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## VIBRATIONAL SPECTROSCOPY, RESONANCE FRACTION AND MOLECULAR MOTION

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**Résumé.** — Les spectres de Raman d'un certain nombre de composés organiques d'étain (IV) sont examinés en détail, principalement dans la région des basses fréquences ( $v \leq 300 \text{ cm}^{-1}$ ) dans le but d'identifier les modes de vibration du réseau de solides covalents et la relation entre ces modes et le facteur Mössbauer-Debye-Waller de la résonance de <sup>119</sup>Sn. La nature complémentaire des deux techniques expérimentales est développée en détail pour les solides contenant 2 N (N = 1. 2, ...) molécules par maille. On montre que cette corrélation peut être utilisée pour expliquer la dynamique inter- et intra-moléculaire des solides covalents.

Abstract. — The Raman spectra of a number of organotin (IV) compounds have been examined in detail, especially in the low frequency ( $\nu \leq 300 \text{ cm}^{-1}$ ) region, with a view to identifying the lattice modes of covalent solids and the relationship between these modes and the Mössbauer-Debye-Waller factor for the corresponding <sup>119</sup>Sn resonance. The complementary nature of the two experimental techniques is developed in detail for solids containing 2 N (N = 1, 2, ...) molecules per unit cell, and it is shown that the resulting correlation can serve to elucidate the inter- and intra-molecular dynamics of molecular solids.

1. Introduction. - The complexity of many molecular solids makes it difficult to achieve a detailed description of the molecular dynamics using conventional neutron scattering techniques. Although limited in scope, extremely useful information may be obtained by means of optical spectroscopy, which provides frequencies and polarizations of inter- and intramolecular vibrations at the  $q \rightarrow 0$  limit of the vibrational dispersion curves. Such information can be utilized in a normal mode analysis in the context of a theoretical vibrational model. However, the number of experimental frequencies which can be extracted from such spectra, is substantially smaller than the number of adjustable parameters in the model. This difficulty is minimized by reducing the number of adjustable parameters by explicitly (or implicitly) setting some of the parameters equal to constants. The choice of these constants is based on complementary information or is often made in a rather ad hoc fashion. The Mössbauer-Debye-Waller factor provides one experimental parameter which can be compared with the results of the analysis of the optical spectra. The usefulness of this parameter is due to the high selectivity of the Mössbauer technique which monitors the dynamical behavior of a specific atom in the lattice.

The complementary nature of the data obtained by Mössbauer and optical techniques has been previously demonstrated for several cases of molecular and covalent solids such as  $SnI_4$  [1] and the iron cyanides [2] in which the Mössbauer data have been compared with optical spectra available for the region of intramolecular vibrations. The development of laser Raman spectroscopy has made it possible and convenient to extend such spectral studies to the region of intermolecular vibrations. In the present investigation results are presented for several monomeric organotin molecular solids which have two molecules per unit cell. The requirement of internal consistency in the simultaneous interpretation of the optical and Mössbauer data makes it possible to identify the Raman active intermolecular mode which corresponds to the  $q \rightarrow 0$  limit of the antitranslational vibration of two molecular species against each other, as well as to ascertain the effective molecular mass associated with this vibration. In addition, some observations are made concerning the nature of the intermolecular frequency

distribution function in these solids and the discussion is then extended to solids with 2N molecules per unit cell.

2. The effective mass approximation. - It is useful to describe the motion of an atom in a molecular solid in terms of a superposition of the motion of the molecular center of mass and the relative motion of the specific atom with respect to the molecular center of mass. The validity of this approximation is a consequence of the distinct separation between the two sets of frequencies describing the inter- and intra-molecular vibrations, which is characteristic of molecular solids. A distinction must be made in a discussion of this kind between atoms situated at or very close to the molecular center of mass and the ligands. In the latter case, low frequency rotational and torsional vibrations of the ligands may contribute substantially to the dynamical behavior of the Mössbauer probe atom. This effect has been demonstrated and discussed in detail for SnI<sub>4</sub> using data for <sup>119</sup>Sn and <sup>129</sup>I as probe atoms [1, 3]. In the present paper we restrict our discussion to solids in which to a good approximation the Mössbauer probe atom may be considered as being situated at the molecular center of mass.

The Mössbauer-Debye-Waller factor, f, is given by

$$\ln f = -\frac{E_{\gamma}^2}{mc^2} \int_0^{\omega_{\max}} \frac{G(\omega)}{\hbar\omega} \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1}\right) d\omega \quad (1)$$

where the frequency distribution function  $G(\omega)$ , which is normalized to unity, i. e. :

$$\int_{0}^{\omega_{\max}} G(\omega) \, \mathrm{d}\omega = 1$$

describes the dynamical behavior of the specific probe atom and may differ substantially from the frequency distribution function of the entire solid. Not all of the vibrational modes of the solid will contribute to the motion of the Mössbauer probe atom. Coupling between two vibrational modes of different energy will depend on the energy difference : the larger this difference (i. e. : the greater the mismatch of the two corresponding frequencies) the smaller will be the mode coupling. Moreover, even for two modes of (nearly) equal energy, the symmetry of the motions must be such that energy transfer between them is possible. It is for this reason that frequently vibrational ligand intra-molecular motions and translational inter-molecular motions within the unit cell do not couple effectively, thus simplifying the resultant vibrational mode analysis.

The atomic frequency distribution function may be rewritten [2] to reflect the separation between the inter- and intramolecular frequencies

$$G(\omega) = A_{\rm I}^2 G_{\rm I}(\omega) + A_{\rm h}^2 G_{\rm h}(\omega)$$

where l and h denote the low and high frequency regions.

The two partial distribution functions are normalized

$$\int G_{\rm I}(\omega) \, \mathrm{d}\omega = \int G_{\rm h}(\omega) \, \mathrm{d}\omega = 1 \, .$$

The weight factors  $A_1^2$  and  $A_h^2$  have been introduced so that all the frequency distribution functions are normalized to unity. So that

$$4_{1}^{2} + A_{h}^{2} = 1$$

to be consistent with the normalization of  $G(\omega)$ .

The usefulness of such a normalization scheme may be demonstrated by considering the extreme case where all the atoms in the molecule are rigidly attached to the molecular center of mass. Under such circumstances the contribution from the high frequency region (intramolecular vibrations) to the Debye-Waller factor may be ignored and the motion of the probe atom may be strictly associated with the motion of the molecular center of mass, with the molecular mass Mas an effective mass. Eq. (1) may be rewritten as

$$\ln f = -\frac{E_{\gamma}^2 A_1^2}{mc^2} \int \frac{G_1(\omega)}{h\omega} \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1}\right) d\omega .$$
 (2)

The contribution to the Debye-Waller factor from the intermolecular vibrations is consequently described in terms of the expression for an atomic solid in which the atomic mass, m, has been replaced by the molecular mass, M, consistent with the relationship

$$\frac{1}{M} = \frac{A_1^2}{m}.$$

The contribution to the Debye-Waller factor from the intramolecular motion of the Mössbauer probe atom with respect to the molecular center of mass is given by a similar expression using the  $G_{\rm h}(\omega)$  frequency distribution function and an effective mass given by

$$\frac{1}{M} = \frac{A_{\rm h}^2}{m} = \frac{M-m}{mM}$$

The effective mass approximation is valid for nonrigid molecules as long as there is a distinct separation between the two frequency regions associated with the inter- and intramolecular motion and there is no coupling between them.

3. Contribution from intramolecular vibrations. — The bulk of the <sup>119</sup>Sn Mössbauer effect data to be considered show that there is a linear dependence of  $\ln f$  on the temperature in the region of interest [4]. This indicates that the data may be discussed in the context of the high temperature limit of eq. (1)

$$\ln f = -\frac{E_{\gamma}^2 kT}{mc^2 \hbar} \int \frac{G(\omega)}{\omega^2} d\omega \qquad (3)$$

and that the contributions from the much higher lying intramolecular frequencies may be ignored. This observation may be justified also in terms of some simple theoretical considerations.

Intramolecular motion (that is, the discrete normal modes of a molecule) is generally characterized by distinct resonance lines observed by optical (i. e. : infrared and Raman) spectroscopy. These vibrations are of low dispersion and thus are well represented by the observed optical frequencies. It is possible, therefore, to consider the intramolecular contributions in terms of these specific discrete frequencies rather than by a broad distribution. Each frequency has to be assigned a weight factor in a way which is consistent with the normalization procedure discussed above

or

$$\frac{1}{M'} = \sum_{i} \frac{1}{M''_{i}}$$

 $A_{\rm h}^2 = \sum_j A_{\rm hj}^2$ 

where the  $M''_{j}$  are effective masses associated with the individual intramolecular vibration modes. Each of the  $A^2_{hj}$  weight factors must be substantially smaller than  $A^2_h$  and, similarly, each of the individual effective masses must be much bigger than M'.

The contribution to the Debye-Waller factor at the high temperature limit from a specific vibration mode is proportional to the inverse square of the frequency of the vibration as well as the inverse of the respective effective mass. It is apparent that contributions from intramolecular vibrations of frequencies which are one order of magnitude higher than the characteristic intermolecular vibrations will be reduced by more than two orders of magnitude by virtue of both the dependence on the frequency and the effective mass. Consideration must be given, however, to those intramolecular frequencies which are quite low and comparable with some of the intermolecular frequencies.

The high temperature limit for the intermolecular contribution may be given in terms of the Debye approximation

$$\ln f = -\left(\frac{3 E_{\gamma}^2 T}{M c^2 k}\right) \left[\frac{1}{\theta_{\rm D}^2} + \frac{1}{36 T^2} + \cdots\right]$$
(4)

$$= aT + bT^{-1} + \cdots \tag{5}$$

or in terms of the Einstein approximation

$$\ln f = -\left(\frac{E_{\gamma}^{2} T}{Mc^{2} k}\right) \left[\frac{1}{\theta_{\rm E}^{2}} + \frac{1}{12 T^{2}} + \cdots\right] .$$
 (6)

In this and the subsequent discussion it has been assumed that the effective lattice temperature (corresponding to  $\theta_D$  or  $\theta_E$  in (4) and (5)) is temperature independent in the high temperature limit, and that a single temperature independent parameter can be used over the temperature interval probed in the experiment. The adequacy of this assumption can be inferred from the linearity of the  $d \ln f/dT$  plot, as will be discussed below, and must be experimentally verified for each material under study.

In some respects the Debye approximation better represents the intermolecular vibrations because these vibrations are associated with a continuous rather than a discrete frequency distribution function. On the other hand, the Debye temperature represents an upper cutoff frequency rather than an average one. The Debye approximation assumes that the frequency distribution function is proportional to  $\omega^2$ , as shown in figure 1, with the highest density of modes close to the



FIG. 1. — Relationship between the Debye cut of frequency,  $\omega_{\rm m}$ , and the Einstein frequency,  $\omega_{\rm E}$ , in the Debye model approximation.

cutoff frequency,  $\omega_{max}$ . The Debye-Waller factor, on the other hand, provides a measure of a weighted average of  $G(\omega)$ , where the weight factors are proportional to the inverse of  $\omega^2$  thus compensating for the  $\omega^2$  dependence of  $G(\omega)$ . Consequently, a substantial contribution to the Debye-Waller factor is from frequencies much lower than the Debye cutoff frequency. For any meaningful comparison with low lying intramolecular vibrations an average frequency will better represent the intermolecular vibrations than the Debye cutoff frequency. Such an average is provided by the Einstein approximation which assumes that the observed Debye-Waller factor is due to a single oscillator of frequency  $\omega_{\rm E}$ .  $\omega_{\rm E}$  represents a weighted average of the actual frequency distribution, with a weighting factor proportional to  $\omega^{-2}$ . This relationship is shown in figure 1. Both approximations provide a one parameter fit to the same data and the ratio between the Debye cutoff frequency and the Einstein frequency, as derived from the high temperature Debye-Waller factor, is

$$\theta_{\rm D}^2 = 3 \ \theta_{\rm E}^2$$

The relative contribution of a low-lying intramolecular vibration to the Debye-Waller factor is given by

$$\frac{M\theta_{\rm E}^2}{M_j''\,\theta_j^2} = \frac{1}{3}\,\frac{M\theta_{\rm D}^2}{M_j''\,\theta_j^2} \tag{7}$$

where  $M_j^r$  is the effective mass associated with the vibration and  $\theta_j$  is related to the vibrational frequency. Because of symmetry considerations, some low-lying intramolecular vibrations do not contribute at all to the dynamics of the molecular center of mass and other may contribute to some extent. A rigorous evaluation of the actual contribution of such a mode to the dynamics of the Mössbauer probe atom requires a full normal mode analysis. Such an analysis must be carried out independently for each of the molecules under consideration and is outside the scope of the present paper.

For a crude evaluation of the possible range of contribution from such low-lying modes let us assume  $M''_j/M = 5$  and  $\theta_j/\theta_D = 2$ . Inserting these values into Eq. (7) results in a contribution of the order of two percent. It would therefore be safe to assume in the following discussions that ignoring the intramolecular vibrations introduces a possible error of less than 5 percent. With this value in mind, the Debye approximation, with the molecular mass as the effective mass, will be applied in the analysis of the Debye-Waller factor in molecular solids.

4. Raman active intermolecular vibrations. - An appropriate model [5] for a molecular solid, made up of monomeric molecular units in which intermolecular bonding forces are very much weaker than intramolecular bonding forces, is provided by a monatomic lattice in which each polyatomic molecule can be represented by a rigid (spherical) atom in an assembly of identical atoms. In the one dimensional case, the dynamics of a linear monatomic chain of atoms, each separated from its nearest neighbor by the internuclear distance a, can be described [3] in terms of standing waves of the form  $x(t) = e^{i\omega t} \sin nka$ , where x(t) is the time dependent displacement of the atoms, and kis the wave vector  $(k = 2 \pi / \lambda)$ . The relationship between the wave vector and the frequency is characterized by a dispersion curve (Fig. 2a). The frequency distribution function  $g(\omega)$ , which represents a projection of the dispersion curve on the frequency axis (Fig. 2b), is a continuous function of the frequency over the range  $0 \le \omega \le \omega_{max}$ . In the Debye approximation the frequency distribution function is assumed to be proportional to  $\omega^2$  and the maximum frequency is denoted by  $\theta_{\rm D} = \hbar \omega_{\rm max}/k$ .

Because of the relationship  $\sin ka = \sin (\pi - ka)$ , the functional relation between  $\omega$  and k needs to be specified only over the range  $0 \le k \le \pi/a$ . Furthermore, since  $\sin \left[ na \left( \frac{\pi}{a} - k \right) \right] = -\cos (n\pi) \sin (nka)$ , it is possible to represent the wave vectors lying in the



FIG. 2a. — Dispersion curves (schematic) for a solid containing 2 N molecules per unit cell under the assumptions discussed in the text. The frequency dependence of the optical and acoustic modes on the wave vector, q, is indicated by the subscripts R and D, respectively.

FIG. 2b. — Frequency distribution,  $g(\gamma)$ , for various compositions of the unit cell of a covalent solid.

region where  $k > \pi/2 a$  in terms of those lying in the region where  $0 \le k \le \pi/2 a$  by reversing the sign of the amplitude of vibrations of every alternate atom in the chain. In other words, it is possible to describe the dispersion relation  $\omega$  vs k of a monatomic chain by folding the dispersion curve about the mid-point  $k = \pi/2 a$ . In this representation each k value is associated with two vibrational modes, the lower of which may be described as the acoustic vibrations of primitive cells each containing a pair of atoms, and the higher one is associated with the intracell vibrations of the two atoms in the unit cell.

Insofar as no physical distinction is being made between the two atoms participating in the *unit cell*, the two descriptions are entirely equivalent from the physical point of view. The artificial choice of a unit cell containing two equivalent atoms should not result in any change in the dynamical properties of the chain, and the frequency distribution function (Fig. 2b) should be the same whether derived from a single acoustic branch extending up to  $k = \pi/a$ , or from the dualbranch description extending only to  $k = \pi/2 a$ .

In the context of the discussion of molecular solids, the two molecules in the unit cell will be of the same mass and have neutral charge. It is only when the two molecules in the unit cell are of different mass that the two branches of the dispersion relations will be separated at the  $k = \pi/2 a$  limit (Fig. 2). In this case the corresponding acoustic and optical bands of the frequency distribution function will be separated by a frequency gap. With the two molecules crystallographically distinct but otherwise identical, no such frequency gap is expected and it becomes convenient to extend the Debye approximation to describe the total intermolecular frequency distribution (Fig. 2b).

It is possible to introduce a physical distinction

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between the two molecules when three dimensional considerations are taken into account. For example, in the case of molecules of lower than spherical molecular symmetry, the relative orientation of the molecular symmetry axes may distinguish between the two molecules. For spherical molecules, three dimensional packing considerations may produce a physical distinction between the component molecules of the unit cell.

The introduction of physical distinction between the molecules in the unit cell will produce a distinction between the two models described above, since the « optical » branch may become optically active and may be probed by Raman scattering techniques. Optical spectroscopy probes only the long wavelength limit  $(q \rightarrow 0)$  of the optical dispersion curves, thus the Raman active vibration mode will represent the cutoff frequency of the frequency distribution function, or in the context of the Debye approximation, the Raman frequency  $\omega_R$  corresponds to a frequency equivalent to the Debye temperature (Fig. 2b).

A straight forward solution [5] of the dynamical equations for a one dimensional molecular chain with two molecules of equal mass per unit cell yields

$$\omega_{\rm R} = 2 \left(\frac{\beta}{M}\right)^{1/2} \tag{8}$$

indicating that the cutoff frequency depends on the molecular mass M and an equilibrium force constant  $\beta$ .

This one dimensional model may be extended to the three dimensional case by applying the same analysis to each of the principal symmetry axes in the lattice. The Raman frequency given by eq. (8) corresponds to the antitranslational motion of half of the molecules in the entire lattice against the other half. This is the simplest optical vibration in the lattice from the symmetry point of view and is therefore extremely insensitive to the details of the symmetry of the unit cell. The equilibrium intermolecular force constant  $\beta$ . in the molecular solids under consideration, is due to the van der Waals interaction. It is unlikely to display any significant anisotropy even in cases where there is a large anisotropy of the unit cell dimensions. This statement is equivalent to the assumptions made in the model, i. e. : that the molecules in the solid can be envisioned as behaving like (spherical) point masses, with no significant coupling between inter- and intramolecular vibrational modes. Anisotropies in the unit cell dimensions in van der Waals solids are mostly due to packing considerations reflecting the asphericity of the constituent molecules. Without any significant anisotropy of the effective force constant  $\beta$ , governing this long wave length optical vibration, the corresponding Raman frequency is expected to remain degenerate in the three dimensional case and be represented by a single frequency.

5. Extension to 2 N molecules per unit cell. — The analysis of the case of 2 N molecules per unit cell

follows the same reasoning as the discussion given above for the bi-molecular unit cell. Considering the one dimensional molecular chain, it is possible to assign arbitrarily a unit cell containing 2 N molecules. With all molecules being equivalent, the artificial assignment of a large unit cell should not affect the actual frequency distribution, which may be derived either from the one-branch dispersion curve associated with a one-molecule description or from a 2 N-branch description of the same (one dimensional) motion, The 2 N branches may be obtained simply by folding the acoustic dispersion curves of the bi-molecular model at the point where  $k = \pi/2$  Na. This procedure will leave the uppermost Raman frequency unchanged both in magnitude and identity while introducing N-1 additional doubly degenerate (at  $q \rightarrow 0$ ) optical frequencies associated with the 2N-2optical branches. Unlike the uppermost Raman frequency, which corresponds to the simple optical vibration where half of the molecules in the lattice vibrate in unison against the other half, the additional optical frequencies are of much lower symmetries which directly relate to the symmetry elements of the unit cell. Consequently, the properties of these vibrations will strongly depend on the details of the symmetry of the unit cell.

A detailed discussion of the three dimensional case must include also the transverse branches of the dispersion curves. Typically these are expected to lie below the corresponding longitudinal ones and will add to the complexity of the derived frequency distribution function below the cutoff frequencies. The question whether they will become optically active will depend on the behavior of the polarizability tensor associated with each of these modes.

The important features which emerge out of this analysis are that the intermolecular frequency distribution, in molecular solids with 2 N molecules per unit cell, will be a continuous function characterized by a cutoff frequency corresponding to the optical vibration in which half of the molecules in the lattice oscillate against the other half. Depending on the nature of the deformation of the charge densities associated with this mode, it may become optically active and be monitored by Raman spectroscopy. The upper Raman frequency is given by equation (8) and is insensitive to the symmetry of the unit cell apart from the constraint that it has an even number of molecules. A comparison between this cutoff frequency and the one obtained from the analysis of the Mössbauer-Debye-Waller factor may shed more light on the nature of the intermolecular dynamics in molecular solids.

6. Comparison between Mössbauer and Raman data. The Debye approximation is better suited for a comparison between the Mössbauer-Debye-Waller factor and the Raman spectra because the latter, as discussed above, may provide an independent measure of the cutoff frequency of the continuous frequency distribution function. The Mössbauer data provide a measure of a weighted average of the actual frequency distribution, which may be related to a cutoff frequency if a specific continuous distribution is assumed. It is common to assume a Debye distribution which results in an estimate for the Debye cutoff frequency,  $\omega_D$ , or the Debye temperature  $\theta_D$ . This estimate may be derived from the high temperature Mössbauer-Debye-Waller data using eq. (4), which may be rewritten as

$$Mv_{\rm D}^2 = -\frac{3 E_{\gamma}^2 k}{\hbar^2 c^2} \cdot \frac{1}{a}$$
(9)

where the constant *a* is the variation of ln *f* with respect to the temperature, that is  $a = -d \ln f/dT$ . The reciprocal of this parameter provides a measure of  $Mv_D^2$  which may be compared to the experimental value obtained from the Raman spectra for  $Mv_R^2$ . It should be emphasized that while the Mössbauer data provide a measure of the product of the appropriate mass *M* and the square of the Debye frequency, the Raman spectra provide the frequency  $v_R$  directly. The relationship between frequency and the Debye temperature is, of course, given by  $v_D = k\theta_D/h$ .

Figure 3 presents the Mössbauer-Debye-Waller data for the molecular solid tetraphenyltin in the temperature range 78 < T < 300 K. The linear dependence of



FIG. 3. — Recoil-free fraction data (normalized to unity in the low temperature limit) of tetraphenyltin.

In f on the temperature in this interval is quite apparent and demonstrates the validity of the analysis of these data in terms of the high temperature approximation. The corresponding Raman spectrum is shown in figure 4. The Debye frequency derived from the slope of  $\ln f$  is in excellent agreement with the Raman frequency of 39 cm<sup>-1</sup> shown in figure 4. Any appreciable contribution from the Raman frequencies at  $64 \text{ cm}^{-1}$  (corresponding to a temperature of ~ 100 K) and above should have caused a leveling off of the  $\ln f$ 



FIG. 4. — Room temperature Raman spectrum of tetraphenyltin in the low frequency region. The mode at  $39 \text{ cm}^{-1}$  has been identified as an *intra*-unit cell, *inter*-molecular vibration on the basis of the model discussed in the text.



FIG. 5. — Correlation between  $Mv_{\rm R}^2$  (from Raman data) and -1/a (from <sup>119</sup>Sn Mössbauer data) for twelve organotin covalent solids. The solid line represents the theoretical slope  $3 E_y^2 k/c^2 \hbar^2$ . The dashed line represents a 10 % error in M and illustrates the mass resolution which is possible under the assumptions of the theoretical model. The data points in this plot refer to the following compounds (T = tropolonato, C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>):

۱.	$(C_6H_5)_2SnT_2$	cis	$O_h$	7. $(C_6H_5)_3$ SnCN		Τď
2.	$(C_4H_9)_2SnT_2$	trans	$O_h$	8. $(C_{3}H_{7})_{2}SnT_{2}$	trans	$\mathbf{O}_{h}$
3.	$(C_6H_5CH_2)_2SnT_2$	cis	$O_h$	9. $[(C_6H_5)_3Sn]_2$		Td
1.	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnCl		Td	10. $[(C_6H_5)_3Sn]_2CN_2$		?
5.	$(C_2H_5)_2SnT_2$	trans	Od	11. $(CH_3)_2SnT_2$	?	$\mathbf{O}_{h}$
5.	$(C_6H_5)_4Sn$		$T_{d}$	12. $(CH_3)_2SnI_2$		$T_d$

curve at the lower temperature region of the figure. The lack of any curvature in the experimental data supports the arguments given above concerning the negligible contribution from low lying intramolecular vibrations.

Figure 5 summarizes a correlation [6] between the <sup>119</sup>Sn Mössbauer data (the a term in eq. (5)) and the Raman data  $(Mv^2)$  where v is the optical frequency in  $cm^{-1}$  for twelve organotin molecular solids. It is important to recognize that included in this correlation is a wide variety of molecular structures and symmetries, including both 4 and 6 coordinate tin atoms as well as cis and trans octahedral species. The Raman data are expressed in terms of  $Mv^2$ , where M is the molecular mass corresponding to one formula weight, while the Mössbauer results are presented in terms of the reciprocal of d ln f/dT.

Two important features of this correlation should be noted :

a) To a very good approximation, the data are fitted by a straight line intersecting the origin, demonstrating the functional relationship between the two plotted parameters, despite the wide range of molecular masses, symmetries and the two different coordinations referred to above. Thus, as is implied in the hardsphere approximation, the model is structure independent.

b) The linear fit through the twelve data points is not a regression fit through the data but rather corresponds to the numerical value of  $d(Mv^2)/d(a^{-1})$ , which, from eq. (9) is seen to be equal to  $3 E_{\gamma}^2 k/c^2 \hbar^2$ . For the 23.8 keV gamma radiation of <sup>119</sup> Sn, this constant is equal to  $1.024 \times 10^4$ . A least squares linear regression analysis of the data summarized in figure 5 yields a value for the slope of  $1.0 \times 10^4$  in excellent agreement with the calculated value, which, in view of the rather crude assumptions made in the model, is somewhat surprising.

Deviations from such a correlation could have arisen mainly from three sources : contributions from low lying intramolecular vibrations, deviations of the actual frequency distribution from the assumed Debye distribution function, and possible anharmonic effects. The observed correlation indicates that either there is a mutual cancellation of errors or that the individual contributions are too small to significantly affect the experimental results. A mutual cancellation effect is quite unlikely to be operative over such a wide range of molecular and crystalline structures, and at the present

state of refinement it may be inferred that the theoretical model adequately represents the available experimental data.

Finally, it is important to recognize that in this data analysis, it is not always the lowest frequency Raman mode which is utilized in the correlation. In fact, one of the major exploitations to be made of the correlation discussed in the present study, is that it permits the selection among several Raman active bands lying in the lattice mode region for covalent solids (that is below about  $250 \text{ cm}^{-1}$ ) of *that* band which arises from the intra-unit cell, inter-molecular motion referred to above. As a case in point, it may be noted that several of the compounds included in the summary of figure 4 are organotin tropolonates. The Raman spectra of these compounds show a band at ~  $24 \text{ cm}^{-1}$ , that is, well below the frequency associated with the intermolecular motion which accounts for the Debye-Waller-Mössbauer factor of the <sup>119</sup>Sn atom. One may now ask why this mode (at  $24 \text{ cm}^{-1}$ ) does not affect the vibrational data analysis extracted from the Mössbauer spectra, for which another optical frequency, lying in the range  $30-50 \text{ cm}^{-1}$  for the organotin tropolonates, has been employed. The reasons are two-fold : a) the particular mode at  $24 \text{ cm}^{-1}$  for the organotin tropolonates has been identified with a librational motion of the  $C_7H_6O_2$  fragment and this motion does not significantly effect the center of mass position of the molecule as a whole; b) as has been noted above, for two motions to couple, it is necessary not only for the energies to be reasonably similar, but it is also required that the symmetries of the two motions be the same (i. e. : related either by an identity element or by a symmetry sub-set). Since this condition does not obtain between the intermolecular vibration of two molecules within the unit cell and the librational motion of the tropolone ring, this latter motion can be ignored with respect to the frequency value used in the data analysis discussed above.

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#### References

- HAZONY, Y., J. Chem. Phys. 49 (1968) 159.
  HAZONY, Y., J. Chem. Phys. 45 (1966) 2664.
- [3] BUKSHPAN, S. and HERBER, R. H., J. Chem. Phys. 46 (1964) 3375.
- [4] See for example, HAZONY, Y. and HERBER, R. H., in « Mössbauer Effect Methodology », I. Gruverman, Ed., Vol. 8 (Plenum Press, New York) 1973;
- HERBER, R. H., LEAHY, M. F. and HAZONY, Y., J. Chem. Phys. 60 (1974) 5070.
- [5] KITTEL, C., «Introduction to Solid State Physics» (John Wiley and Sons, New York) 1960, Chapter 5.
- [6] Taken in part from the PhD thesis of A. J. Rein, Rutgers University, 1974.