calculated, resulting in

$$Z \doteq Z_0 [1 + (\hbar\Omega/kT) \coth^2 (\hbar\omega^2/2kT)]. \qquad (14)$$

Z_0 is the simple harmonic oscillator ($\lambda = 0$) partition function. The ensemble averages of the occupation numbers in (12) can then be evaluated, giving

$$\langle \theta^2 \rangle = \frac{\hbar}{2I\omega_0} \coth (x/2) \qquad (15)$$
$$+ \frac{\hbar\Omega}{I\omega_0^2} \left[\coth^2\left(\frac{x}{2}\right) + \left(\frac{x}{2}\right) \coth\left(\frac{x}{2}\right) \operatorname{cosech}^2\left(\frac{x}{2}\right) \right].$$

If the crystal has more than one molecule per unit cell, then θ is some linear combination of normal coordinates q_j:

$$\theta = \sum_j A_j q_j, \quad (j = 1, \ldots, M), \qquad (16)$$

where M is the number of librational degrees of freedom per unit cell, and the coefficients are determined by the intermolecular potential symmetry. It follows from (16) that

$$\langle \theta^2 \rangle = \sum_j A_j^2 \langle q_j^2 \rangle, \quad (\theta = \theta_X, \theta_Y), \qquad (17)$$

and we assume that every $\langle q_j^2 \rangle$ has the same form as $\langle \theta^2 \rangle$ in (15), i.e., every q_j is an independent anharmonic oscillator. The NQR frequency is then calculated by combining (3), (15) and (17):

$$(18)$$
$$\nu_Q(T) = \nu_0 \left\{ 1 - \frac{3\hbar}{4} \sum_{j=1}^{M} \frac{A_j^2}{I_j \omega_j} \left[\coth\left(\frac{x_j}{2}\right) + \frac{2\Omega_j}{\omega_j} F(x_j) \right] \right\}.$$

I_j is equal to I_X or I_Y, $F(x)$ is the expression inside the brackets in (15), $x_j = \hbar\omega_j/kT$, and ω_j, Ω_j are obtained through the analysis of Raman spectral line frequencies according to the anharmonic libration model [10].

The NQR frequency at $T = 0$ shows a residue of the anharmonic part of the rotational potential energy:

$$\nu_Q(0) = \nu_0 \left\{ 1 - \frac{3\hbar}{4} \sum_{j=1}^{M} \frac{A_j^2}{I_j \omega_j} \left[1 + \frac{2\Omega_j}{\omega_j} \right] \right\}. \qquad (19)$$

On the other hand, in the "high" temperature region

$$\nu_Q(T) \approx \nu_0 \{ 1 - a(\omega_j) T - b(\omega_j, \Omega_j) T^2 \}. \qquad (20)$$

For axially symmetric molecules it may be possible to have a reasonably good fitting to experiment of (18)

rewritten with just one average pair of parameters $\bar{\omega}$ and $\bar{\Omega}$.

2. Two Coupled Oscillators

Two identical and axially symmetric molecules undergo anharmonic librations about the same axis connected by harmonic couplings. Their instantaneous angular displacements are θ_1 and θ_2, and the rotational potential energy is assumed to be

$$V(\theta_1, \theta_2) = (1/2) I \omega_0^2 (\theta_1^2 + \theta_2^2) + (1/2) I K_1^2 (\theta_1 + \theta_2)^2 + (1/2) I K_2^2 (\theta_1 - \theta_2)^2 - \lambda (\theta_1^4 + \theta_2^4), \quad (21)$$

where $I K_{1,2}^2$ are force constants associated to the symmetric and antisymmetric oscillation mode couplings. By introducing the moment of inertia weighted normal coordinates

$$q_1 = (I/2)^{1/2} (\theta_1 + \theta_2) \quad \text{and}$$
$$q_2 = (I/2)^{1/2} (-\theta_1 + \theta_2), \quad (22)$$

the potential energy is transformed into

$$V = (1/2) \omega_1^2 q_1^2 + (1/2) \omega_2^2 q_2^2 - (\lambda/2 I^2)(q_1^4 + q_2^4 + 6 q_1^2 q_2^2), \quad (23)$$

where $\omega_i^2 = \omega_0^2 + 2 K_i^2$ $(i = 1, 2)$, and the complete separation of variables is frustrated by the quartic term. A perturbation calculation is carried out through the same steps as those in the single oscillator case, and after a tedious algebra the following results are obtained:

(a) Eigenenergies:
$$E(n_1 n_2) = \hbar \omega_1 (n_1 + \tfrac{1}{2}) + \hbar \omega_2 (n_2 + \tfrac{1}{2}) - \tfrac{1}{2} \hbar \Omega_1 (n_1 + 1/2)^2 - \tfrac{1}{2} \hbar \Omega_2 (n_2 + 1/2)^2 - \tfrac{1}{2} \hbar (\Omega_1 \Omega_2)^{1/2} (n_1 + \tfrac{1}{2})(n_2 + \tfrac{1}{2}) - \tfrac{1}{8} \hbar (\Omega_1 + \Omega_2), \quad (n_1, n_2 = 0, 1 \ldots), \quad (24)$$

where
$$\Omega_j = 3 \hbar \lambda / 2 I^2 \omega_j^2, \qquad (j = 1, 2). \quad (25)$$

(b) Partition Function:

$$Z \doteq Z_{01} Z_{02} \left[1 + \frac{\hbar \Omega_1}{2kT} \coth^2 (\hbar \omega_1 / 2kT) + \frac{\hbar \Omega_2}{2kT} \coth^2 (\hbar \omega_2 / 2kT) \right. \quad (26)$$
$$\left. + \frac{\hbar (\Omega_1 \Omega_2)^{1/2}}{4kT} \coth (\hbar \omega_1 / 2kT) \coth (\hbar \omega_2 / 2kT) \right].$$

$Z_{01} \cdot Z_{02}$ is the $\lambda = 0$ partition function.

(c) Expectation value of the square normal coordinate amplitude:

$$\langle \psi_{n1, n2} | q_1^2 | \psi_{n1, n2} \rangle = \frac{\hbar}{\omega_1} \left(n_1 + \frac{1}{2} \right) + \frac{\hbar \Omega_1}{\omega_1^2} \left(n_1 + \frac{1}{2} \right)^2 + \frac{\hbar \Omega_1}{4 \omega_1^2}, \quad (27)$$

and a similar expression for q_2^2.

(d) Mean square normal coordinates amplitudes:

$$\langle q_1^2 \rangle = \frac{\hbar}{2\omega_1} \coth(x_1/2) + \frac{\hbar \Omega_1}{2 \omega_1^2} F(x_1) + \frac{\hbar (\Omega_1 \Omega_2)^{1/2}}{2 \omega_1^2} G(x_1, x_2),$$

$$\langle q_2^2 \rangle = \frac{\hbar}{2\omega_2} \coth(x_2/2) + \frac{\hbar \Omega_2}{2 \omega_2^2} F(x_2) + \frac{\hbar (\Omega_1 \Omega_2)^{1/2}}{2 \omega_2^2} G(x_2, x_1), \quad (28)$$

where $F(x)$ still is defined as in (15) and the two frequencies function $G(x_1, x_2)$ is

$$G(x_1, x_2) = \left(\frac{x_1}{2} \right) \operatorname{cosech}^2 (x_1/2) \coth(x_2/2). \quad (29)$$

When the oscillation about the other axis is also reckoned, the pair of molecules ends up with four degrees of freedom. Equation (3) for v_Q can then be combined with (22) and (28) to yield a general expression for the temperature dependence of NQR frequency:

$$v_Q(T) = v_0 \left\{ 1 - \left(\frac{3\hbar}{8I} \right) \sum_{j=1}^{4} \frac{1}{\omega_j} \left[\coth(x_j/2) + \frac{\Omega_j}{\omega_j} F(x_j) + \frac{(\Omega_j \Omega_k)^{1/2}}{\omega_j} G(x_j, x_k) \right] \right\}, \quad (30)$$

where $x_j = \hbar \omega_j / kT$; x_k refers to the frequency which is mixed with ω_j in the anharmonic part of the potential energy expression (23).

Application: Solid Chlorine

Solid chlorine is a suitable substance for testing the validity of the theory presented herein. It is a diatomic molecular crystal with a face-centered orthorhombic lattice structure, arranged in layers parallel to the bc crystallographic plane. The relative orientations of the

EFG principal axes and those of the inertia tensor closely meet the assumptions made in the beginning of the preceding section. A thorough description of the molecular arrangement and the application of group theory to find the libration mode eigenvectors may be found in a paper by McEnnan and Schempp [11]. This system has an additional feature that makes it a very convenient one for our purpose: the internal (stretching) and libration modes are well separated in frequency, so any mode-coupling can be neglected. Also the rigid molecule picture gets stronger support, and no averaging of the EFG principal component eq needs to be taken into account. However, there is one drawback to deal with: only three libration frequencies have been observed and independently confirmed by different authors, out of the four Raman active modes expected. This led to discrepancies about the assignment of the frequencies to the four libration eigenvectors. An extended discussion about this can be found in pages 40 and 41 of [11]. We shall apply our theory to the ^{35}Cl NQR frequencies measured by N & C [8] to evaluate the location of the missing band in solid chlorine Raman spectra.

1. Choice of the Temperature Range

The graph of the $v_Q(T)$ curve given, e.g., by (18) has a characteristic shape which agrees with most of the v_Q versus T graphs of systems showing no phase transition: dv_Q/dT is negative and monotonically decreasing, and $d^2 v_Q/dT^2$ is always negative, approaching a constant value for increasing temperatures. The N & C data were checked for this behavior by calculating the ratios $(\Delta v_Q/\Delta T)$ for all temperature intervals. Its graph follows a smooth decreasing curve, except for two small bumps close to 100 K and 130 K, but large fluctuations happen as one gets close to the melting point by less than 20 K. An estimation of the second derivative shows an almost constant negative value until it begins to jump between positive and negative values in the same temperature region. In order to avoid this "irregular" behavior, only $v_Q(T)$ for $T < 150$ K was considered.

2. Single Frequency Picture

Equations (18) and (19), rewritten for a molecule with one doubly degenerate libration frequency, were used first the evaluate v_0 and the effective frequencies ω and Ω (actually the wavenumbers $\bar{v}$ and $\bar{\Omega}$) by

means of an iterative procedure, as follows. Equation (18) was fitted to the v_Q versus T graph with v_Q substituted by $v_Q(0)$. The fitting yielded $\bar{v}$ and $\bar{\Omega}$, which were taken into (19), and a new v_0 was calculated. The sequence was repeated and converged after a few steps. The calculated curve fits very well to the experimental points along the whole temperature range. The best fit parameters are

$$v_0 = 54.937 \text{ MHz},$$
$$\bar{v} = 118 \pm 3 \text{ cm}^{-1},$$
$$\bar{\Omega} = 18.5 \pm 2.5 \text{ cm}^{-1},$$

leading to the $T = 0$ NQR frequency $v_Q(0) = 54.487$ MHz. These v_0 and $v_Q(0)$ are in perfect agreement with those calculated by N & C, who analysed only the region $T < 60$ K, where Bayer's equation was satisfactory in describing v_Q data. Moreover, if we make in (19) the substitution

$$\frac{1}{\bar{v}_{eq}} = \frac{1}{\bar{v}} \left[1 + \frac{2\bar{\Omega}}{\bar{v}} \right], \tag{31}$$

we find $\bar{v}_{eq} = (90 \pm 3) \text{ cm}^{-1}$, also in agreement with N & C. The same procedure carried out for ^{37}Cl gave

$$v_0 = 43.300 \text{ MHz}, \qquad \bar{v} = 99 \pm 1 \text{ cm}^{-1},$$
$$\bar{v}_{eq} = 89.5 \pm 1.5 \text{ cm}^{-1}, \quad v_Q(0) = 42.945 \text{ MHz},$$
$$\bar{\Omega} = 5.2 \pm 1 \text{ cm}^{-1}.$$

3. Single Oscillators Picture

Once again (18) and (19) were combined, v_0 was eliminated and $v_Q(T)$ expressed in terms of $v_Q(0)$ and the contributions of all four anharmonic libration modes. Since only three have been detected, their $\bar{v}$ and $\bar{\Omega}$ values calculated in [10] were substituted into the expression of $v_Q(T)$ and substracted from it. The remaining values were fitted to the functional form of the unknown fourth mode contribution. This fitting can be achieved through more than one combination of $\bar{v}_4$ and $\bar{\Omega}_4$, some of them visually gratifying but with doubtful parameter values. We show two acceptable solutions in Figures 1 and 2. In the first we have $\bar{v}_4 = 98 \text{ cm}^{-1}$ and $\bar{\Omega}_4 = 17.5 \text{ cm}^{-1}$, which means that the unobserved mode must have a wavenumber of 63 cm^{-1} close to zero temperature and its large anharmonic character is responsible for a wide line with a strong temperature dependence as shown in Figure 3. A less satisfactory possibility, as far as the goodness of fit is used as a criterium, is the couple $\bar{v} = 70.5 \text{ cm}^{-1}$,
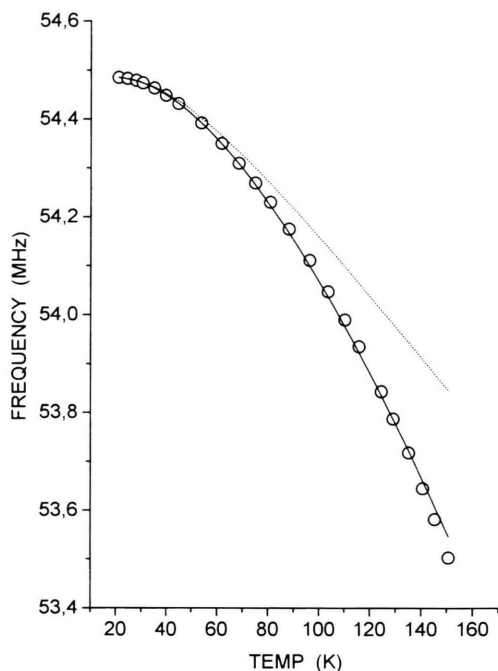
Fig. 1. ^{35}Cl NQR frequencies and calculated curves: (· · · ·) Bayer's model with N & C fitting for $T < 60$ K and extended up to 150 K; (——) four single oscillators model, (18), $\bar{v}_4 = 98$ cm^{-1}, $\bar{\Omega}_4 = 17.5$ cm^{-1}.
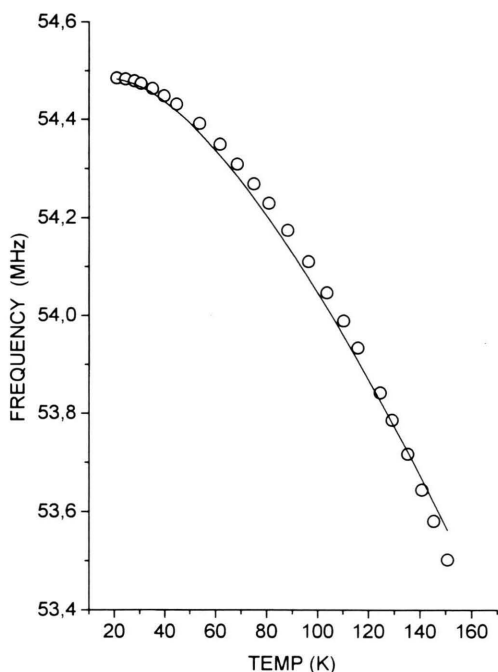

Fig. 2. ^{35}Cl NQR frequencies and calculated curve, four single oscillators model, $\bar{v}_4 = 70.5$ cm^{-1}, $\bar{\Omega}_4 = 2.0$ cm^{-1}

$\bar{\Omega}_4 = 2.0$ cm^{-1}, whose zero temperature frequency is 66 cm^{-1} and has a mild temperature dependence, also shown in Figure 3. This coincides with Cahill and Leroi's proposal [9], based on the comparison with solid bromine Raman spectra with four visible libration bands, and also with the point by point calculation made by Obermyer and Jones [12].

4. Two Coupled Oscillators

The expression for $v_Q(T)$ given by (30) was applied to the ^{35}Cl isotope NQR frequency in solid chlorine with the same purpose of finding the temperature dependence of the missing libration band in Raman spectra. We assigned the two upper lines, 119 and 100 cm^{-1} for $T = 15$ K, to the symmetric and antisymmetric modes in the bc plane, respectively. Their parameters, calculated through the coupled oscillators model [10] are, in cm^{-1},

$\bar{v}(0)$	$\bar{v}$	$\bar{\Omega}$
119	148	17.6
110	119	7.7

We are then left with four parameters to be calculated for the other two lines, assigned to the inter-planes coupled oscillations, one of them satisfying the known temperature dependence. The fitting of NQR data under this condition lead to the following parameters, also in cm^{-1}:

$\bar{v}(0)$	$\bar{v}$	$\bar{\Omega}$	
83	88.3	0.85	(symmetric, observed)
62.5	91.5	24.5	(antisymmetric, not observed),

in agreement with the solid curve in Figure 3. The calculated temperature dependence of ^{35}Cl NQR frequencies using these fitting parameters in (30) is shown in Figure 4.

Discussion

With the addition of a quartic term in the rotational potential for the molecular libration we could work out expressions for the NQR frequency that reproduce the shape of the v_Q versus T graph of solid chlorine and shows that, if there is any possibility of observing the up till now undetected libration mode, it must be searched near 63 cm^{-1} at very low temperatures.
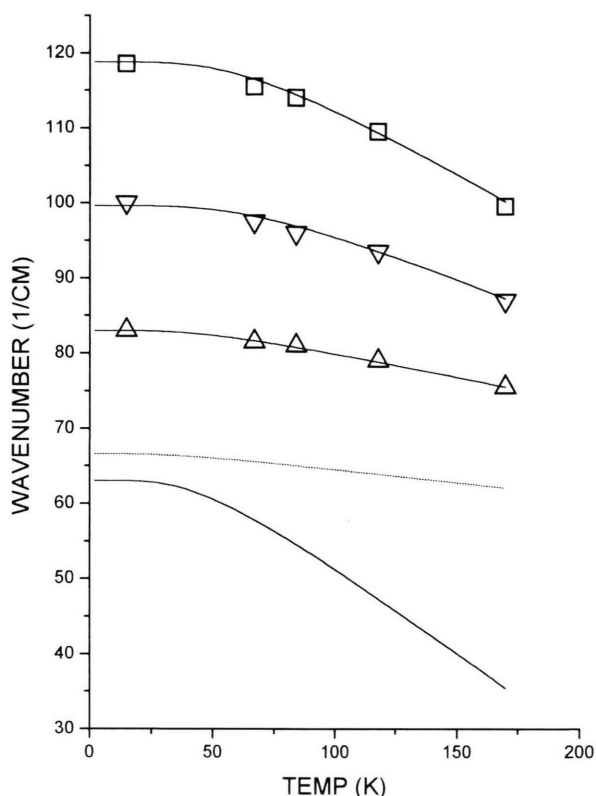
Fig. 3. Libration mode frequencies measured by C & L (□, ▽, △) and the fitting curves given by the anharmonic libration model [10]. Below are plotted the possible temperature dependences of the missing band: the solid (dotted) curve yields the fitting in Figure 1 (2).
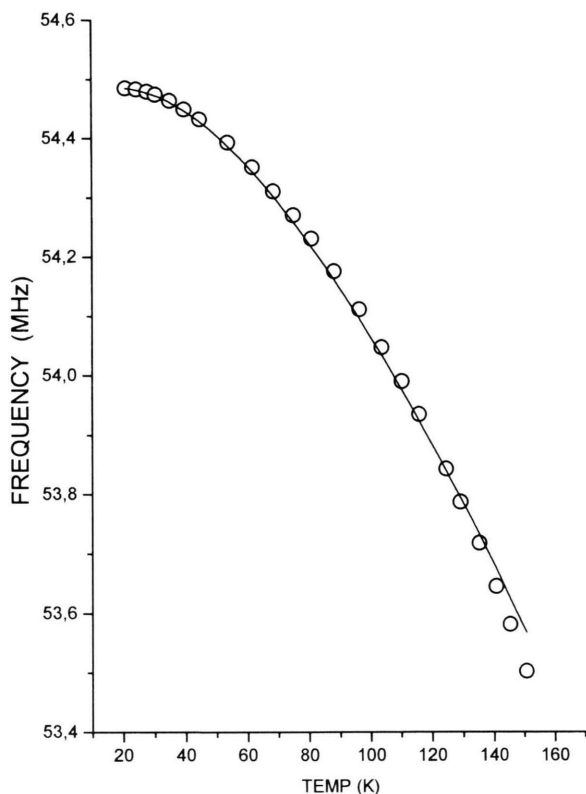

Fig. 4. ^{35}Cl NQR frequencies and calculated curve by the two coupled anharmonic rotators model, (30).

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[1] A. Abragam, The Principles of Nuclear Magnetism, Ch. VI, Clarendon Press, Oxford 1961.
[2] T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Solid State Physics, Suppl. I, Academic Press, New York 1950.
[3] H. Bayer, Z. Physik **130**, 227 (1951).
[4] T. Kushida, J. Sci. Hiroshima Univ. Sci. A **19**, 327 (1955).
[5] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).
[6] R. J. C. Brown, J. Chem. Phys. **32**, 116 (1960).
[7] J. R. Brookeman, M. M. McEnnan, and T. A. Scott, Phys. Rev. B **4**, 3661 (1971).

[8] N. Nakamura and H. Chihara, J. Phys. Soc. Japan **22**, 201 (1967).
[9] J. E. Cahill and G. E. Leroi, J. Chem. Phys. **51**, 4514 (1969).
[10] C. Mendonça and S. R. Rabbani, Z. Naturforsch. **51 a**, 718 (1996).
[11] M. M. McEnnan and E. Schempp, J. Magn. Reson. **11**, 28 (1973).
[12] R. T. Obermyer and E. P. Jones, Can. J. Phys. **51**, 2300 (1973).