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TEMPERATURE DEPENDENCE OF NQR  
FREQUENCY**

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# ANHARMONIC LIBRATIONS AND THE TEMPERATURE DEPENDENCE OF NQR FREQUENCY

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Running title: Anharmonic Librations and NQR Frequency

The temperature dependence of NQR frequencies of nuclei in molecules undergoing quasi-harmonic rotational oscillations was 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 calculated for the change in NQR frequency can be grouped into two terms, the first one related to the harmonic part of the potential, already present in Bayer's equation, while the second one is related to the quartic term. In the absolute zero it yields a nonzero contribution to  $\langle\theta^2\rangle$ , and for high temperatures it reproduces the nonlinear character of the  $\nu_Q(T)$  curve observed experimentally. The model has been tested with the measurements in solid  $\text{Cl}_2$  performed by Nakamura and Chihara, combined with libration mode frequencies measured in Raman spectroscopy by Cahill and Leroi and analysed according to the anharmonic libration picture we propose elsewhere. The fitting of our equation to experimental data supports Cahill and Leroi's hypothesis about the existence of an undetected libration mode in  $\text{Cl}_2$  Raman spectra of frequency near  $60 \text{ cm}^{-1}$ .

Keywords: NQR, Bayer's Model, Anharmonic Vibrations.

## INTRODUCTION

Nuclear quadrupole resonance (NQR) frequency is temperature dependent because molecular overall and internal vibration bring about time modulation of the energy of interaction between the quadrupole moment of the resonant nucleus (nuclear spin  $I \geq 1/2$ ) and the electric field gradient (EFG) produced by the static charge distribution in the neighborhood. In the principal axes system the EFG tensor has cartesian components  $V_{xx}$ ,  $V_{yy}$  and  $V_{zz}$ , and the nuclear quadrupole Hamiltonian can be written as [1]

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

where, according to the usual notation,  $eQ$  is the nuclear quadrupole moment,  $eq = V_{zz}$  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 torsion oscillations or 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 equation (1), with the parameters  $eq$  and  $\eta$  replaced by their time-averaged values. For the common case of a spin  $3/2$  nucleus in an electric field of small asymmetry parameter the NQR frequency is

$$\nu_Q = e^2 Qq/2h \quad (2)$$

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

$$\nu_Q = \nu_0 [1 - (3/2)\langle\theta_x^2\rangle - (3/2)\langle\theta_y^2\rangle], \quad (3)$$

where  $\nu_0 = (e^2 Qq_0/2h)$  is the resonant frequency which would be observed in a stationary molecule and  $\theta_x$ ,  $\theta_y$  are very small angular displacements with respect to the equilibrium orientations of X, Y axes. It follows that  $\nu_Q$  is temperature dependent through the mean square libration amplitudes. NQR frequency thus provides informations 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 equation (3) into a temperature dependence based on the following assumptions: (a) the EFG is averaged only by 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  $eq_0$  is not affected by the motion, hence  $\eta = 0$ . It follows from the statistical mechanics of quantum harmonic oscillators that mean square angular amplitudes are

$$\langle \theta_k^2 \rangle = (\hbar/2I_k \omega_k) \coth(\hbar\omega_k/2kT) \quad (4)$$

and the NQR frequency, according to Bayer, is written in the form

$$\nu_Q(T) = \nu_0 \left[ 1 - \left( \frac{3\hbar}{4} \right) \sum_k \frac{\coth(\hbar\omega_k/2kT)}{I_k \omega_k} \right] \quad (5)$$

where  $k = X, Y, I_k$  are the corresponding molecular moments of inertia and  $\omega_k$  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  $\nu_0$  and the  $\omega_k$  could in principle be calculated as best fit parameters, but this procedure does not yield reliable results. In fact, that equation 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 instead, and an increasing deviation is observed. Also the  $\omega_k$  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 about motional averaging of the nuclear quadrupole Hamiltonian, equation (3), 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 equation (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  $\omega_k$  to the volume which, combined with the equation of state, led to a pressure and temperature dependence of  $\nu_Q$ . Brown [6] introduced into Bayer's equation an empirical linear relationship  $\omega_k = \omega_{k0}(1 - gT)$  which is observed in Raman spectra taken in the high temperature region and is imputed to lattice vibrations

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 arise from its value, which is also dependent upon the temperature range. In another approach, intended to introduce nonlinear vibration effects, Brookeman, McEannan and Scott [7] extended equation (3) by adding terms up to sixth power in  $\theta$ , obtained from the cosine function power series expansion.

Nakamura and Chihara (N & C) [8] measured  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  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  $\nu_0$  from  $\nu_Q(T)$  for  $T < 60$  K equation (5) was solved for  $\omega_k$  at each temperature, showing that it changes from  $90 \text{ cm}^{-1}$  to  $74 \text{ cm}^{-1}$  in a nonlinear pattern. Later, Cahill and Leroi (C & L) [9] measured the libration mode frequencies of solid  $\text{Cl}_2$  by Raman spectroscopy in a wide temperature range. The plot of their  $\omega_k$  versus  $T$  data suggest a plateau at low temperatures and a linear decrease of  $\omega_k$  in the higher temperature range.

The authors of this present work demonstrated in another paper [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, and the decrease of libration mode frequencies with temperature increase is connected to the  $V_4$  coefficient. In this work the same rotational potential well is employed to evaluate the mean square angular amplitudes of equation (3) and to get an expectedly improved version of Bayer's formula applicable in simple molecular crystals.

## THEORY

### I. Single Oscillator

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

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

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 same procedure described in [10] we write the energy levels for the anharmonic rotator

$$E_n = \hbar\omega_0 \left( n + \frac{1}{2} \right) - \hbar\Omega \left( n + \frac{1}{2} \right)^2 - \hbar\Omega/4 \quad (n = 0, 1, \dots) \quad (7)$$

where

$$\Omega = (3\hbar/2I^2\omega_0^2)\lambda \quad (8)$$

The corresponding eigenstates are

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

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

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

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

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

obtaining

$$\theta_n^2 = \frac{\hbar}{I\omega_0} \left( n + \frac{1}{2} \right) + \frac{2\hbar\Omega}{I\omega_0^2} \left( n + \frac{1}{2} \right)^2 + \frac{\hbar\Omega}{2I\omega_0^2} \quad (12)$$

after use of equation (8). The partition function

$$Z = \sum_n e^{-E_n/kT} = e^{\epsilon/4} \sum_n e^{-\lambda(n+1/2)} e^{\lambda(n+1/2)^2} \quad (13)$$

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

$$Z \doteq Z_0 \left[ 1 + (\hbar\Omega/kT) \coth^2(\hbar\omega_0/2kT) \right] \quad (14)$$

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

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

If the crystal has more than one molecule per unit cell then  $\theta$  is some linear combination of normal coordinates  $q_j$

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

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 equation (16) that

$$\langle \theta^2 \rangle = \sum_j A_j^2 \langle q_j^2 \rangle \quad (\theta = \theta_x, \theta_y) \quad (17)$$

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

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

$I_j$  is equal to  $I_X$  or  $I_Y$ ,  $F(x)$  is the expression inside brackets in equation (15),  $x_j = \hbar\omega_j/kT$ , and  $\omega_j, \Omega_j$  are obtained through the analysis of Raman spectral lines 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

$$v_0(O) = v_0 \left\{ 1 - \frac{3\hbar}{4} \sum_{j=1}^M \frac{A_j^2}{I_j \omega_j} \left[ 1 + \frac{2\Omega_j}{\omega_j} \right] \right\} \quad (19)$$

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

$$v_0(T) \approx v_0 \{ 1 - a(\omega_j) T - b(\omega_j, \Omega_j) T^2 \} \quad (20)$$

For axially symmetric molecules it may be possible to have a reasonably good fitting to experiment of equation (18) rewritten with just one average pair of parameters  $\bar{\omega}$  and  $\bar{\Omega}$ .

## II. 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  $\theta_1$  and  $\theta_2$  and the rotational potential energy is assumed to be

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

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

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

The potential energy is transformed into

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

where  $\omega_1^2 = \omega_0^2 + 2K_1^2$  and  $\omega_2^2 = \omega_0^2 + 2K_2^2$ , 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

$$E(n_1, n_2) = \hbar \omega_1 \left( n_1 + \frac{1}{2} \right) + \hbar \omega_2 \left( n_2 + \frac{1}{2} \right) - \frac{1}{2} \hbar \Omega_1 \left( n_1 + \frac{1}{2} \right)^2 - \frac{1}{2} \hbar \Omega_2 \left( n_2 + \frac{1}{2} \right)^2 - \frac{1}{2} \hbar (\Omega_1 \Omega_2)^{1/2} \left( n_1 + \frac{1}{2} \right) \left( n_2 + \frac{1}{2} \right) - \frac{1}{8} \hbar (\Omega_1 + \Omega_2) \quad (n_1, n_2 = 0, 1, \dots) \quad (24)$$

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

### (b) Partition Function

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

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

### (c) Expectation value of square normal coordinate amplitude

$$\langle \psi_{n_1, n_2} | q_1^2 | \psi_{n_1, n_2} \rangle = \frac{\hbar}{\omega_1} \left( n_1 + \frac{1}{2} \right) + \frac{\hbar \Omega_1}{\omega_1^2} \left( n_1 + \frac{1}{2} \right)^2 + \frac{\hbar \Omega_1}{4\omega_1^2} \quad (27)$$

and a similar expression for  $q_2^2$ .

### (d) Mean square normal coordinates amplitudes

$$\langle q_1^2 \rangle = \frac{\hbar}{2\omega_1} \coth(x_1/2) + \frac{\hbar \Omega_1}{2\omega_1^2} F(x_1) + \frac{\hbar (\Omega_1 \Omega_2)^{1/2}}{2\omega_1^2} G(x_1, x_2) \quad (28)$$

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

where  $F(x)$  still is defined as in equation (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 end up with four degrees of freedom. Equation (3) for  $\nu_Q$  can then be combined with (22) and (28) to yield a general expression for the temperature dependence of NQR frequency:

$$\nu_Q(T) = \nu_0 \left\{ 1 - \left(\frac{3\hbar}{8I}\right) \sum_{j=1}^4 \frac{1}{\omega_j} \left[ \coth(x_j/2) + \frac{\Omega_j}{\omega_j} F(x_j) + \frac{(\Omega_j \Omega_k)^{1/2}}{\omega_j} G(x_j, x_k) \right] \right\} \quad (30)$$

where  $x_j = \hbar\omega_j/kT$ ;  $x_k$  refers to the frequency which is mixed with  $\omega_j$  in the anharmonic part of the potential energy expression, equation (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 modes 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 modes 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 it can be found in pages 40/41 of reference [11]. We shall apply our theory to the  $^{35}\text{Cl}$  NQR frequencies measured by N&C [8] to evaluate the location of the missing band in solid chlorine Raman spectra.

#### I. Choice of the Temperature Range

The graph of the  $\nu_Q(T)$  curve given, e.g., by equation (18) has a characteristic shape which agrees with the most of the  $\nu_Q$  versus  $T$  graphs of systems showing no phase transition:  $d\nu_Q/dT$  is negative with a monotonically decreasing value and  $d^2\nu_Q/dT^2$  is always negative approaching a constant value for increasing temperatures. The N&C data were checked for this behavior by calculating the ratios  $(\Delta\nu_Q/\Delta T)$  for all temperature intervals. Its graph follows a smooth decreasing curve, except for the 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  $\nu_Q(T)$  for  $T < 150$  K were considered.

#### II. Single Frequency Picture

Equations (18) and (19), rewritten for a molecule with one doubly degenerate libration frequency, were used first to evaluate  $\nu_0$  and the effective frequencies  $\bar{\omega}$  and  $\bar{\Omega}$  (actually the wavenumbers  $\bar{\nu}$  and  $\bar{\Omega}$ ) by means of an iterative procedure, as follows. Equation (18) was fitted to the  $\nu_Q$  versus  $T$  graph with  $\nu_Q$  substituted by  $\nu_Q(0)$ . The fitting yielded  $\bar{\nu}$  and  $\bar{\Omega}$ , which were taken to equation (19) and a new  $\nu_0$  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, and the best fit parameters are

$$\begin{aligned} \nu_0 &= 54.937 \text{ MHz}, \\ \bar{\nu} &= 118 \pm 3 \text{ cm}^{-1}, \\ \bar{\Omega} &= 18.5 \pm 2.5 \text{ cm}^{-1}, \end{aligned}$$

leading to the  $T = 0$  NQR frequency  $\nu_Q(0) = 54.487$  MHz. These  $\nu_0$  and  $\nu_Q(0)$  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  $\nu_Q$  data. Moreover, if we make in equation (19) the substitution

$$\frac{1}{\bar{\nu}_{eq}} = \frac{1}{\bar{\nu}} \left[ 1 + \frac{2\bar{\Omega}}{\bar{\nu}} \right] \quad (31)$$

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

$$v_0 = 43.300 \text{ MHz} \quad \bar{\nu} = 99 \pm 1 \text{ cm}^{-1} \quad \bar{\nu}_{eg} = 89.5 \pm 1.5 \text{ cm}^{-1}$$

$$v_Q(0) = 42.945 \text{ MHz} \quad \bar{\Omega} = 5.2 \pm 1 \text{ cm}^{-1}$$

### III. Single Oscillators Picture

Once again equations (18) and (19) were combined,  $v_0$  eliminated and  $v_Q(T)$  expressed in terms of  $v_Q(0)$  and the contribution of all four anharmonic libration modes. Since only three have been detected, their  $\bar{\nu}$  and  $\bar{\Omega}$  values calculated in reference [10] were substituted into the expression of  $v_Q(T)$  and subtracted from it. The remainder values were fitted to the functional form of the unknown fourth mode contribution. This fitting can be achieved through more than one combination of  $\bar{\nu}_4$  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  $\bar{\nu}_4 = 98 \text{ cm}^{-1}$  and  $\bar{\Omega}_4 = 17.5 \text{ cm}^{-1}$ , which means that the unobserved mode must have a wavenumber of  $63 \text{ cm}^{-1}$  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  $\bar{\nu}_4 = 70.5 \text{ cm}^{-1}$ ,  $\bar{\Omega}_4 = 3.9 \text{ cm}^{-1}$ , whose zero temperature frequency is  $66 \text{ cm}^{-1}$  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].

### IV. Two Coupled Oscillators

The expression for  $v_Q(T)$  given by equation (30) was applied to the  $^{35}\text{Cl}$  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  $100 \text{ cm}^{-1}$  for  $T = 15 \text{ K}$ , to the symmetric and antisymmetric modes in the  $bc$  plane, respectively. Their parameters, calculated through the coupled oscillators model [10] in  $\text{cm}^{-1}$ , are

$\bar{\nu}(0)$	$\bar{\nu}$	$\bar{\Omega}$
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 parameter, also in  $\text{cm}^{-1}$ :

$\bar{\nu}(0)$	$\bar{\nu}$	$\bar{\Omega}$	
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.

### 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  $63 \text{ cm}^{-1}$  at very low temperatures.

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## FIGURES CAPTIONS

- Figure 1 - <sup>35</sup>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, equation (18),  $\bar{\nu}_4 = 98 \text{ cm}^{-1}$ ,  $\bar{\Omega}_4 = 17,5 \text{ cm}^{-1}$ .
- Figure 2 - <sup>35</sup>Cl NQR frequencies and calculated curve, four single oscillators model,  $\bar{\nu}_4 = 70,5 \text{ cm}^{-1}$ ,  $\bar{\Omega}_4 = 3,9 \text{ cm}^{-1}$
- Figure 3 - Libration modes frequencies measured by C&L (□, ▽, Δ) and the fitting curves given by the anharmonic libration model, reference [10]. Below are plotted the possible temperature dependences of the missing band: the solid (dotted) curve yields the fitting in Figure 1 (2).
- Figure 4 - <sup>35</sup>Cl NQR frequencies and calculated curve by the two coupled anharmonic rotators model, equation (30).





