

**METHYL GROUP ROTATION IN CRYSTALS
AT LOW TEMPERATURES**

H. den Adel

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Kast dissertaties

METHYL GROUP ROTATION IN CRYSTALS AT LOW TEMPERATURES

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METHYL GROUP ROTATION IN CRYSTALS
AT LOW TEMPERATURES

Promotor : Prof.Dr. W.J. Huiskamp

Co-promotores: Dr. Z. Dokoupil

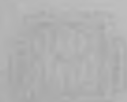
Dr. H.B. Brom

De verrijking van de groep van Dokoupil en
Huiskamp en de bijdragen van Brom en
Dokoupil aan de kennis van de
methylgroeprotatie in kristallen
zijn de voorwerpen van de dissertatie
van Dr. Z. Dokoupil, die is
afgeleverd aan de Faculteit der
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CHAPTER 1

GENERAL INTRODUCTION

The rotational motion of molecules ¹⁾ has been studied extensively; these studies have been carried out for example in the gaseous and in the condensed phase. In addition to the rotation of the entire molecule, internal rotation ²⁾ can also occur if the molecule possesses a light molecular group having discrete rotational symmetry. This internal rotation is hindered by intramolecular interactions, which can be expressed as a potential barrier. In the gaseous phase, each molecule can be treated independently of the surrounding molecules, since the intermolecular interactions are negligible. Under such conditions, the many experimental results, concerning in particular the energy levels of the molecule as obtained by for example microwave and infrared spectroscopy, can be well described by theory, for instance ab initio calculations of the potential barrier within molecules containing methyl groups ³⁾. In a more detailed analysis of the recorded spectra, deformations of the molecule also have to be taken into account.

The hindered internal rotation in the solid state offers the possibility of studying additional phenomena, based on the presence of intermolecular interactions. In some cases, these interactions may complicate the analysis of the experimental data, but on the other hand, when the crystal structure is known, the crystal symmetry facilitates the disentangling of the rotational energy levels. It is also of considerable interest to investigate to what

extent the internal rotation is related to the occurrence of phase transitions, or even might induce or trigger them. When extending the measurements to low temperatures, we are able to strongly restrict the number of thermally populated levels and concomitantly obtain a substantial simplification of the data analysis. The experimental techniques used in the solid state are different from those used in the gaseous phase. Inelastic neutron spectroscopy⁴⁾ measures the energy differences between the rotational levels. Furthermore, nuclear magnetic resonance⁵⁾, quasi-elastic neutron scattering⁶⁾, and dielectric measurements⁷⁾ may provide information about the dynamics of the rotational system. The measurement of low-temperature specific heat may provide not only the energy levels, but may also inform us about the degeneracies of the levels (see for example chapter 5). Furthermore, the time dependence of the thermal relaxation process within the system of rotational levels (see for instance chapter 4) can be studied. Meaningful relaxation measurements are limited to the case that the relaxation time is longer than the time needed to reach internal temperature equilibrium in the sample, this being typically 10 s. The combination of the above methods is a powerful tool to fathom the mechanisms of internal rotation. Apart from a better understanding of the behaviour of molecular groups in a solid itself, the need for knowledge about the rotational motion in the solid state was also felt in the field of magnetic interactions⁸⁾ in metal-organic compounds and in organic (super) conductors^{9,10)}.

The quantum mechanical hamiltonian of a hindered rotating molecular group contains, in addition to the kinetic energy, also a potential energy term of a well-defined symmetry. For the determination of the energy levels, the application of group theory is indispensable. It facilitates the calculation of the eigenvalues and the associated eigenfunctions; these calculations became feasible by the availability of high-speed and large-memory computers, with an appropriate software support. Hence the use of perturbation theory has become almost obsolete. We shall discuss in chapter 2 several experimental and computational techniques which have been applied in the study of the internal rotation in solids.

In chapter 3, we describe the specific-heat, NMR, and dielectric measurements on dimethyl-tin-difluoride, $(\text{CH}_3)_2\text{SnF}_2$. This is a simple compound, with well-known properties; the crystal structure¹¹⁾ was resolved at room temperature, while low-temperature elastic neutron scattering⁶⁾ suggested the presence of a phase transition. Furthermore, by quasi-elastic⁶⁾ and inelastic¹²⁾

neutron scattering techniques, the barriers against internal rotation were found to be low. The specific-heat measurements confirmed the phase transition at 70.4 K; the change of potential barrier plays a dominant role in this transition. The deduced barrier heights are in agreement with the heights as determined by the neutron measurements.

A similar comparison has been made for the mono-methyl-pyridines in chapter 4. In these compounds, the potential barriers are also low and highly symmetric. In addition to the specific-heat measurements, the slow thermal relaxation in 4-methyl-pyridine, as caused by the symmetry properties of the methyl group, has been observed in a calorimetric experiment, and is shown to be consistent with the NMR ¹³⁾, specific-heat, and neutron data ⁴⁾. In order to obtain more information about the methyl-group rotation in these compounds, one of them (4-methyl-pyridine) was partly deuterated. The specific-heat, dielectric, and inelastic neutron scattering data of this compound are discussed in the last chapter. Around 5.4 K a phase transition occurs. The experimental entropy above this transition is directly related to the total degeneracy of the energy levels, and it is found to be in agreement with the theoretically calculated entropy. The height of the barrier as derived from the specific-heat data is also sufficient to describe the entropy data. For the interpretation of the experimental results below 5.4 K, several models have been examined. A definite interpretation is still lacking, due to insufficient experimental data.

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CHAPTER 2

EXPERIMENTAL AND COMPUTATIONAL TECHNIQUES

1. *EXPERIMENT*

1.1 *Introduction*

Calorimetry is widely used in physics, in particular for gaining information on properties of condensed matter, as well as in other branches of science. Low-temperature calorimetry, although it has been developed into a standard method, is much more restricted in use. This is due to the technical requirements as to, obviously, the availability of liquid helium, proper vacuum equipment etc. It is also related to the circumstance, that its use is aimed at obtaining precise, quantitative information as to be able to extrapolate to zero kelvin and so to determine for instance the entropy content as a function of temperature. An advantage of low-temperature calorimetry is that we can study weak interactions without the disturbance of strong lattice vibrations. Furthermore, specific heat is not only a function of the mutual energy differences between the energy levels, but it also depends on their degeneracies, as determined by the quantum-mechanical symmetries. The effects of these degeneracies on the specific heat become specially noticeable at low temperatures, which makes low-temperature calorimetry a suitable method to investigate these symmetries. From the experimental point of view, the straightforward measuring procedure allows a high degree of automatization.

1.2 *The experimental set-up.*

The cylindrical copper calorimeter is 19 mm in diameter and 35 mm long. It is provided with a vane which can be clamped between the jaws of a mechanical heat switch, which is linked to a thermal bath, e.g. liquid helium. The german-silver bottom is provided with a feedthrough for the carbon thermometer. Inside the calorimeter case there are two sets of four radial vanes, the first set soldered to the case itself, the other set consists of a cross, soldered on a rod, which passes through the bottom of the calorimeter. The thermometer is attached to this rod. Heat is supplied to the cell via a 200 Ω Evanohm resistance wire. The copper parts of the calorimeter are gold plated.

For the measurements on 4-methyl-pyridine a heat shield is used, because the time required to take one data point is very long in this sample, see chapter 4. This shield consists of a cylindrically shaped copper case, 45 mm long and 40 mm in diameter. There is a hole in the bottom, 10 mm in diameter, to evacuate the space inside the shield. An extra radiation shield is placed in front of this hole. At the lid a vane is silver soldered, which can be clamped between the jaws of the heat switch. The calorimeter can be thermally connected to the heat shield by helium gas. The shield is provided with a resistance heater and a carbon thermometer, similar to the one used with the calorimeter. The thermometer is mounted inside the shield. All electrical wires passing through the shield are thermally anchored to it by strips made of printed-circuit board. The temperature of the shield can be kept constant within a few mK during at least 24 hours, by a proportional and integral regulator. For the evaluation of the thermal drift before and after a heat pulse we refer to chapter 4.

1.2.1 *The empty calorimeter.*

The heat capacity of the empty calorimeter is measured beforehand. Its value at 1 K, 10 K, 20 K, 50 K and 100 K amounts approximately to 0.25, 20, 125, 1100 and 2700 mJ/K respectively. Since the calorimeter mainly consists of metal parts, the low-temperature heat capacity, $K(T)$, is determined by the electronic and the phonon contribution. This would lead to a dependence on temperature given by :

$$K(T) = aT + bT^3 \quad (1)$$

At temperatures above 6 K, deviations from the behaviour described by eq.(1) are found. The empty-calorimeter heat capacity will be approximated by a polynomial in odd powers of the temperature, cf. Osbornes "reference equation" for the specific heat of copper ¹⁾. This formula increases the convergence of the approximation process:

$$K(T) = \sum_{i=1}^n a_i T^{(2i-1)} \quad (2)$$

In order to facilitate the determination of the coefficients a_i in eq.(2) by a least-square fit of the experimental data (the values extend over two decades in temperature and four decades in heat capacity) this fit is made in two intervals, i.e. from 1 K to 16 K and from 10 K to 100 K. The overlap ensures, that the heat capacity around 13 K, the switching point between the two approximations, varies only smoothly as function of temperature. Furthermore a weighting function is used, defined by:

$$g_i = 1/(K_i T_i^2) \quad (3)$$

Besides the increase in convergence, this weighting factor emphasises the low-temperature data. In the part below 16 K an experimental point (T_i, K_i) is rejected in the least-square fit calculations if the relative deviation amounts to more than 1%. Above 16 K the rejection criterion is chosen to be 1.5%. The mean deviation of the polynomial from the experimental data is 0.3%.

Above 35 K the heat capacity of the empty calorimeter varies less rapidly and hence fewer input data are required. However, the acquisition time for a data point, increases strongly above 35 K. The total measuring time for the thermal data of an empty calorimeter can be substantially reduced, if we collect our data above 35 K in alternating temperature intervals of about 8 K. These intervals suffice to describe the empty-calorimeter heat capacity without loss of accuracy. This is shown by means of a numerical test for some arbitrary calorimeters, of which the heat capacity has been measured from 1 K to 100 K. When in the approximation some intervals are omitted, the calculated and experimental values of the omitted points are found not to exceed a relative error of 0.5%.

1.2.2 The compounds.

The samples, investigated in this thesis, have been obtained commercially. $(\text{CH}_3)_2\text{SnF}_2$ is a solid at room temperature. The specimen, in the form of a white powder, is compressed into the calorimeter at a pressure of about 0.1 MPa. This ensures (a) a high degree of filling and therefore a better ratio between the heat capacity of the sample and that of the container and (b) a better heat contact within the sample, leading to a shorter period of time to reach internal equilibrium after a temperature variation. Because of the compression, the vanes in the calorimeter are deformed, and so the container becomes less suited to be reused, after the removal of the previous sample.

The mono-methyl-pyridines are liquids at room temperature. For the 4- CH_2D -pyridine an improved type of calorimeter has been applied, see chapter 5. Instead of vanes, copper brushes are used to increase the heat distribution in the sample.

1.2.3 Thermometry.

The carbon-film thermometers used, are described elsewhere ²⁾. They are able to measure temperatures between 0.2 K and at least 100 K. In each run the thermometer is calibrated against the saturated vapour pressure of ^3He , ^4He , $n\text{-H}_2$ and O_2 . For oxygen and normal hydrogen the IPTS-68 scale ³⁾ is used, for ^3He the 1962 scale ⁴⁾ and for ^4He the 1958 scale ⁵⁾. The pressure of the bath is stabilized by a manostat. Below 1.5 K we use a vapour pressure cell, containing a small amount of ^3He . In the overlapping region of ^3He and ^4He thermometry, the temperatures, determined in both ways, are the same within 1 mK. We take 14 calibration points between 0.9 K and 4.2 K.

For the ten calibration points between 14 K and 20 K we use normal hydrogen. This liquid is not in thermal equilibrium, since conversion from ortho hydrogen to para hydrogen takes place. We have determined the conversion time in our set-up experimentally. In spite of the scatter and irregularities in the data, the conversion process, observed in our set-up as the lowering of the temperature of the liquid hydrogen at constant vapour pressure, is described by an exponential decay, rather than a function, inversely proportional ^{6,7)} to the time, t , elapsed after liquefaction:

$$\Delta T(t) = \Delta T(0) \exp(-t/\tau) \quad . \quad (4)$$

$\Delta T(t)$ is the difference in temperature between converting normal hydrogen and completely converted equilibrium hydrogen, at constant pressure; τ is the conversion time. $\Delta T(0)$ is $\Delta T(t)$ at $t=0$; its value amounts to 115 mK. τ is found to be 150 ± 25 hours. It should be noted that in our set-up only the first 100 hours of the conversion process could be observed.

The thermometer calibration in the hydrogen range occurs within eight hours after liquefaction, so the temperature correction for the ageing of the hydrogen is less than 5 mK, being about twice as large as the absolute accuracy of the determined temperature value in this region.

In spite of the fact that the triple point of oxygen is as low as 55.8 K, the temperature region below 80 K is of less interest for our calibration purpose, since it is rather tedious to achieve a stable equilibrium pressure. Therefore we take three calibration points only between 80 K and 90 K.

The resistance values of a typical thermometer versus temperature are given in table 1. The R-T data are usually fitted by an expression of $\ln T$ as a polynomial in $\ln R$ ²⁾

$$\ln T = \sum_{i=0}^n a_i (\ln R)^i \tag{5}$$

Table 1

Data of a typical thermometer

T(K)	R(k Ω)	Deviations (mK)
1	22	1
4	8.7	2
14	4.7	5
20	4.0	5
80	2.5	100
90	2.4	100

Numerical tests have shown, that good results can be obtained with $n=5$. If only a few calibration points are available, e.g. when measurements are

performed in several magnetic fields, better results are obtained using a fit to the expression:

$$T^{-1/2} = \sum_{i=0}^n a_i (\ln R)^i . \quad (6)$$

Numerical tests have shown that eq.(6) with $n=2$ approximates the helium range (0.9 K to 4.2 K) or the hydrogen range (14 K to 20 K) to the same accuracy as eq.(5) with $n=5$. Also for the purpose of extrapolations, eq.(6) is more suitable than eq.(5).

The calibration data of an arbitrary thermometer are displayed in fig. 1 where $\ln R$ is plotted versus $\ln T$ and versus $^{8)} T^{-1/2}$. The typical deviations of the experimental data from the least-square fitted values are also listed in table 1.

1.2.4 Determination of the heat capacity.

We use a discontinuous way to measure the heat capacity, i.e. the heat-pulse method. The thermometer is included in a branch of a wheatstone bridge. This bridge is usually not in equilibrium. Its unbalance is periodically read by a digital data collecting system ⁹⁾. The thermal data before and after the heat pulse, are approximated by straight lines. From the extrapolation of these lines to half the heating time, the voltage rise, ΔH , due to the heat pulse, is determined. After each point, the comparative resistor, i.e. a decabox included in the same branch as the thermometer, is readjusted. From the variation in resistance, ΔR , and the corresponding change in output voltage of the bridge, ΔU , the bridge sensitivity is derived. For a wheatstone bridge eq.(7) is fulfilled:

$$G = \Delta R / (R \Delta U) = \text{constant} . \quad (7)$$

G is the reduced bridge sensitivity, R is the mean value of the comparative resistor. For nearly all data points G is determined. The experimental value of G is slightly dependent on R ; the total variation amounts to $\approx 1\%$ of its mean value. The G values are described by a linear dependence on R :

$$G(R) = aR + b . \quad (8)$$

From equations (5) or (6) dT/dR is calculated; finally the temperature change

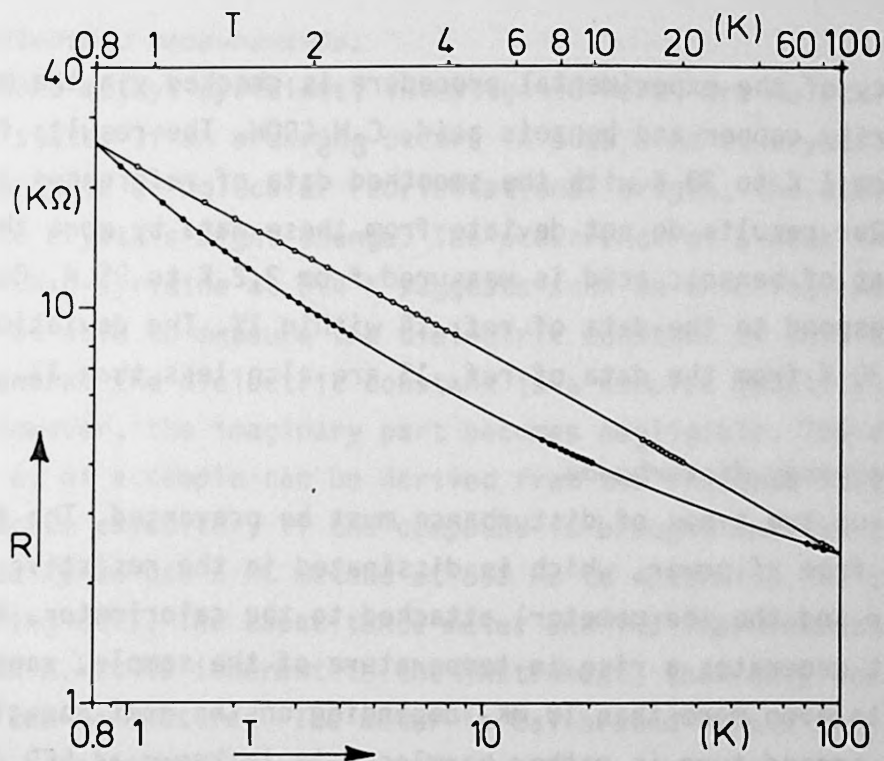


Fig. 1 The resistance of an arbitrary home made carbon thermometer against the temperature. The vertical scale displays logarithmically the resistance R in $k\Omega$. On the lower scale the temperature is displayed logarithmically. The corresponding data points are marked by dots. On the upper scale the temperature is displayed according to a $T^{-1/2}$ scale. The scale marks between 10 and 100 K are drawn in the same sequence as those between 1 and 10 K. The corresponding data points are marked by circles. The full lines are the least square fits to the equations (5) and (6) for dots and circles respectively.

ΔT is given by :

$$\Delta T = (dT/dR)GR\Delta H \quad (9)$$

The heat capacity is derived from the ratio between the applied energy and ΔT .

1.2.5 Accuracy.

The accuracy of the experimental procedure is checked via the measurement of high purity copper and benzoic acid, C_6H_5COOH . The results for Cu are compared from 1 K to 30 K with the smoothed data of references 1, 10, 11, 12 and 13. Our results do not deviate from these data by more than 1%. The specific heat of benzoic acid is measured from 2.2 K to 95 K. Our data below 30 K correspond to the data of ref. 14 within 1%. The deviations of our data above 30 K from the data of ref. 15 are also less than 1%.

1.2.6 Radio frequency disturbance.

In our set-up two types of disturbance must be prevented. The first type originates from rf power, which is dissipated in the resistive elements (e.g. the heater and the thermometer) attached to the calorimeter. Below 10 K this effect generates a rise in temperature of the sample, ranging from less than 1 mK to even more than 10 mK, depending on the heat capacity of the sample. The second type is rather harmless; it is known as LFD (low frequency detection): strong rf voltages or currents will be detected in the non-linear elements (e.g. diodes or transistors) of the measuring instruments, and change the function of those particular elements in the electrical circuit.

The sources of our troubles are the transmitters of the adjacent police station and their patrol cars, operating in the VHF band around 80 MHz and 160 MHz. The rf leaks into our equipment via the shielded cables, inside and outside the cryostat. The first precautions taken, were to shield the cryostat and to apply an extra shielding around the cables. With a grid dip oscillator, operating around 80 MHz and 160 MHz extra "leaks" in the system of the cables are found. By means of π -networks (0.3 nF as parallel capacitors and 30 μ H as serial inductor) the electrical leads of the heating system and the thermometer are provided with strong attenuators for rf induced currents. Finally the feedthroughs of the measuring space are provided with a L-network (0.3 nF as parallel capacitor and 30 μ H as serial inductor), giving extra rf attenu-

ation.

The second type of interference, which appears in the dc preamplifier and the x-t recorder, is also prevented by π -networks. Our set-up is now able to withstand a rf field, generated from a 1 W FM transmitter at 145 MHz, operating in our experimental room.

1.2.7 Dielectric measurements.

The mono-methyl-pyridines, investigated here, are molecular crystals in the solid state. If an ordering occurs in such kind of crystals, e.g. of a crystallographic or molecular reorientational origin, the dielectric properties of the crystals might change. The occurrence of a peak in the specific heat of 4-CH₂D-pyridine at 5.4 K suggests such an ordering. We modified the set-up to be able to measure the dielectric constant of this compound.

In general the dielectric constant is a complex quantity. At low frequencies however, the imaginary part becomes negligible. The dielectric constant, ϵ , of a sample can be derived from the increase in capacitance of a known vacuum capacitor, if the compound is brought between the plates. Experimentally we use a RC method at 850 Hz to determine the capacitance of the measuring cell. The capacitance meter and its improvements are described in appendix A. It is inherent to the instrument, that only non-conducting compounds can be measured. The meter is calibrated versus the capacitance of some known capacitors. The absolute accuracy in our set-up is about 1 pF; the relative accuracy is much better, being about 0.05%. Since our main interest concerns the temperature dependence of the dielectric constant, we will use arbitrary units for the capacitance of the measuring cell. The given values are corrected for the lead capacitance and the (temperature dependent) empty-cell capacitance.

1.2.8 Measuring cells.

We have designed two cylindrically shaped capacitors. The first one, a glass capacitor, is specially suited for liquids. For a drawing and more details about its construction, see chapter 5. Its capacitance was checked as a function of the dielectric constants¹⁶⁾ of air, n-hexane, c-hexane, carbon tetrachloride, benzene, m-xylene and chloro-benzene, all at room temperature. The capacitance of a cylindrically shaped vacuum capacitor is given by:

$$C = 2\pi\epsilon_0 l / \ln(r_2/r_1) \quad (10)$$

l is the length of the cylinder, r_2 the outer radius, r_1 the inner radius. The measuring space of the cell is the central capacitor of a system of three, switched in series. The outer and inner one consist of the glass walls, extending themselves between r_u and r_2 , and, r_1 and r_i , for the outer wall and inner wall respectively (see fig. 2 of chapter 5). The measuring space is confined between r_2 and r_1 . As a consequence of the serial circuitry of the capacitors, there exists a linear relation between the reciprocal of the total capacitance, $1/C_t$, and the reciprocal of the relative dielectric constant, $1/\epsilon$:

$$1/C_t = \ln(r_u r_1 / r_i r_2) / 2\pi\epsilon_0 l \epsilon_g + \ln(r_2 / r_1) / 2\pi\epsilon_0 l \epsilon = a + b/\epsilon \quad (11)$$

ϵ_g is the relative dielectric constant of the glass used and l is the length of the cell. Fig. 2 displays the experimental results of the calibration and the results of a calculation based upon the dimensions of the capacitor as designed. Since it is not feasible to measure directly the dimensions of the cell after its realization, specially the thickness of the glass walls and the measuring space, we determine these values from the data in fig. 2. If we compare the deduced and planned thickness of the glass and the measuring space, we only have to assume deviations from the designed values amounting to 0.1 or 0.2 mm to explain our results; such deviations are likely to occur. Furthermore there is an extra contribution to the capacitance, originating from the bottom of the cell, where both tubes are melted together, leading to a parallel capacitance of about 2 pF, which is independent of the dielectric constant of the calibration compounds. We may conclude that the data are consistent with the calculations. For the determination of ϵ we use the experimentally deduced relation between C_t and ϵ . From eq.(11) we derive the sensitivity of this cell for a change in the dielectric constant:

$$dC_t/d\epsilon = bC_t^2/\epsilon^2 \quad (12)$$

If $\epsilon \approx 1.6$ (a value found at 4 K for both 4-CH₃-pyridine and 4-CH₂-pyridine), $dC_t/d\epsilon$ amounts to 7 pF.

The second capacitor, mainly made of metal parts, is specially suited for powders. It consists of two coaxial german-silver tubes, 35 mm long. The

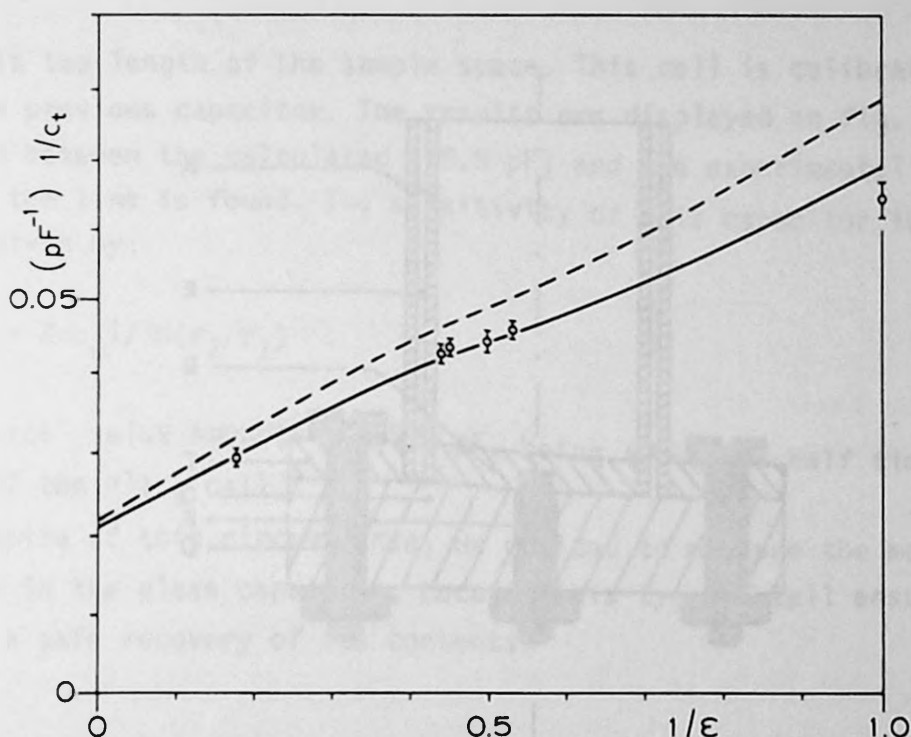


Fig. 2 The inverse capacitance $1/c_t$ of the glass capacitor vs. the inverse relative dielectric constant, $1/\epsilon$ in the fig., of the sample space. The dashed line is the prediction based upon the dimensions of the original design. The full line corresponds to the relation between $1/c_t$ and $1/\epsilon$, see eq.(11).

inner tube has an outside diameter, r_1 , of 20 mm and the outer tube has an inside diameter, r_2 , of 22 mm. Both tubes are soldered to a base plate, which allows their fixation via a teflon mount. The tubes were centered with respect to each other by a 5 mm high teflon ring, see fig. 3. The available sample space, as determined by the length and diameters of the cylinders, is the same as that of the first (glass) capacitor. For this capacitor there is a linear relation between its capacitance and the dielectric constant of the

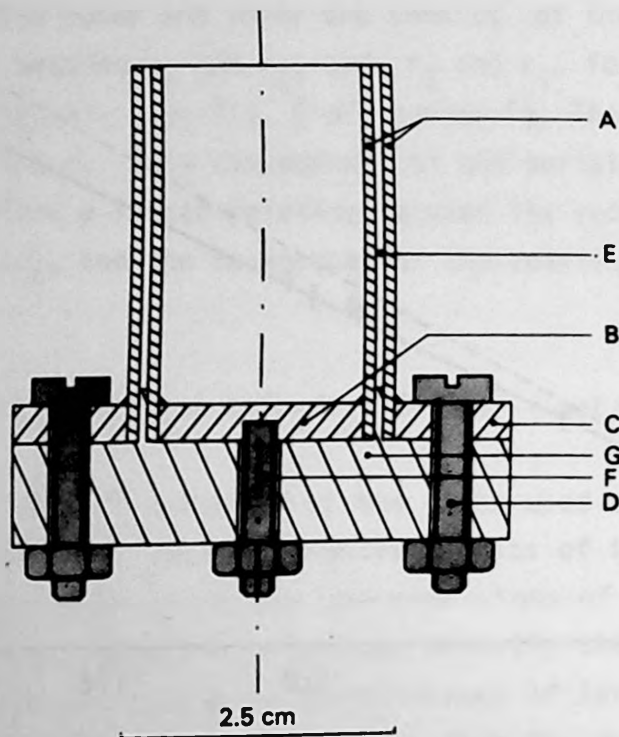


Fig. 3 The metal capacitor.

A German-silver tubes

B Brass plate for the inner cylinder

C Brass ring as support for the outer cylinder

D Attachment bolt with nut and electrical connection to the outer plate

E Measuring space

F Bolt with nut for the inner cylinder; it is also used as electrical connection

G Teflon base plate, ensuring the fixation of both cylinders

sample in the measuring space:

$$C = 2\pi\epsilon_0 l \epsilon / \ln(r_2/r_1) \quad , \quad (13)$$

where l is the length of the sample space. This cell is calibrated analogously to the previous capacitor. The results are displayed in fig. 4. A good agreement between the calculated (18.5 pF) and the experimental (18.1 ± 0.5 pF) slope of the line is found. The sensitivity of this capacitor for a change in ϵ is given by:

$$dC/d\epsilon = 2\pi\epsilon_0 l / \ln(r_2/r_1) \quad . \quad (14)$$

Its numerical value amounts to 18.1 pF, being two and a half times as large as that of the glass cell.

In spite of this circumstance, we decided to measure the mono-methylpyridines in the glass capacitor, because this type of cell ensures a constant mass and a safe recovery of its contents.

2. THEORY

2.1 Collective lattice contributions.

The lattice specific heat is described by the Debye model. Since the molecules of our compounds consist of several atoms, in general we will need more than one Debye function to describe the lattice specific heat. In keeping with other experimental results, the lattice specific heat can sufficiently accurately be represented by Debye functions only. In many cases two functions are sufficient. In addition, the contributions of these (e.g. two) Debye functions, are to be multiplied by a factor depending on the structure of the molecule and its surroundings. Then the lattice specific heat, $C_L(T)$, is given by:

$$C_L(T) = 3R \times \left[n_1 D(\theta_1/T) + n_2 D(\theta_2/T) \right] \quad , \quad (15)$$

where D is the Debye function, θ_1 and θ_2 two different Debye temperatures, n_1 and n_2 the multiplicities and T the temperature. It should be noted that the sum of the multiplicities must be smaller than the number of atoms in

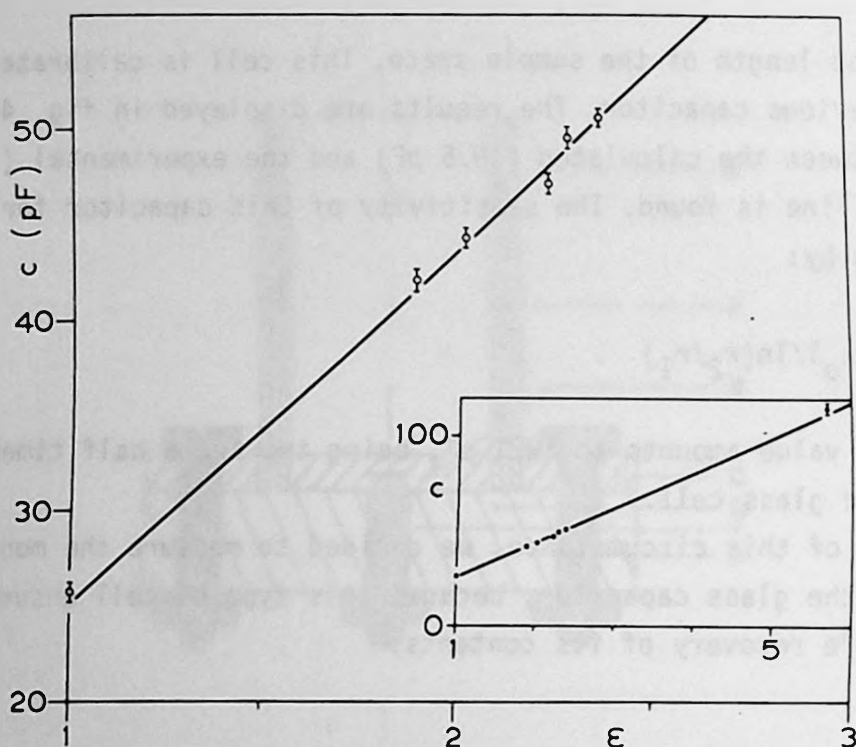


Fig. 4 The capacitance c of the metal capacitor against the relative dielectric constant ϵ of the measuring space. The full line is the prediction based upon the actual dimensions of the capacitor. The insert also displays the results for ϵ larger than 3.

a molecule. The combination of two or more Debye functions leads also to a dependence of the lattice specific heat on the temperature cubed, as is observed experimentally. Expressions using simple series expansions in stead of the formulae in infinitesimal form for the Debye free energy, entropy and specific heat are given in appendix B.

2.2 *Non-collective lattice contributions.*

It is assumed that they originate from the internal vibrations in a molecule. These motions are independent of the motions in adjacent molecules, so each molecule can be treated isolated from the others. The associated specific heat is described by the Einstein model. Also the contribution to the lattice specific heat of the optical branch of the phonon spectrum can be approximated by this model. The Einstein free energy, entropy and specific heat are also given in appendix B.

2.3 *Rotational contribution.*

The methyl groups of the compounds, investigated in this thesis, will exhibit hindered planar rotations. For the calculation of the thermodynamical properties related to these rotations, we need the energies, which are determined by the Schrödinger equation:

$$\mathcal{H}\psi = E\psi \quad , \quad (16)$$

with

$$\mathcal{H} = -(\hbar^2/2I)d^2/d\phi^2 + V(\phi) \quad . \quad (17)$$

$V(\phi)$ is the angular dependent potential barrier, which impedes the motion of the methyl group, E is the energy, ψ is the eigenfunction and I is the principal moment of inertia of the methyl group. The hindrance in motion finds its origin in both intermolecular and intramolecular interactions.

When we substitute in eq.(17) for the potential barrier a purely cosine function,

$$V(\phi) = (V/2)(1+\cos\phi) \quad , \quad (18)$$

the Schrödinger equation reduces to the Mathieu equation^{17,18)}. When we

assume that the barrier consists of the sum of two cosine shaped functions,

$$V(\phi) = (V_3/2)(1 + \cos 3\phi) + (V_6/2)(1 + \cos 6\phi) \quad , \quad (19)$$

we obtain the Whittacker-Hill equation¹⁹⁾. We will discuss in chapter 5, that the symmetry of the methyl group was broken by partly deuterating the rotor. This has influence on the symmetry of the interacting potential. Therefore we had to solve the Schrödinger equation using a more general form for the barrier,

$$V(\phi) = \sum_{l=1}^N (V_{nl}/2)(1 - (-1)^{P_{nl}} \cos nl\phi) \quad , \quad (20)$$

with $P_{nl} = 0$ or 1. It is usually assumed that at $\phi = 0$ the distinct contributions to the barrier possess their minimal or maximal values; they are not shifted with respect to each other over an arbitrary angle. The potential barrier in eq.(20) is composed of several contributions, each of them being invariant to certain symmetry elements, which form a group. The sum of the contributions is invariant to only those elements, which form part of the intersection of these groups. For the second part of the hamiltonian, $V(\phi)$, the element of the highest order in this group, C_{nv} , is a n -fold rotation. The kinetic energy operator, $(\hbar^2/2I)d^2/d\phi^2$, possesses axial symmetry, so the total hamilton operator is also invariant under the operations of C_{nv} . Hence the eigenfunctions of eq.(20) can be characterized by the irreducible representations of the group C_{nv} . From the physical point of view it is sufficient to consider C_n in stead of C_{nv} , because the mirror operations are not feasible.

The eigenfunctions of a hindered planar rotor can be expanded in an infinite series of the free planar rotor eigenfunctions:

$$\psi_{s,m} = \sum_{k=-\infty}^{+\infty} a_k \exp(i\phi(nk+m)) \quad , \quad (21)$$

where m is the free rotor quantum number and s is a binary variable related to the irreducible representation of the eigenfunction, see below. Considering a free planar rotor, all energy levels are doublets, except the ground state singlet, which is defined by $m = 0$. Some of these doublets are splitted up by the barrier into two singlets. We will restrict ourselves to the groups C_{1v} to C_{6v} (C_{1v} is isomorphous to C_{1h}).

When we apply a projection operator of representation Γ of the group C_{nv} to an eigenfunction, described in eq.(21), it projects out the eigenfunction in a different mathematical form, unless the result is zero. In this new form, the function is adapted to the irreducible representation Γ , i.e. if we reapply the projection operator of Γ to the new eigenfunction, the resulting function remains the same. When the representation corresponds to a degenerate state, the projection operator transforms the eigenfunction into a linear combination of the mutually orthogonal basis-functions. For a singlet state, the combination is trivial, being the basisfunction itself. The characterization of the eigenfunctions is given in table 2. We describe three cases for the eigenfunctions separately.

Table 2
 Characterization of the eigenfunctions.

C_{nv}		$m(\bmod n)$	0	1	2	3	4	5
n								
1			A_1, A_2					
2			A_1, A_2	B_1, B_2				
3			A_1, A_2	E	E			
4			A_1, A_2	E	B_1, B_2	E	E_1	
5			A_1, A_2	E_1	E_2	E_2	E_1	E_1
6			A_1, A_2	E_1	E_2	B_1, B_2	E_2	

(a) $m \equiv 0 \pmod n$, type A_1 or A_2
 The eigenfunction belonging to A_1 is labeled: $1,m$ and the one to A_2 : $2,m$. The general form of eq.(21) is changed by the projection operators into

$$\psi_{1,m} = a_{k_0} + \sum_{k=k_0+1}^{\infty} a_k \left[\exp(i\phi(nk+m)) + \exp(-i\phi(nk+m)) \right] \quad , \quad (22)$$

and

$$\psi_{2,m} = \sum_{k=k_0+1}^{\infty} a_k \left[\exp(i\phi(nk+m)) - \exp(-i\phi(nk+m)) \right], \quad (23)$$

with $k_0 = -(m/n)$, for A_1 and A_2 -type eigenfunctions respectively. These types of eigenfunctions always occur, independently of the value of n .

(b) $2m \equiv 0 \pmod{n}$, type B_1 or B_2 .

The eigenfunction of the type B_1 is labelled with $s=1$, the one of type B_2 with $s=2$. Likewise eq.(21) can be adapted to the characters of B_1 and B_2 , by writing:

$$\psi_{1,m} = \sum_{k=k_0+1}^{\infty} a_k \left[\exp(i\phi(nk+m)) + \exp(-i\phi(nk+m)) \right], \quad (24)$$

and

$$\psi_{2,m} = \sum_{k=k_0+1}^{\infty} a_k \left[\exp(i\phi(nk+m)) - \exp(-i\phi(nk+m)) \right], \quad (25)$$

where $k_0 = -(2m+n)/2n$. The B-type eigenfunctions only occur if n is even, see table 2.

(c) m is unequal to the values used in (a) and (b).

This only occurs for $n \geq 3$. The eigenvalue is doubly degenerate. The two eigenfunctions can be characterized by E , E_1 or E_2 , depending on the symmetry and the rotor quantum number. The projection operators of these representations produce from eq.(21) two types of functions:

$$\psi_{1,m} = \sum_{k=-\infty}^{\infty} a_k \exp(i\phi(nk+m)), \quad (26)$$

and

$$\psi_{2,m} = \sum_{k=-\infty}^{\infty} a_k \exp(-i\phi(nk+m)). \quad (27)$$

These two functions form an orthogonal basis for the E-type eigenfunctions.

In addition to these eigenfunctions we use auxiliary functions $\omega_{s,1,p}$ defined by:

$$\omega_{s,1,p} = \exp(i\phi(nl+p)) - (-1)^s \exp(-i\phi(nl+p)). \quad (28)$$

They can be classified analogously to the functions $\psi_{s,m}$. When solving the Schrödinger equation, it is convenient to define the inproduct of two

arbitrary functions ψ_a and ψ_b as :

$$(\psi_a, \psi_b) = \int_0^{2\pi} \psi_a^* \psi_b d\phi \quad . \quad (29)$$

The asteriks indicates that the complex-conjugated function of ψ_a should be used. It is now easy to calculate the eigenvalues by the application of the following operation:

$$(\omega_{s,1,p}, \mathcal{H}(\psi_{s,m})) = E(\omega_{s,1,p}, \psi_{s,m}) \quad . \quad (30)$$

Since $\omega_{s,1,p}$ is an arbitrary function with $1 \geq k_0$ for singlet representations and 1 is completely free for the doublet representations, we can derive from eq.(30) an infinite set of equations, which can be formally represented by:

$$G \cdot \underline{a} = E \underline{a} \quad . \quad (31)$$

$\underline{a}$ is the vector of the coefficients a_k and G is a matrix, which contains all coefficients of the equations in a_k . For the determination of the matrix G , see appendix C.

Functions belonging to different irreducible representations are mutually orthogonal. Also the eigenfunctions of the doublet levels are orthogonal, as can be found by the application of eq.(29). When we apply the hamilton operator to a function $\psi_{s,m}$, belonging to an irreducible representation $\Gamma^{(sm)}$, the result of this operator is another function of the same representation $\Gamma^{(sm)}$. Combining this fact with the orthogonality of the representations, we only have to calculate eq.(30 using functions $\omega_{s,1,p}$ of the same representation as $\psi_{s,m}$, which reduces the calculations in solving eq.(31). It is an eigenvalue and eigenvector problem, which we have solved numerically²⁰⁾. G is a hermitian non diagonal matrix. Using Householders method²¹⁾, G is reduced by similarity transformations to a tridiagonal matrix, of which the eigenvalues, E , are easily found. The transformed eigenvectors $\underline{a}_t$ are calculated from the tridiagonal matrix, and the original $\underline{a}$ is found by the application of the inverse similarity transformation to $\underline{a}_t$.

The results for purely cosine shaped barriers are checked against the tables of references 17 and 18 and for the mixed barriers of threefold and sixfold symmetry against the tables of reference 19. The rotational degeneracy is determined by the irreducible representations of the eigenfunctions. For

the thermodynamic properties also the nuclear spin degeneracies must be taken into account.

2.4 Nuclear spin degeneracy.

Since the protons in the methyl group possess a half-integer nuclear spin value ($\vec{I} = \frac{1}{2}$), they must be treated as fermions. The total eigenfunction, here the product of nuclear and rotational eigenfunctions, must be anti-symmetric for a permutation of two protons. A single permutation produces a mirror reflection of the frame ²²⁾ of the proton triangle, an operation which is not compatible with pure rotations. Two subsequent proton permutations leave the frame of the proton triangle invariant, and this is compatible with a rotation. Hence we consider only an even number of permutations, which form a group isomorphous to C_n . In order to calculate those combinations of nuclear and rotational eigenfunctions, which are not excluded by the Pauli principle, we examine the product group of the rotational and nuclear symmetry operations. If the rotational barrier has a threefold symmetry, both groups are C_3 . By means of the projection operators belonging to C_3 , we can classify ²³⁾ the nuclear eigenfunctions according to the irreducible representations of C_3 , see table 3. The A-type eigenfunctions are fourfold degenerate ($\vec{I} = 3/2$), while the E-type eigenfunctions are doubly degenerate, as far as the nuclear spin ($\vec{I} = \frac{1}{2}$) is concerned.

Table 3

The nuclear spin eigenfunctions of CH_3

A-type functions	E_a and E_b -type functions
$ +++>$	$\frac{1}{3}\sqrt{3}(+->+\omega^2 -++>+\omega ++->)$
$\frac{1}{3}\sqrt{3}(+->+ -++>+ ++->)$	$\frac{1}{3}\sqrt{3}(-+->+\omega^2 +-->+\omega --->)$
$\frac{1}{3}\sqrt{3}(-+->+ +-->+ --->)$	$\frac{1}{3}\sqrt{3}(+->+\omega -++>+\omega^2 ++->)$
$ --->$	$\frac{1}{3}\sqrt{3}(-+->+\omega +-->+\omega^2 -++>)$
	$\omega = \exp(2i\pi/3)$

Since the total eigenfunction must be symmetric for an even number of proton permutations, its representation must be A. We can read from the product group table, see table 4, that rotational and nuclear E-type eigenfunctions combine to an A-type eigenfunction; the same is found for the A-type nuclear and rotational eigenfunctions. As a result all levels are equally degenerate.

Table 4

The product group table of $C_3 \times C_3$

	A	E_a	E_b
A	A	E_a	E_b
E_a	E_a	E_b	A
E_b	E_b	A	E_a

It should be noted that the symmetry group of the cosine shaped rotational barrier is C_{3v} . However, if we describe this potential by C_3 , the energies and also the rotational eigenfunctions, calculated from eq.(17) remain of course the same. However, the singlets, now all A-type, possess two different kind of functions, characterized by A_1 and A_2 of the group C_{3v} : the first one is an even function, the other is odd. The E-type eigenfunctions are the same, even in formal notation, since the character of the mirror class σ_v in the E representation is zero ²⁴⁾. Now that the energies and degeneracies of the levels are known, we can calculate the corresponding specific heat, see e.g. the appendix of chapter 5.

APPENDIX A

The electrical circuit of the linear capacitance meter ²⁵⁾ is shown in fig. 5. The principle of operation is as follows. The first timer (555) generates a block signal with a repetition frequency of 850 Hz. The second timer is triggered by this signal and this timer generates a pulse having the same repetition frequency. Its pulse width is a linear function of the (unknown) capacitor C_x and the resistor R , both connected to the second timer.

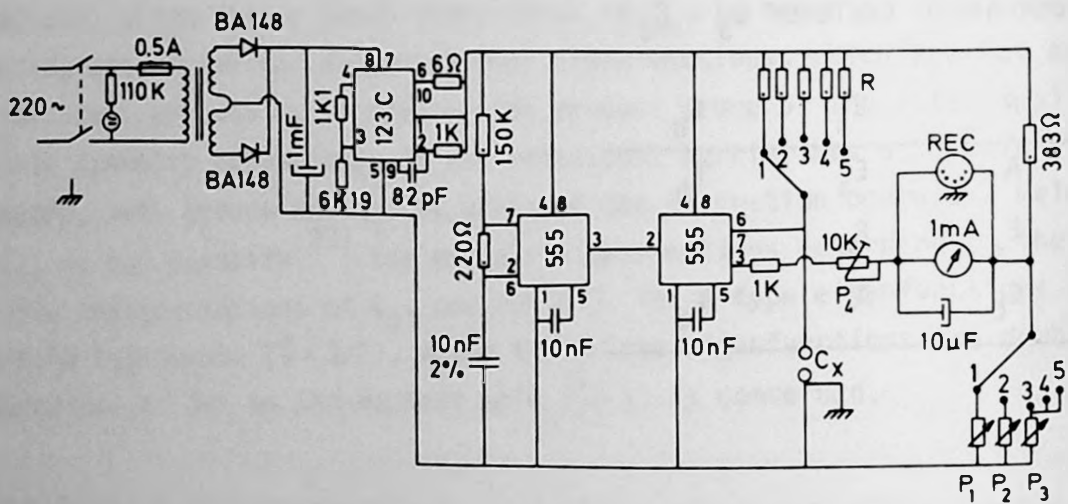


Fig. 5 The electrical circuit of the capacitance meter used. C_x represents the capacitance to be measured. The resistors, indicated by a dot, are 1% precision resistors.

Since the resistor R has a constant value, the time averaged dc voltage at the output terminal is therefore a linear function of the unknown capacitor. By a stepwise change of the resistor R , different capacitance ranges can be chosen. The parasitical stray capacitance at the connecting terminals is

compensated to zero by the variable resistors P_1 , P_2 and P_3 , for the lowest three successive ranges. After connection of a known standard capacitor, the mA meter is set to the desired meter deflection by the variable resistor P_4 .

It was necessary to modify the original circuit ²⁵⁾ slightly in order to meet our experimental requirements. As can be seen from fig. 5, the value of the supply voltage influences the meter deflection. Therefore we provided the circuit with a standard stabilized power supply, using the integrated circuit 123 C. During test measurements on thermostated capacitors, it turned out that the reading of the capacitance meter depended on the temperature of the electronic circuit. The value of this dependence amounts 0.1 pF/K on the 100 pF scale. Therefore we thermally isolated the box containing the electronic components. If the measurements require a sensitive determination of the change of the measuring-cell capacitance, the x-t recorder, switched parallel to the mA meter, is used as detector. The voltage at the dc terminals is compensated by an auxiliary network. In this way, short time variations in the connected capacitor of the order of 10^{-5} of the full scale deflection can be observed.

APPENDIX B

We summarize here the series expansions used for the calculation of the free energy, F , entropy, S , internal energy, U , and the specific heat, C in the Debye and Einstein model. All quantities are given per degree of freedom and concern 1 mol. In the Debye model

$$(F-F_0)/RT = \ln(1-\exp(-x)) - 4\pi^4/15x^3 + \sum_{n=1}^{\infty} \left[\frac{1+3/nx+6/(nx)^2+6/(nx)^3}{n \exp(nx)} \right], \quad (B.1)$$

$$(U-U_0)/RT = 4\pi^4/15x^3 - 3 \sum_{n=1}^{\infty} \left[\frac{1+3/nx+6/(nx)^2+6/(nx)^3}{n \exp(nx)} \right], \quad (B.2)$$

$$S/R = 4\pi^4/15x^3 - \ln(1-\exp(-x)) - 4 \sum_{n=1}^{\infty} \left[\frac{1+3/nx+6/(nx)^2+6/(nx)^3}{n \exp(nx)} \right], \quad (B.3)$$

$$C/R = 4\pi^4/5x^3 -$$

$$\sum_{n=1}^{\infty} \left[3nx + 12 + 36/nx + 72/(nx)^2 + 72/(nx)^3 \right] / (n \exp(nx)), \quad (B.4)$$

with $x = \theta_D/T$, θ_D being the Debye temperature. The index 0 indicates a temperature of zero kelvin. The equations (B.2) and (B.4) are the same as those in ref. 26; equations (B.1) and (B.3) seem to differ from those in ref. 26, but since

$$\sum_{n=1}^{\infty} 1/(n \exp(nx)) = -\ln(1 - \exp(-x)) \quad , \quad (B.5)$$

they are essentially the same. These series expansions converge rapidly; the terms for $nx > 20$ produce contributions of the order of 10^{-10} or less to the final result.

The formulae used in the Einstein model are:

$$(F-F_0)/RT = \ln(2\sinh(y)) \quad , \quad (B.6)$$

$$S/R = y \coth(y) - \ln(2\sinh(y)) \quad , \quad (B.7)$$

$$C/R = x^2 \exp(x)/(\exp(x)-1)^2 \quad , \quad (B.8)$$

with $y = \theta_E/2T$ and $x = 2y$.

APPENDIX C

In this appendix we describe the comprehensive mathematical operations, which are necessary to determine the elements of the G matrix. The method followed here, is analogous to the one used by Gloden¹⁹⁾ for the determination of the eigenvalues of the Whittacker-Hill equation with threefold symmetry. However, in our description we take advantage of the results of group theory applied to the eigenfunctions and the auxiliary functions. In this way we evade the numerical confusion between two nearly coinciding eigenvalues. A second difference is that this formulation of the rotor problem allows us to determine the eigenvalues and eigenfunctions of one, or the sum of more than one cosine shaped barrier(s), with arbitrarily rotational symmetry.

We start with some abbreviations, used for the eigenfunctions and the potential barrier, introducing two functions, $c(x)$ and $s(x)$.

$$c(x) = \exp(ix) + \exp(-ix) , \quad (C.1)$$

$$s(x) = \exp(ix) - \exp(-ix) . \quad (C.2)$$

Some properties of these functions are summarized in the equations (C.3) until (C.7).

$$s(k) \times s(l) = c(k+l) - c(k-l) , \quad (C.3)$$

$$s(k) \times c(l) = s(k+l) + s(k-l) , \quad (C.4)$$

$$c(k) \times c(l) = c(k+l) + c(k-l) , \quad (C.5)$$

$$\int_0^{2\pi} c(\phi(k-l)) d\phi = 4\pi \delta_{k,l} , \quad (C.6)$$

with $\delta_{k,l}$ the Kronecker delta, and finally:

$$\int_0^{2\pi} s(\phi(k-l)) d\phi = 0 . \quad (C.7)$$

The potential barrier, see eq.(20) can be reorganized to:

$$V(\phi) = \sum_{l=1}^N (V_{nl}/2) + \sum_{l=1}^N \beta_{nl} c(nl\phi) , \quad (C.8)$$

with β_{nl} given by:

$$\beta_{nl} = -(V_{nl}/4)(-1)^{P_{nl}} . \quad (C.9)$$

In eq.(C.8) $V(\phi)$ can be divided into a constant part and an angular dependent part. The constant part can be brought to the right side of the equals sign in eq.(17) leading to:

$$-(\hbar^2/2I)d^2\psi/d\phi^2 + \left\{ \sum_{l=1}^N \beta_{nl} c(nl\phi) \right\} \psi = \eta \psi , \quad (C.10)$$

and

$$\eta = E - \sum_{l=1}^N (V_{nl}/2) \quad . \quad (C.11)$$

The singlet eigenfunctions are normalized to 4π , resulting from the requirement in the eigenfunction subroutine ²⁰⁾ that:

$$\sum_{k=1}^{\infty} a_k^2 = 1 \quad , \quad (C.12)$$

while e.g. for an A_2 -type eigenfunction:

$$|\psi_{2,m}|^2 = \int_0^{2\pi} \sum_{k=k_0+1}^{\infty} \sum_{l=k_0+1}^{\infty} b_k b_l \left[-c(\phi(n(k+1)+2m)) + c(\phi(n(l-1))) \right] d\phi =$$

$$4\pi \sum_{l=k_0+1}^{\infty} b_l^2 = 4\pi \sum_{k=1}^{\infty} a_k^2 \quad , \quad (C.13)$$

where $a_1 = b_{k_0+1}$ etc; after substitution of eq.(C.12) into (C.13), the norm of $\psi_{2,m}$ becomes 4π .

We will now derive the elements of the G matrix, using the different types of eigenfunctions according to their irreducible representations, i.e. A_1 , A_2 , B_1 , B_2 and E .

A_1 eigenfunctions.

The eigenfunction, see eq.(22) can be rewritten to:

$$\psi_{1,m} = a_{k_0} + \sum_{k=k_0+1}^{\infty} a_k c(\phi(nk+m)) \quad , \quad (C.14)$$

with $k_0 = -m/n$.

Since a_{k_0} is an angular independent number, not yet determined, it may be multiplied by $\sqrt{2}$ in order to arrange a convenient normalization.

$$|\psi_{1,m}|^2 = \int_0^{2\pi} \psi_{1,m}^* \psi_{1,m} d\phi = 2\pi(2a_{k_0}^2 + 2\sum_{k=k_0+1}^{\infty} a_k^2) = 4\pi \sum_{k=k_0}^{\infty} a_k^2 \quad . \quad (C.15)$$

This equation allows an easy substitution of eq.(C.12) leading to a norm of $\psi_{1,m}$ of 4π , so eq.(C.14) is now replaced by:

$$\psi_{1,m} = a_{k_0} \sqrt{2} + \sum_{k=k_0+1}^{\infty} a_k c(\phi(nk+m)) \quad . \quad (C.16)$$

A similar problem occurs for $\omega_{1,l,m}$, see eq.(28). The norm of these functions is also 4π if $l \neq k_0$, but 8π if $l = k_0$ ($\omega_{1,k_0,m} = 2$). As a result $\omega_{1,k_0,m}$ is chosen to be $\sqrt{2}$, leading to a norm of 4π . Now $\psi_{1,m}$ and all functions $\omega_{1,l,m}$ have the same norm. The l -th row of G is denoted by G_l ,

$$G_l = (\omega_{1,l,m}, \mathcal{H}\psi_{1,m}) \quad . \quad (C.17)$$

If we apply the hamiltonian operator to $\psi_{1,m}$, we obtain:

$$\mathcal{H}\psi_{1,m} = (\hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 c(\phi(nk+m)) + a_{k_0} \sqrt{2} \sum_{l=1}^N \beta_{nl} c(nl\phi) + \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} \left[c(\phi(n(k+1)+m)) + c(\phi(n(k-1)+m)) \right] \quad . \quad (C.18)$$

So:

$$G_{k_0} = (\sqrt{2}, \mathcal{H}\psi_{1,m}) = 4\pi \sqrt{2} \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} \delta_{k-k_0, l} \quad , \quad (C.19)$$

when $j \geq k_0+1$ we derive

$$G_j = (4\pi \hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 \delta_{k,j} + 4\pi a_{k_0} \sqrt{2} \sum_{l=1}^N \beta_{nl} \delta_{j-k_0, l} + 4\pi \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} \beta_{nl} a_k (\delta_{k,j+1} + \delta_{k,j-1} + \delta_{k, l-j+2k_0}) \quad . \quad (C.20)$$

At the right side of eq.(30) we find the term:

$$\eta(\omega_{1,j,m}, \psi_{1,m}) = 4\pi n a_j \quad . \quad (C.21)$$

All rows of G and all elements of eq.(C.21) have a factor of 4π in common, so it can be written as:

$$G \cdot (4\pi \underline{a}) = \eta(4\pi \underline{a}) \quad , \quad (C.22)$$

being equivalent to eq.(31). For the solution of eq.(C.22) this factor of 4π can be neglected.

As an illustrative example, we will assume a potential barrier described by an arbitrarily chosen number of four terms:

$$V(\phi) = \sum_{l=1}^4 \{V_{nl}/2\} (1-(-1)^{P_{nl}} \cos(nl\phi)) \quad (C.23)$$

Using this barrier, a part of the matrix G is shown in table 5.

With the appropriate subroutines the energy levels and, if needed, the eigenfunction coefficients can be determined.

Table 5

The upper part of the G matrix in the A_1 representation.
 $J = \hbar^2/2I$, $V(\phi) = \sum_{l=1}^4 \{(V_{nl}/2) + \beta_{nl} c(nl)\}$ and $\beta_{nl} = -(V_{nl}/4)(-1)^{P_{nl}}$.

		$\sqrt{2}\beta_{n1}$	$\sqrt{2}\beta_{n2}$	$\sqrt{2}\beta_{n3}$	$\sqrt{2}\beta_{n4}$	0	0	0	.	.	.
0	$\sqrt{2}\beta_{n1}$	$J + \beta_{n2}$	$\beta_{n1} + \beta_{n3}$	$\beta_{n2} + \beta_{n4}$	β_{n3}	β_{n4}	0	0	.	.	.
$\sqrt{2}\beta_{n1}$	$J + \beta_{n2}$	$\beta_{n1} + \beta_{n3}$	$4J + \beta_{n4}$	β_{n1}	β_{n2}	β_{n3}	β_{n4}	0	.	.	.
$\sqrt{2}\beta_{n2}$	$\beta_{n1} + \beta_{n3}$	$4J + \beta_{n4}$	β_{n1}	$9J$	β_{n1}	β_{n2}	β_{n3}	β_{n4}	.	.	.
$\sqrt{2}\beta_{n3}$	$\beta_{n2} + \beta_{n4}$	β_{n1}	β_{n1}	β_{n1}	$16J$	β_{n1}	β_{n2}	β_{n3}	.	.	.
$\sqrt{2}\beta_{n4}$	β_{n3}	β_{n2}	β_{n2}	β_{n2}	β_{n1}	β_{n1}	β_{n1}	β_{n1}	.	.	.
0	β_{n4}	β_{n3}	β_{n3}	β_{n3}	β_{n2}	β_{n1}	β_{n1}	$36J$	β_{n1}	$49J$	.
0	0	β_{n4}	β_{n4}	β_{n4}	β_{n3}	β_{n2}	β_{n1}	.	.	.	.
0	0	0	0	0	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.

A_2 eigenfunctions.

These functions are:

$$\psi_{2,m} = \sum_{k=k_0+1}^{\infty} a_k s(\phi(nk+m)) \quad (C.24)$$

with $k_0 = -m/n$.

If we apply the hamilton operator to $\psi_{2,m}$ we get:

$$\mathcal{H}\psi_{2,m} = (\hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 s(\phi(nk+m)) + \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} \left[s(\phi(n(k+1)+m)) + s(\phi(n(k-1)+m)) \right] \quad (C.25)$$

For $\omega_{2,j,m}$ we use now:

$$\omega_{2,j,m} = s(\phi(nj+m)) \quad , \quad (C.26)$$

leading to G_j for each $j(\geq k_0+1)$:

$$G_j = (4\pi\hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 \delta_{k,j} + 4\pi \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} (\delta_{k,j+1} - \delta_{k,j-1} - \delta_{k,l-j+2k_0}) \quad (C.27)$$

The equation to be solved, is again eq.(C.22). G is partly displayed in table 6 for $N=4$ as a limit to the barrier expansion.

Table 6

The upper part of the G matrix in the A_2 representation.

$J = \hbar^2/2I$ and β_{nl} is the same as in table 5.

				β_{n4}	0	0	0	.	.	.
			β_{n3}	β_{n4}	β_{n4}	0	0	.	.	.
$J - \beta_{n2}$	$\beta_{n1} - \beta_{n3}$	$\beta_{n2} - \beta_{n4}$	β_{n2}	β_{n3}	β_{n3}	β_{n4}	0	.	.	.
$\beta_{n1} - \beta_{n3}$	$4J - \beta_{n4}$	β_{n1}	β_{n1}	β_{n2}	β_{n2}	β_{n3}	β_{n4}	.	.	.
$\beta_{n2} - \beta_{n4}$	β_{n1}	$9J$	$16J$	β_{n1}	β_{n1}	β_{n2}	β_{n3}	β_{n4}	.	.
β_{n3}	β_{n2}	β_{n1}	β_{n1}	$25J$	β_{n1}	β_{n2}	β_{n3}	β_{n4}	.	.
β_{n4}	β_{n3}	β_{n2}	β_{n2}	β_{n1}	$36J$	β_{n1}	β_{n2}	β_{n3}	.	.
0	β_{n4}	β_{n3}	β_{n3}	β_{n2}	β_{n1}	$49J$	β_{n1}	β_{n2}	.	.
0	0	β_{n4}	β_{n4}	β_{n3}	β_{n2}	β_{n1}	$64J$	.	.	.
0	0	0	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.

B_1 eigenfunctions.

They are derived from eq.(24) as

$$\psi_{1,m} = \sum_{k=k_0+1}^{\infty} a_k c(\phi(nk+m)) \quad , \quad (C.28)$$

with $k_0 = -(2m+n)/2n$, k_0 being an integer. After the application of the hamilton operator to $\psi_{1,m}$ we obtain:

$$\begin{aligned} \mathcal{H}\psi_{1,m} = & (\hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 c(\phi(nk+m)) + \\ & \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} \left[c(\phi(n(k+l)+m)) + c(\phi(n(k-l)+m)) \right] \quad . \quad (C.29) \end{aligned}$$

The auxiliary functions $\omega_{1,j,m}$ are:

$$\omega_{1,j,m} = c(\phi(nj+m)) \quad . \quad (C.30)$$

So for the j -th row of G we obtain:

$$\begin{aligned} G_j = & (4\pi\hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 \delta_{k,j} + \\ & 4\pi \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} (\delta_{k,j+l} + \delta_{k,j-l} + \delta_{k,1-j+2k_0+1}) \quad . \quad (C.31) \end{aligned}$$

Expanding the barrier into four terms, the upper part of G is given in table 7. The $\pm$ sign must be read as $+$ for the B_1 levels.

Table 7

The upper part of the G matrix in the $B_1(+)$ and $B_2(-)$ representation.

$K = n^2 h^2 / 8I$, β_{n1} is defined in eq.(C.9).

					0	0	0	.	.	.
				β_{n4}		0	0	.	.	.
$K + \beta_{n1}$	$\beta_{n1} + \beta_{n2}$	$\beta_{n2} + \beta_{n3}$	$\beta_{n3} + \beta_{n4}$	β_{n4}	β_{n4}	0	0	.	.	.
				β_{n3}	β_{n3}	β_{n4}	0	.	.	.
$\beta_{n1} + \beta_{n2}$	$9K + \beta_{n3}$	$\beta_{n1} + \beta_{n4}$	β_{n2}	β_{n2}	β_{n3}	β_{n4}	β_{n4}	.	.	.
		25K	β_{n1}	β_{n1}	β_{n2}	β_{n3}	β_{n4}	.	.	.
$\beta_{n2} + \beta_{n3}$	$\beta_{n1} + \beta_{n4}$		49K	β_{n1}	β_{n2}	β_{n3}	β_{n4}	.	.	.
		β_{n1}		81K	β_{n1}	β_{n2}	β_{n3}	.	.	.
$\beta_{n3} + \beta_{n4}$	β_{n2}	β_{n2}	β_{n1}		121K	β_{n1}	β_{n2}	.	.	.
	β_{n3}	β_{n2}	β_{n2}	β_{n1}		169K	β_{n1}	.	.	.
β_{n4}	β_{n4}	β_{n3}	β_{n3}	β_{n2}	β_{n1}	β_{n2}	225K	.	.	.
0	0	0	β_{n4}	β_{n3}	β_{n2}	β_{n1}		.	.	.
0	0							.	.	.
0	0							.	.	.
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.

B_2 eigenfunctions.

The eigenfunctions corresponding to the B_2 representation are

$$\psi_{2,m} = \sum_{k=k_0+1}^{\infty} s(\phi(nk+m)) ; \quad (C.32)$$

the ω functions of interest are:

$$\omega_{2,j,m} = s(\phi(nj+m)) . \quad (C.33)$$

Analogously we obtain for G_j :

$$G_j = (4\pi\hbar^2/2I) \sum_{k=k_0+1}^{\infty} a_k (nk+m)^2 \delta_{k,j} + 4\pi \sum_{l=1}^N \sum_{k=k_0+1}^{\infty} a_k \beta_{nl} (\delta_{k,j+1} + \delta_{k,j-1} - \delta_{k,l-j+2k_0+1}) \quad (C.34)$$

Using the same barrier as for B_1 -levels, the upper part of the G matrix is also displayed in table 7; we should read now - for the $\pm$ sign.

E eigenfunctions, doublet states.

The two eigenfunctions are:

$$\psi_{1,m} = \sum_{k=-\infty}^{+\infty} a_k \exp(i\phi(nk+m)) \quad (C.35)$$

and

$$\psi_{2,m} = \sum_{k=-\infty}^{+\infty} a_k \exp(-i\phi(nk+m)) \quad (C.36)$$

We use $\psi_{1,m}$ only. As a result $\omega_{s,j,p}$ is also simplified to:

$$\omega_{1,j,m} = \exp(i\phi(nj+m)) \quad (C.37)$$

A disadvantage is that these functions are normalized to 2π . We proceed similarly as for the singlets.

$$\mathcal{H}\psi_{1,m} = (\hbar^2/2I) \sum_{k=-\infty}^{+\infty} a_k (nk+m)^2 \exp(i\phi(nk+m)) + \sum_{l=1}^N \sum_{k=-\infty}^{\infty} a_k \beta_{nl} \left[\exp(i\phi(n(k+1)+m)) + \exp(i\phi(n(k-1)+m)) \right] \quad (C.38)$$

and so:

$$G_j = (2\pi\hbar^2/2I) \sum_{k=-\infty}^{+\infty} a_k (nk+m)^2 \delta_{k,j} + 2\pi \sum_{l=1}^N \sum_{k=-\infty}^{+\infty} a_k \beta_{nl} (\delta_{k,j+1} + \delta_{k,j-1}) \quad (C.39)$$

The equation now to be solved, is:

$$G \cdot (2\pi a) = \eta(2\pi a) \quad (C.40)$$

In this case we divide by 2π , and so eq.(C.40) becomes eq.(31). The central part of the matrix is shown in table 8.

Table 8

The central part of the G matrix in the E , E_1 or E_2 representation.
 $L = \hbar^2/2I$ and β_{n1} is the same as in table 5.

[illegible]

Numerical considerations.

Here we shall address ourselves to the question how far the expansion of the eigenfunctions into the planar free-rotor eigenfunctions has to be extended. Therefore we carried out numerical tests in case of low barriers (below 1000 K). We assume for a methyl group $\hbar^2/2Ik$ to be 7.6 K²⁷⁾. Relative changes less than 10^{-11} are found in the eigenvalues up to 3000 K, if we truncate the eigenfunction expansion after 40 terms.

All eigenvalue and eigenvector calculations were performed on an Amdahl 470 V7B computer, using a Fortran program, in combination with the NAG²⁰⁾ subroutines F01AJF, F02AMF, F01AGF and F02AVF. The determination of the eigenvalues up to 3000 K takes about 0.5 s; when also the eigenfunction coefficients are needed, the calculations last 3 s.

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CHAPTER 3

METHYL GROUP ROTATION IN $(\text{CH}_3)_2\text{SnF}_2$

Synopsis.

Dimethyl-tin-difluoride has a structural phase transition at 70.4 K as observed in heat-capacity, NMR and dielectric measurements. The information about the rotational motion of the methyl groups, obtained by nuclear relaxation and heat-capacity measurements, is discussed and compared with neutron-scattering results. The entropy of the system is shown to be directly related to the value of the high-temperature barrier ($V_3/k = 160$ K). The proton relaxation rate in the high-temperature phase is dependent on transitions between a number of levels, closely separated in energy. As a result one has to expect an almost zero value of the activation energy, as is found experimentally. For this phase NMR, neutron-scattering and heat-capacity data are in agreement. For the low-temperature barrier, the neutron-scattering result is at the lower end of the range, set by the heat-capacity data. In this case NMR possibly probes a fast relaxing minority of the methyl groups with a barrier, which is higher than that felt by the majority.

1. *Introduction.*

The internal molecular degrees of freedom of symmetric groups of atoms like methyl groups, ammonium groups etc., in the solid state has already been a subject of experimental and theoretical interest for a number of decades. Although considerable progress has been made in the understanding of many phenomena in these systems, a still existing problem is the interpretation of the activation energies (magnitude and temperature dependence) as found by NMR, especially in low-barrier systems and the role of the internal molecular degrees of freedom in (structural) phase transitions.

For our study of these points of interest we were looking for a simple well-defined system, where enough additional data could be obtained from the literature. Dimethyl-tin-difluoride, $(\text{CH}_3)_2\text{SnF}_2$, appeared to be a suitable candidate. In this compound a phase transition occurs around 70 K¹⁾. Above the phase-transition temperature, T_p , the crystal structure is known²⁾, being $I4/mmm$; the sample has two equivalent methyl groups and possesses no paramagnetic ions (no magnetic relaxation or ordering). Quasielastic (QNS) and elastic (ENS) neutron scattering data^{1,3)} are available above and below the phase transition; the tunnelling splitting of the ground state is determined by inelastic neutron-scattering (INS)³⁾ at liquid helium temperatures. In the successive sections of this chapter the techniques used in this study and the properties of the material, known e.g. from X-ray and neutron-scattering experiments are given. Then the theory for the analysis of the heat-capacity and NMR data is discussed, whereafter the experimental data are presented and analyzed. In the next section a comparison is made of the results obtained by both techniques and the neutron data; the final results are summarized in the conclusion.

2. *Apparatus and material.*

The specific heat was measured from 0.95 to 95 K in an adiabatic set-up via the heat pulse method. The temperature was measured by means of a carbon thermometer, which was calibrated against the vapour pressure of normal H_2 , ^4He , ^3He and O_2 . The temperature was determined within 0.1%. The thermometer was soldered on a gold-plated calorimeter. A mechanical heat switch provided

the heat contact between the calorimeter and the cryogenic coolant if needed. No helium exchange gas was used. As a heater a resistance wire was wound around the calorimeter. The empty sample container was measured first, so its heat capacity was known. The powdered sample was compressed into the container at a pressure of 0.2 MPa. Extra specific-heat measurements were performed in a adiabatic demagnetization set-up from 150 mK to 1 K ⁴⁾. The sample was mixed with Apiezon N-grease for the internal heat contact.

The proton relaxation measurements were performed using a Bruker CXP 4-100 pulse spectrometer at a frequency of 38.166 MHz using a 90° - τ - 90° pulse sequence with a pulse time of about 2 μ s. The stabilized temperatures in the measured interval (100 K - 50 K) were obtained in a flow cryostat with platinum thermometry.

In the same cryostat as the one used for specific heat, we measured the dielectric constant ϵ . Our aim was to detect sudden changes in ϵ , possibly associated with a phase transition. The capacitor consisted of two coaxial gold-plated german-silver tubes, 35 mm long and about 20 mm in diameter. The plate distance was 1.0 mm. Both tubes were soldered to a ring, screwed on a teflon base mount for the necessary support. The cell parameters were determined at room temperature by means of the dielectric measurements of cyclohexane, carbon tetrachloride, m-xylene, benzene and chloro-benzene. The temperature, which could be varied by a resistance heater, was determined with a platinum resistance thermometer with an accuracy of 0.5%.

The direct reading capacitance meter ⁵⁾, using a RC method at 850 Hz, produced a dc output, registered on a stripchart recorder. The sensitivity is about 1 fF with the possibility to offset between 0 and 150 pF. The reading and sensitivity were checked against several capacitors. Also the empty cell and its leads were measured as function of temperature, so we could subtract the empty-cell capacitance.

The dimethyl-tin-difluoride used was a white powder, supplied by ALFA chemicals. The crystal structure and the thermal motions of the atoms were determined at room temperature by X-ray ²⁾. The crystal structure is found to be of space group I4/mmm. The cell parameters are $a = 0.424$ nm and $c = 1.416$ nm, see fig. 1. The thermal motions of the carbon atoms correspond with a nearly isotropic vibration. The motion of the tin and fluorine atoms are anisotropic. The tin atoms vibrate mostly perpendicular to the $a - a$ plane; the fluorine atoms vibrate strongly in or parallel to the $a - a$ plane, but perpendicular to the Sn - F bond. The motions of the tin and fluorine atoms

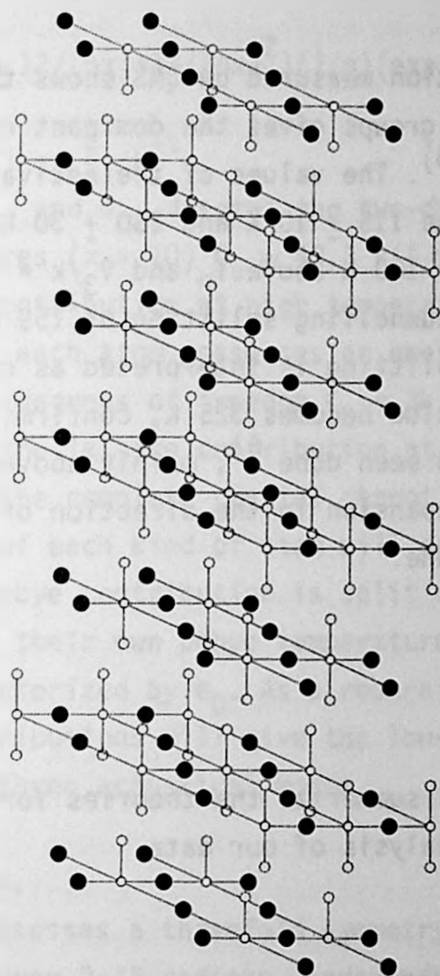


Fig. 1 The crystal structure of dimethyl-tin-difluoride $(\text{CH}_3)_2\text{SnF}_2$ at room temperature. The a -axes ($a = 0.424 \text{ nm}$) lay along the dotted lines between the solid open circles in a horizontal plane. In the vertical direction two Sn - F planes, separated by an interstitial Sn - F plane, are connected by the c -axes ($c = 1.416 \text{ nm}$).

Sn Open solid circle

C Dashed open circle

F Black circle

in or parallel to the $a - a$ plane along the bond are of equal amplitude. From the diffraction pattern ¹⁾ seen by ENS it is clear that the symmetry of the space group changes between 78 K and 61 K, indicating the existence of a phase transition.

The intensity distribution measured by QNS shows that threefold reorientation of the methyl groups gives the dominant contribution to the quasi-elastic scattering ^{1,3)}. The values of the activation energies above and below T_p were found to be 115 ± 10 K and 250 ± 30 K. For a pure threefold barrier this leads to $V_3/k = 160$ K above T_p and $V_3/k = 325$ K below the phase transition. INS revealed a tunnelling splitting of 159 mK in the low-temperature phase ³⁾. When this splitting is interpreted as caused by a pure threefold barrier, the barrier value becomes 325 K, confirming the QNS result.

Mössbauer work has also been done ⁶⁾, mainly above T_p ; it has been proposed that the thermal expansion in the direction of the c -axis is much larger than in the $a - a$ plane.

3. *Theory.*

In this section we will summarize the theories for specific heat and NMR as far as used in the analysis of our data.

3.1 *Specific heat.*

There are several mechanisms which lead to contributions in the specific heat. The basic assumption is that all contributions are additive, so each contribution can be dealt with separately. We shall consider here in particular the contributions from the lattice and from the molecular rotations.

3.1.1 *Lattice contributions.*

It will be convenient to discriminate among three temperature regions. The first contribution to be considered will be the lattice contribution at low temperatures. The Debye model for the lattice specific heat C_L , leads to a dependence cubed in temperature, $C_L \propto T^3$, assuming acoustic phonons (2 transversal and 1 longitudinal) in three dimensions. If the propagation of the phonons becomes preferentially two dimensional, C_L becomes proportional to the temperature squared, $C_L \propto T^2$. The two-dimensional specific heat is given by $C_V = 3R \times D_2(x)$. In a straightforward method the following equation

can be derived:

$$D_2(x) = 12Z(3)x^{-2} - \sum_{n=1}^{\infty} (2nx + 6 + 12/(nx) + 12/(nx)^2)(1/n)(\exp(-nx)) , \quad (1)$$

with $x = \theta_{D2}/T$ and $Z(s) = \sum_{k=1}^{\infty} k^{-s}$.

$Z(3) = 1.2020560932\dots$ and θ_{D2} denotes the two-dimensional Debye temperature. At low temperatures ($x > 10$) $C_V \cong 43.3 R(T/\theta_{D2})^2$.

For the lattice contribution at high temperatures the theory is simple. In the classical limit each atom possesses an energy of kT per degree of freedom, so with three degrees of freedom $C_L = 3k$.

Finally we treat the lattice contribution at intermediate temperatures. At these temperatures the complete crystal cannot be described as one entity. The mode of vibration of each kind of atom will depend on its mass and surroundings. The total Debye contribution is split up in several other Debye contributions ⁷⁾, with their own Debye temperatures θ_D ; n denotes the number of phonon modes, characterized by θ_D . As a restraint we will require that all these other Debye contributions will give the low-temperature Debye theta, corresponding to only three acoustical modes.

3.1.2 Methyl rotations.

A methyl group possesses a threefold symmetry. The proton triangle is covered by a rotation over $2\pi/3$ radians, independent of the environment. The symmetry of the eigenstates, with wave functions ψ , can be higher if there is a symmetry caused by the surroundings of the methyl group. The surrounding atoms will hinder the motion of the methyl group. The hindering barrier V , can be expanded in a Fourier series,
 $V(\phi) = \sum_n (V_n/2)(1 - (-1)^{p_n} \cos 3n\phi)$, $p_n = 0$ or 1 ; ϕ denotes the angular position of the protons. The energy states, E , are calculated by solving the Schrödinger equation:

$$-\frac{\hbar^2}{2I} \frac{d^2\psi(\phi)}{d\phi^2} + V(\phi) \psi(\phi) = E \psi(\phi) , \quad (2)$$

which can readily be transformed into the Mathieu equation. The moment of inertia I , being only slightly dependent on environment, is known e.g. from infrared measurements ⁸⁾: I equals $5.3 \times 10^{-47} \text{ kg m}^2$.

The eigenstates are labelled according to the irreducible representation of group C_{nv} . The free rotor quantum number, m , is still used. If $m \equiv 0 \pmod{3}$, ψ is not degenerate. The other ψ 's are twofold degenerate. The nuclear spin of the protons is another source of degeneracy. For instance, by the method of group theory or by projection operator techniques the nuclear degeneracy can be determined. The final result is that all eigenstates are fourfold degenerate.

For a given potential barrier the energies are known and the specific heat can be calculated. If the number of relevant energy levels is $(N+1)$, the specific heat of a system consisting of 1 mol is given by:

$$\frac{C(T)}{R} = \frac{\sum_{i=0}^N g_i (x_i)^2 e^{-x_i}}{\sum_{i=0}^N g_i e^{-x_i}} - \left\{ \frac{\sum_{i=0}^N g_i x_i e^{-x_i}}{\sum_{i=0}^N g_i e^{-x_i}} \right\}^2 ; \quad (3)$$

$x_i = E_i/kT$ and g_i is the degeneracy. The successive energy levels are labelled by i : E_0, E_1 etc.

3.2 NMR theory.

The relaxation behaviour of the Zeeman energy of the proton spins is determined by three systems: the nuclear spin system (Zeeman and dipolar), the rotor system (rotational polarization and tunnelling system), and the phonon system⁹⁾; both spin and rotor states have a specific symmetry. The autorelaxation rate of the proton Zeeman system, S_{ZZ} , which can be derived from or might directly be observed in a relaxation experiment^{10,11)}, is given by:

$$S_{ZZ} = A \left(J(\omega_t - \omega_0, \tau_c) + J(\omega_t + \omega_0, \tau_c) + 4J(\omega_t - 2\omega_0, \tau_c) + 4J(\omega_t + 2\omega_0, \tau_c) \right) . \quad (4)$$

The spectral density function $J(\omega, \tau_c)$ is assumed to be given by $J(\omega, \tau_c) = \tau_c / (1 + \omega^2 \tau_c^2)$, in which τ_c is a correlation time. In eq.(4) we have neglected the contribution of the interrelaxation to the spectral densities at ω_0 and $2\omega_0$, ω_0 being the Larmor frequency of the nuclear spin. The effective tunnelling splitting ω_t -the weighted energy difference between the rotational A and E subsystems- becomes lower for increasing temperatures.

At the lowest temperatures, ω_t equals the tunnelling splitting between the ground and first excited rotational state. In our experiments $\omega_t \gg \omega_0$ and $\omega_t \tau_c \ll 1$, so that $J(\omega, \tau_c) = \tau_c$. The coefficient A, dependent on both intra- and inter-contributions, contains the ratio, p, of the number of proton spins in the methyl groups to the total number of proton spins and an efficiency factor δ^2 , given by:

$$\delta^2 = |\langle \psi(RA) | \exp(2i\phi) | \psi(RE) \rangle|^2, \quad (5)$$

with $\psi(RA) = \{\bar{E}_t |c_t(RA)|^2 |\psi_t(RA)|^2\}^{\frac{1}{2}}$, etc. The weighted population of the A symmetric part (wave function $\psi_t(RA)$) of the t^{th} torsional rotor level is denoted by $|c_t(RA)|^2$. If $\omega_0 \tau_c \ll 1$ the autorelaxation rate of the Zeeman system becomes:

$$S_{ZZ} = K \delta^2 \tau_c. \quad (6)$$

In eq.(6) K is a proportionality constant. Using $\tau_c = \tau_0 \exp(E_a/kT)$, we get the following relation between S_{ZZ} values at two different temperatures T_1 and T_2 , S_{ZZ1} and S_{ZZ2} respectively:

$$E_a/k = (1/T_1 - 1/T_2)^{-1} \times \ln(S_{ZZ1}/S_{ZZ2}) + (1/T_1 - 1/T_2)^{-1} \times \ln(\delta_2^2/\delta_1^2). \quad (7)$$

With eq.(7) the activation energy E_a can be calculated

4. *Experimental data and interpretation.*

We use the same categories as in the previous section.

4.1 *Specific heat.*

First we discuss the low-temperature data. Fig. 2 displays the results of the measurements between 1 and 100 K. A small peak at 70.4 ± 0.2 K is obvious. No thermal hysteresis was observed in the peak temperature between measurements performed at increasing and decreasing temperature, so we conclude the phase transition to be of second order. The insert displays the low-temperature results on a logarithmic scale. Below 4 K there is no linear

relation neither between C and T^3 or between C and T^2 . Above 4 K, C is fairly well proportional to T^3 . The compound possesses two methyl groups, which might exhibit internal rotations. At not too low a value of a threefold barrier, the specific heat at low temperatures can be described by the two lowest energy levels. The energy difference between them is much smaller than 1 K, so the rotational specific heat, C_R , above 1 K is proportional to T^{-2} .

For the total specific heat $C = C_L + C_R$, one obtains depending on the lattice dimensionality $CT^2 = a + bT^5$ or $CT^2 = a + bT^4$. Fig. 3 displays both results in the same temperature region. After the subtraction of an average T^{-2} contribution, the deviations from the theory are in case of T^4 smaller than for T^5 : the dimensionality of the lattice changes as far as acoustic phonons are concerned. When extrapolating the lines a and b in fig. 3, the results for Θ_{D2} , Θ_{D3} , hereafter denoted by Θ_D and a (the coefficient of T^{-2}) are 300 K, 90.3 K and 1.8 mJ K/mol.

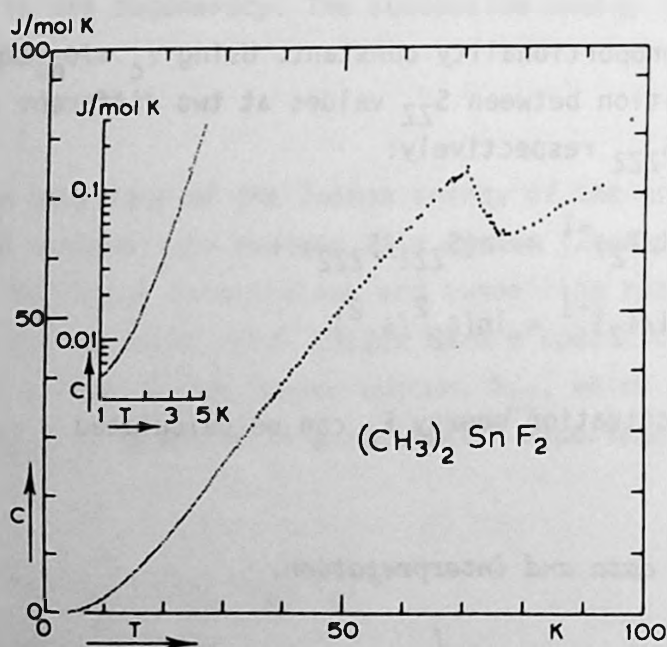


Fig. 2 The specific heat C of $(CH_3)_2 Sn F_2$ as a function of temperature. The insert displays on a logarithmic scale the low-temperature data.

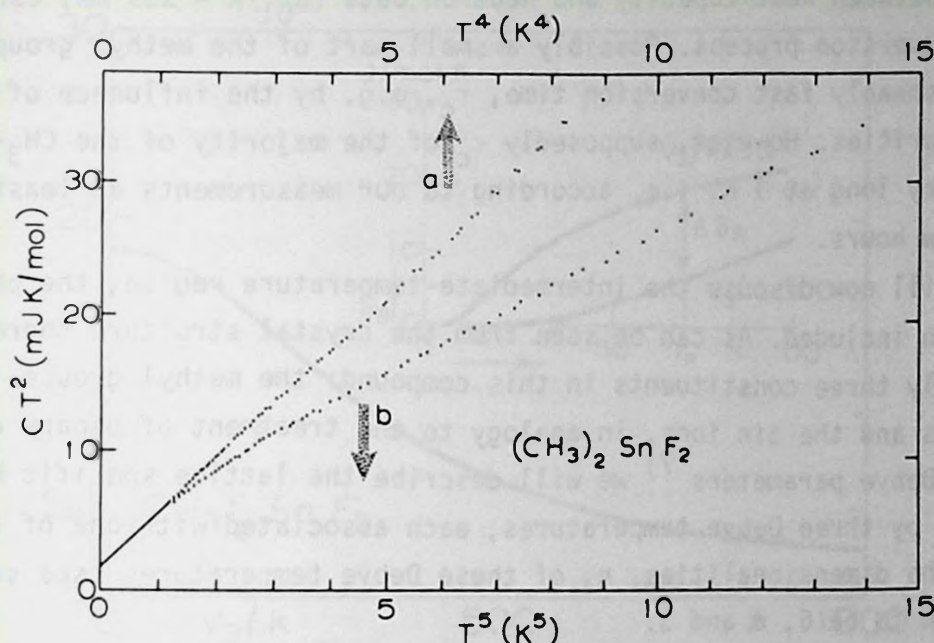


Fig. 3 The specific heat C of $(\text{CH}_3)_2 \text{Sn F}_2$ in a CT^2 vs. T^4 (a) and vs. T^5 (b) plot. The (a) plot displays that C is proportional to T^2 . The solid line below 1 K is the extrapolation of line (a); it displays the high-temperature tail of a Schottky type anomaly.

The symmetry of the methyl group is threefold. The surroundings of the methyl group are dominated by four fluorines, introducing a site symmetry of four. Therefore the total symmetry of the potential well could be twelve. However, QNS experiments revealed that both below as above T_p the total symmetry of the barrier is threefold. The heat-capacity data in the low-temperature region ($T < 20$ K) do not allow us to state the symmetry below T_p . So we follow the results for the symmetry as obtained by the neutron experiments.

From the value of the coefficient of T^{-2} we calculate the energy splitting (Δ_{01}/k) between E_1 and E_0 to be 20 mK. The corresponding threefold barrier, V_3/k will be 500 K. In order to establish Δ_{01}/k more accurately, we measured the specific heat between 150 mK and 1 K in an adiabatic demagnetization set-up. The measurements did not reveal a Schottky anomaly, neither

the maximum, nor its high-temperature tail. An explanation for the discrepancy between heat-capacity and neutron data ($\Delta_{01}/k = 159 \text{ mK}$) can be found in the conversion process. Possibly a small part of the methyl groups ($\approx 2\%$) has a reasonably fast conversion time, τ_c , e.g. by the influence of O_2 or other impurities. However, supposedly τ_c of the majority of the CH_3 -groups may be very long at 1 K, i.e. according to our measurements at least longer than a few hours.

We will now discuss the intermediate-temperature region, the phase transition included. As can be seen from the crystal structure there are essentially three constituents in this compound: the methyl groups, the fluor ions and the tin ions. In analogy to the treatment of binary compounds with two Debye parameters ⁷⁾ we will describe the lattice specific heat in this case by three Debye temperatures, each associated with one of the groups. The dimensionalities, n , of these Debye temperatures (see section 3) are chosen to be 6, 6 and 3.

The values of these three Debye thetas must be determined experimentally. We will fit our experimental data by one rotational and three lattice contributions. The procedure followed was to vary only one parameter. At each measured temperature the theoretical and the experimental specific-heat values were plotted on a video screen and were compared by visual inspection.

It should be remarked that up to a temperature of 30 K, C_L is completely determined by the low-temperature Debye temperature. Since at 30 K the contribution of the phase transition is small, C consists only of C_L and C_R . In order to prevent the calculated specific heat C_{calc} exceeding C_{exp} , there exist a lower limit to V_3/k namely 330 K. Using similar arguments between 80 and 95 K, the range of the values for the high-temperature barrier is 50-200 K. We will describe two models for the explanation of the observed phenomena.

In the first model the rotational barrier changes in the phase transition, whereas the parameters, characterizing the lattice contribution, do not change. If we assume a low barrier above T_p and a high one below T_p , we can see in the insert of fig. 4 that at temperatures above 10 K, there is a considerable difference in entropy between the two barriers. If we change the barrier at a certain temperature, we see that the system can gain entropy when the temperature is rising. The involved entropy is independent whether a gradual or a stepwise change in barrier height occurs; we can use the stepwise change for the ease in the calculations:

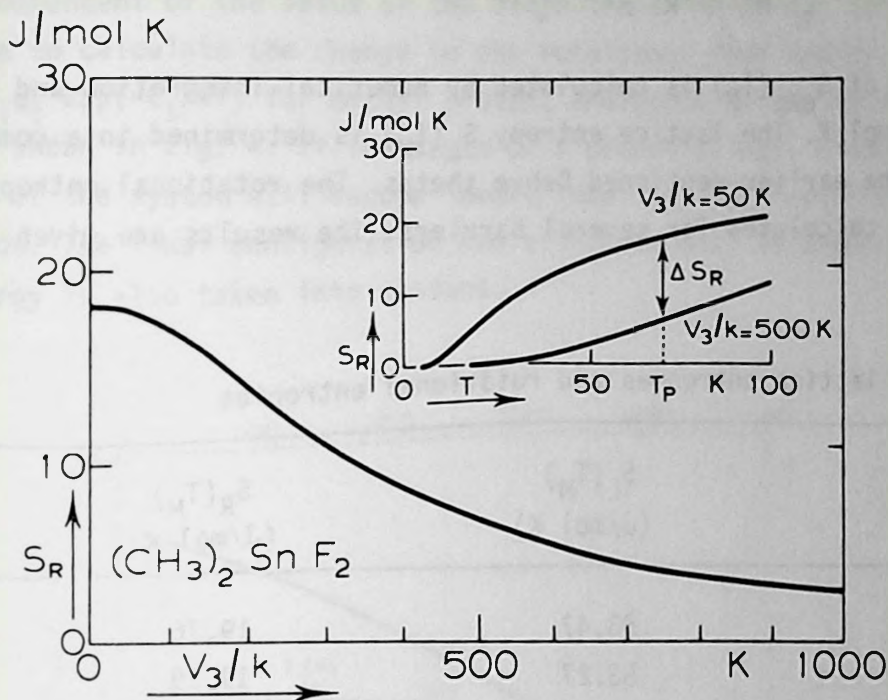


Fig. 4 The rotational entropy S_R of two threefold hindered rotors vs. the barrier V_3/k at a temperature of 70.4 K. The insert displays the rotational entropy gain ΔS_R at the transition temperature T_P , if, supposedly, the barrier is changed from 50 K to 500 K.

$$\Delta S = S_R^H(T_P) - S_R^L(T_P) \quad . \quad (8)$$

The entropy difference given by eq.(8) must be compared with the entropy excess found by taking the experimental entropy at T_M , $S_{\text{exp}}(T_M)$, and subtracting the lattice entropy, $S_L(T_M)$, and the rotational entropy above and below the phase transition, respectively $S_R^H(T_M) - S_R^H(T_P)$ and $S_R^L(T_P)$:

$$\Delta S = S_{\text{exp}}(T_M) - S_L(T_M) - \left(S_R^H(T_M) - S_R^H(T_P) \right) - S_R^L(T_P) \quad . \quad (9)$$

For the correct barriers above and below the phase transition combination of eq.(8) and eq.(9) gives:

$$S_{\text{exp}}(T_M) - S_L(T_M) - S_R^H(T_M) = 0 \quad . \quad (10)$$

The values of $S_{\text{exp}}(T_M)$ is calculated by numerical integration and amounts to 71.3 J/mol K. The lattice entropy $S_L(T_M)$ is determined in a computation based on the earlier mentioned Debye thetas. The rotational entropy, $S_R(T_M)$, is calculated for several barriers. The results are given in table 1.

Table 1

Results of lattice entropies and rotational entropies

V_3/k (K)	$S_L(T_M)$ (J/mol K)	$S_R(T_M)$ (J/mol K)
100	53.47	19.76
110	53.27	19.59
120	53.27	19.40
130	53.09	19.22
140	53.09	19.06
150	52.92	18.88
160	52.59	18.54
170	52.59	18.27
180	52.39	17.98

It follows from eq.(10) that the determination of the barrier above T_p is independent of the barrier value below the phase transition. As already mentioned, the heat-capacity data could be fitted with high-temperature barriers between 50 K and 200 K. From the entropy calculation (eq.(10)) the barrier is determined to be $V_3/k = 160 \pm 10$ K.

In the second model, at the phase transition not only the barrier height but also the Debye thetas characterizing the lattice contribution change. In eq.(9) $S_L(T_M)$ has to be changed to $(S_L^H(T_M) - S_L^H(T_p)) - S_L^L(T_p)$. Using similar arguments for ΔS as in the first model, eq.(10) reduces to:

$$S_{\text{exp}}(T_M) - S_L^H(T_M) - S_R^H(T_M) = 0 \quad , \quad (11)$$

which is independent of the value of the Debye thetas below T_p . It is also illustrative to calculate the change in the rotational free energy $F = -kT \ln \sum_i g_i \exp(-E_i/kT)$ for methyl groups, analogous to the entropy calculation shown in fig. 4. If the depth of a potential well increases, the free energy of the system will become lower, (see fig. 5), favouring this new situation. The final configuration can of course only be predicted if the lattice energy is also taken into account.

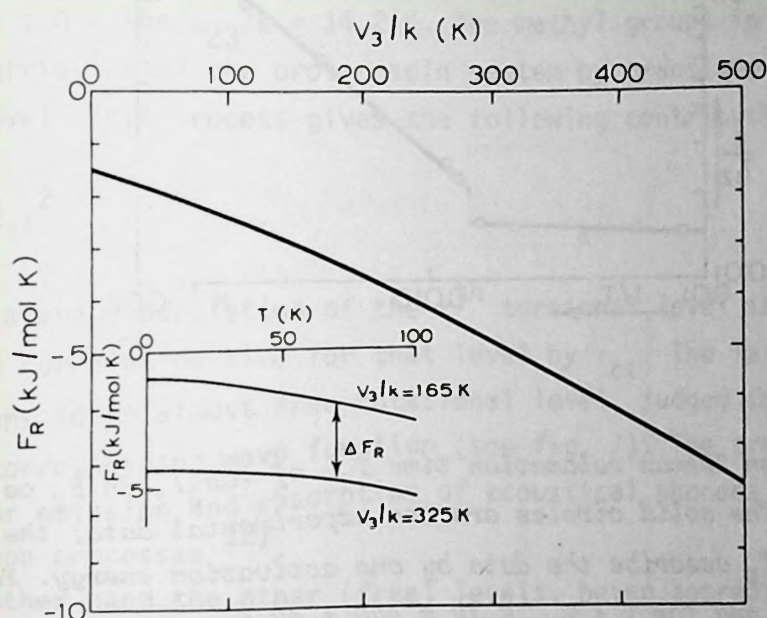


Fig. 5 The rotational free energy F_R at 70.4 K of two threefold hindered rotors for increasing depths of the potential well. The insert shows the decrease in free energy ΔF_R , if, supposedly, the barrier is changed from 165 K to 325 K.

4.2 NMR-data.

The observed Zeeman relaxation times (T_{1Z}) vs. T^{-1} are plotted in fig. 6. The recovery of the magnetization of the proton spins was exponential, probably because of an appreciable intercontribution to the relaxation. No dependence of T_{1Z} on sample rotation was found¹¹⁾. If these T_{1Z} data are analyzed with eq.(6), in which a simple Arrhenius law is supposed for the correlation time τ_c , then the data taken at a temperature above the phase

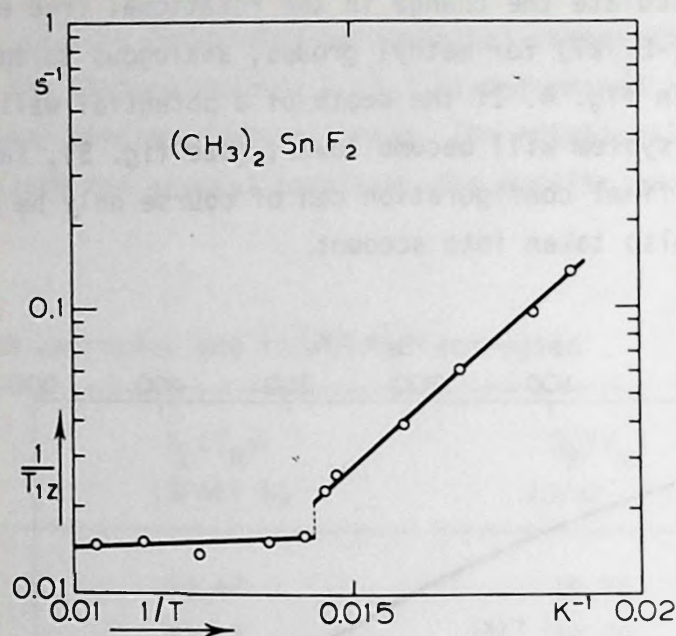


Fig. 6 The proton Zeeman relaxation time T_{1Z} of $(CH_3)_2 Sn F_2$ as a function of temperature. The solid circles are the experimental data; the solid lines above and below T_P describe the data by one activation energy. For $T > T_P$, $E_a/k = 40 \pm 20$ K and for $T < T_P$, $E_a/k = 400 \pm 40$ K.

transition temperature T_P , give an apparent activation energy $E_a/k = 40 \pm 20$ K. In this estimate the efficiency factor is assumed to be temperature independent. On the low-temperature side of T_P the apparent activation energy becomes $E_a/k = 400 \pm 40$ K. The temperature of the phase transition is seen to be at 70 ± 1 K.

5. Comparison of the results.

In this section we will first compare the results in the high-temperature phase and thereafter consider the low-temperature data.

5.1 High-temperature phase.

QNS and heat-capacity data give the same value for the high-temperature barrier: $V_3/k = 160 \pm 10$ K or 1.33 kJ/mol. For the interpretation of the activation energies found by NMR in such a low-barrier system, one has to know the energy level scheme and the wave functions. For the barrier $V_3/k = 165$ K, fig. 7 gives the energy levels and the corresponding wave functions. The energy splitting between the torsional ground state ($t=1$) and the first excited state ($t=2$) is $\Delta E/k = 87$ K, the tunnelling splitting being $\Delta_{01}/k = 1.0$ K and $\Delta_{23}/k = 14.2$ K. The methyl groups in the levels within the barrier relax the proton spin system by transitions to a free rotational level. This process gives the following contribution to S_{ZZ} :

$$S_{ZZ} \propto \left[\sum_t |\bar{c}_t|^2 \tau_{ct}^{-1} \right]^{-1} \quad (12)$$

The weighted average population of the t^{th} torsional level is denoted by $|\bar{c}_t|^2$ and the correlation time for that level by τ_{ct} . The latter is calculated for transitions to an almost free rotational level, judged from the ϕ -dependence of the corresponding wave function (see fig. 7). The transitions are calculated for emission and absorption of acoustical phonons in one or multiple phonon processes ¹²⁾.

On the other hand the other (free) levels, being appreciably populated for a part in this low-barrier system, directly relax the nuclear spin system. Even the second E-level, see figure 7, can be regarded as almost free. If we assume that the correlation times of these free levels depend only slightly on temperature in the temperature range considered, we get:

$$S_{ZZ} \propto \sum_f |c_f|^2 \tau_{cf} \quad , \quad (13)$$

with τ_{cf} independent of T . The index f labels the (almost) free rotor states.

The temperature dependence of S_{ZZ} in the latter class of processes is positive, while the first class give a negative temperature coefficient. The cancellation of the T -dependence of both contributions explains the flat temperature dependence as observed in the high-temperature phase.

The resemblance with another low-barrier system, γ -picoline, is striking. A very flat temperature dependence of T_{12} was also observed in γ -picoline ¹³⁾ over an appreciable temperature region: the apparent activation energy as measured by NMR between 150 K and 25 K did not exceed $E_a/k = 50$ K.

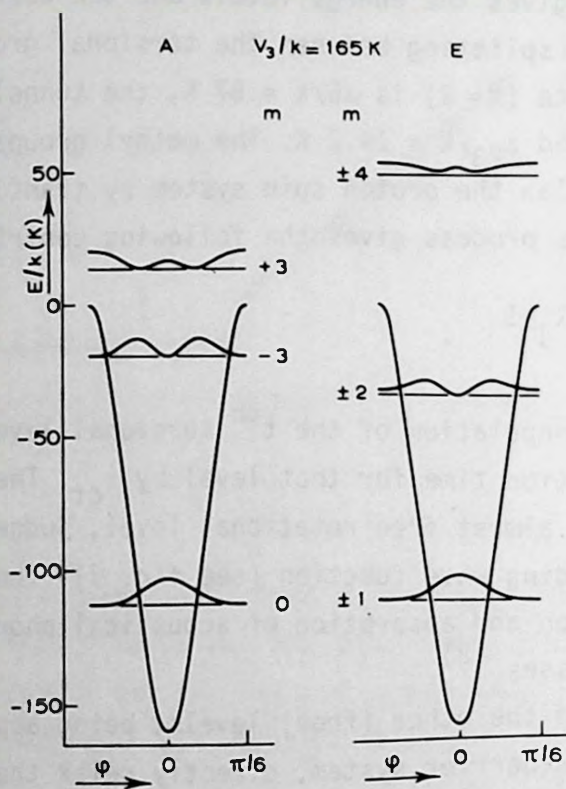


Fig. 7 The energy levels with the corresponding angular distribution of a hindered rotor by a threefold barrier of $V_3/k = 165 \text{ K}$, are shown. The levels are labelled by the free rotor quantum number m .

5.2. Low-temperature phase.

From QNS and INS a low-temperature barrier $V_3/k = 325 \pm 5$ K (see table 2) is deduced. Heat-capacity data supply a lower limit to the height of the barrier of 330 K, if a threefold barrier is assumed. Although the value found from QNS and INS is at the edge of the possible range, set by the heat-capacity measurements, the values found are in agreement. For the NMR data we will follow the same line as in the high-temperature phase and start with the barrier deduced from neutron scattering. The level scheme belonging to $V_3/k = 325$ K and the corresponding wave functions are given in fig. 8.

Table 2

The low-temperature and high-temperature barriers.

Method	$V_3/k, T < T_p$	$V_3/k, T > T_p$
Neutron spectroscopy: quasi elastic ^{1,3)}	325 ± 30 K	160 ± 20 K
inelastic ³⁾	325 ± 5 K	-----
Specific heat	> 330 K	160 ± 10 K
NMR, E_a/k	(400 ± 40) K	(40 ± 20) K

If we then calculate the temperature dependence of the efficiency factor, the activation energy is found to be $E_a/k = 390$ K and $\tau_0 = 3 \times 10^{-15}$ s. Also the correlation times τ_{ct} for the various levels can be calculated, resulting in an overall τ_c , given by eq.(12). A comparison between calculated and experimental data shows that the value of E_a/k is improbably high for the energy level scheme used, while the value of τ_0 is unusually short.

If we assume that only a part of the methyl groups (e.g. 2% i.e. $p=0.02$) is responsible for the observed relaxation, having a barrier which is slightly different from the main one $-V_3/k = 500$ K in stead of 325 K- we get the right E_a/k and $\tau_0 \approx 10^{-13}$ s, a value familiar for the rotational correlation times. That a small part of the methyl groups behaves differently is also seen in the low-temperature tail of the heat-capacity data. It may be noted that a

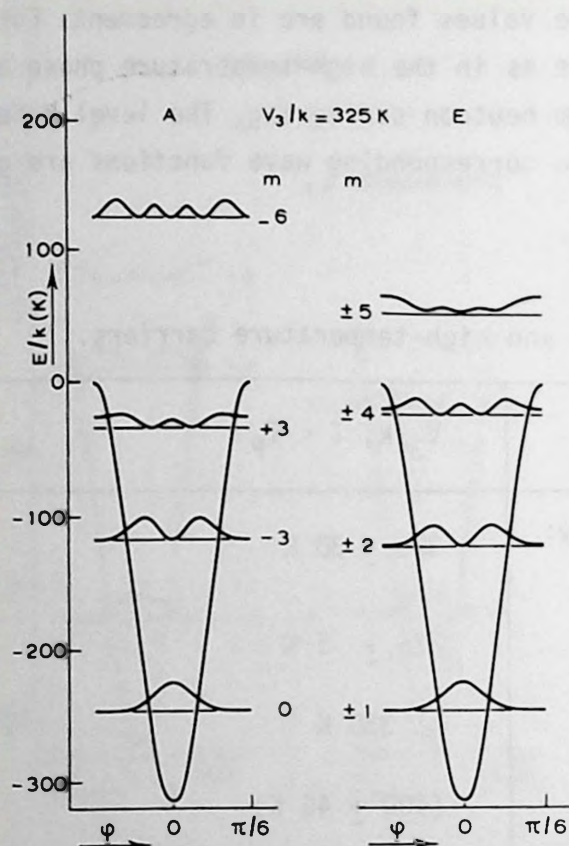


Fig. 8 This figure is essentially the same as fig. 7, however $V_3/k = 325$ K.

simple alternative solution as taking another form of the barrier, e.g. a mixture of V_3 with V_6 , giving the right tunnelling splitting (INS) and the right activation energy (NMR) has to conform to the heat-capacity data too. This appeared as a strong restraint: a barrier like $V_3/k = 424$ K with $V_6/V_3 = 0.39$ is not possible, because it gives excessive specific heat around 30 K.

5.3 Dielectric measurements.

The dielectric constant ϵ is closely related to the electric susceptibility, χ , which bears a strong analogy to the magnetic susceptibility. For polar molecules χ obeys the Curie law, $\chi \propto T^{-1}$. For non-polar molecules χ is temperature independent. Sudden changes in χ give an indication for a phase transition. The measurements were performed between 35 K and 140 K. The recorded capacitance of the filled capacitor, corrected for the empty-cell contribution is displayed in fig. 9. A small peak at 70 K is present, which agrees with the temperature at which the maximum in specific heat occurs. Since the theory for the dielectric behaviour of a system of rotating molecular groups is not well developed, we will not analyze these data in more detail.

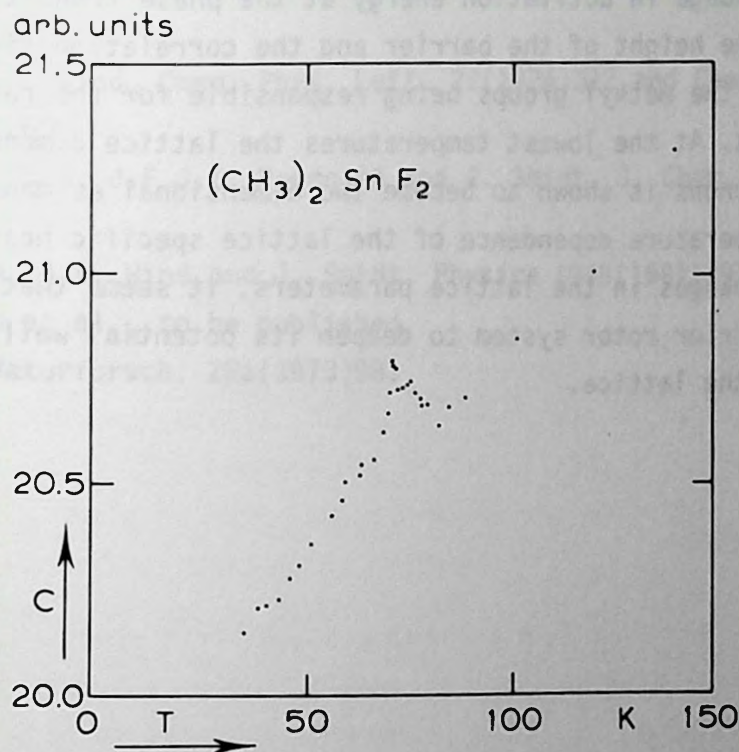


Fig. 9 Plot of Δc of $(\text{CH}_3)_2 \text{Sn F}_2$ vs. temperature. Δc is proportional to the capacitance of the cell filled with $(\text{CH}_3)_2 \text{Sn F}_2$, and is corrected for the empty-cell contribution.

6. Conclusion.

It is shown that the entropy calculations based on the heat-capacity data supply a value for the high-temperature barrier. In that calculation the lattice entropy has to be estimated, which determines the error in the final result. The very low activation energy found by nuclear relaxation measurements above T_p can be understood using the level scheme of the appropriate barrier. In the case of a low-barrier system it is not possible without that knowledge to determine the height or form of the barrier. In the low-temperature phase, inspection of the heat-capacity curve gives the lower limit of the range of barrier heights. Calculation of the total entropy gain in the phase transition -which is clearly seen to occur at $T = 70.4$ K- appeared to be too inaccurate to refine that estimate. NMR clearly shows the change in activation energy at the phase transition. The values found for the height of the barrier and the correlation time τ_0 point to a minority of the methyl groups being responsible for the relaxation of the proton spins. At the lowest temperatures the lattice dimensionality for acoustic phonons is shown to become two dimensional as manifested by the squared temperature dependence of the lattice specific heat. From the absence of abrupt changes in the lattice parameters, it seems that the tendency of this low-barrier rotor system to deepen its potential well is only slightly opposed by the lattice.

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CHAPTER 4

CALORIMETRIC INVESTIGATIONS OF THE MONO-METHYL-PYRIDINES

Synopsis.

The specific heat of 2-, 3- and 4-methyl-pyridine (2MP, 3MP and 4MP) is measured between 1.5 and 90 K. In these compounds the methyl group displays a hindered internal rotation. From the data the barriers against the rotational motion are derived and for 4MP (γ -picoline) the conversion time as a function of temperature is deduced and analyzed. These results are found to be in good agreement with the available data from inelastic neutron scattering and nuclear magnetic resonance experiments.

1. *Introduction.*

4-Methyl-pyridine (γ -picoline) was the first compound, that showed nuclear dipolar polarization upon application of a sudden temperature variation of the lattice ^{1,2)}. This phenomenon appeared to be a direct consequence of the symmetry properties of the rotating methyl group. Since that time a number of NMR ^{3,4)} and inelastic neutron scattering ^{4,5)} (INS) studies have been performed on several members of the methyl-pyridine family. They reveal a large tunnelling splitting in 4MP while in 2MP and 3MP the splitting is appreciably smaller. In this chapter specific-heat measurements are described, that provide additional information for the description of the rotational motion of the methyl group. Since the barriers are low, the molecule will

display internal rotation down to low temperatures, where rotational specific heat dominates the specific-heat contribution of the lattice vibrations.

2. Apparatus and samples.

The specific heat was measured between 1.5 and 90 K in an adiabatic set-up using the heat pulse method. Since the methyl-pyridines are liquids at room temperature, having a vapour pressure of about 1 kPa, reduction of the mass of the sample by the vacuum pumps should be prevented. The compounds, weighing about 10 g, were sealed hermetically in a gold-plated copper calorimeter, which was suspended in vacuo by nylon threads. The container had a weight of 10 g, a diameter of 2 cm and a length of 3 cm. It was equipped with a vane, which could be clamped between the jaws of a mechanical heat switch. Heat was provided by a 200 Ω Evanohm resistance wire. The temperature was measured by a carbon film resistor (10 k Ω at 4 K, 2.5 k Ω at 100 K), which was calibrated against the vapour pressure of liquid helium, normal hydrogen and oxygen. The temperature of the sample was continuously recorded by a strip chart recorder and sampled once per second by a digital data collecting system. The heat capacity of the empty calorimeter was measured beforehand.

The 4MP sample was remeasured between 3.5 and 15 K for reasons, which will be explained in section 4. During this measurement the calorimeter was surrounded by a copper heat shield. Its temperature was measured with a separate carbon resistor. The temperature of the shield, also provided with a resistance heater, could be kept within 2 mK during more than 24 hours by means of a proportional and integrating regulator.

The samples were provided by Baker. Their purity was better than 97%, impurities consisting almost entirely of the related methyl-pyridines. The boiling points ⁶⁾ of 2MP, 3MP and 4MP are respectively 128.8, 144.1 and 144.9 °C and the melting points are at -68.8, -18.3 and 3.8 °C. These liquids are known to be aggressive to organic materials such as plastics and rubbers. It can be stored safely in teflon, pyrex, stainless steel and gold. The densities at 90 K ⁷⁾ are 1134, 1098 and 1163 kg/m³.

The crystal structures were determined ⁷⁾ to be of the monoclinic space group P2/m, P2₁/m and P2₁/c, assigned with the Wyckoff numbers 10, 11 and 14. However the positions of the atoms in the unit cell are not known. 3MP and 4MP contain 4 molecules per unit cell; 2MP contains 8 molecules per unit

cell, but it should be mentioned that the volume of its unit cell is about twice as large as the unit-cell volume of 3MP and 4MP.

Microwave spectra on 2MP and 4MP vapour indicate low barriers for internal rotation. The spectrum of 2MP⁸⁾ was analyzed by means of a barrier $V(\phi) = (V_3/2)(1-\cos 3\phi) + (V_6/2)(1-\cos 6\phi)$ with $V_3/k = 130$ K and $V_6/k = -6$ K. The barrier of 4MP⁹⁾ was described by one term only $V(\phi) = (V_6/2)(1-\cos 6\phi)$ with $V_6/k = 7$ K.

In the solid state INS measurements⁴⁾ on 3MP revealed a barrier [defined by $V(\phi) = (V_3/2)(1-(-1)^p \cos 3\phi) + (V_6/2)(1-(-1)^p \cos 6\phi)$] of $V_6/k = 421$ K and $V_3/k = 120$ K with $p=1$. Also the activation energies derived from nuclear-relaxation data⁴⁾ on 3MP could be understood with the same barrier. For 2MP no barrier could be deduced from the NMR data. For 4MP, INS results⁵⁾ were interpreted by a sixfold barrier $V_6/k = 200$ K.

3. Theory.

There are several contributions to the total observed specific heat. Because they are additive, we can deal with them separately.

3.1 Lattice contribution.

We will divide the temperature range into two regions: the low-temperature and the high-temperature region. In the low-temperature region the Debye model leads to a behaviour of the specific heat proportional to the temperature cubed, $C_L \propto T^3$, under the assumption that only acoustic phonons are present, having two transversal and one longitudinal mode. At higher temperatures deviations between theory and experiment are found. In order to describe the experimental data in this region a phenomenological model is used. In these molecular crystals the specific heat is approximated by two Debye functions:

$$C_L(T)/R = 3D(^1\theta_D/T) + 3D(^2\theta_D/T) \quad , \quad (1)$$

where $^1\theta_D$ and $^2\theta_D$ are the characteristic Debye temperatures. D is given by¹⁰⁾

$$D(x) = (0.8\pi^4/x^3) -$$

$$\sum_{n=1}^{\infty} \left(3nx + 12 + 36/nx + 72/(nx)^2 + 72/(nx)^3 \right) / \left(n \exp(nx) \right) \quad , \quad (2)$$

with $x = \theta_D/T$. Furthermore we require that the specific heat, obtained in this way, continuously changes into the observed low-temperature specific heat. Hence the following relation exists among θ_D , $^1\theta_D$ and $^2\theta_D$:

$$\theta_D^{-3} = (^1\theta_D)^{-3} + (^2\theta_D)^{-3} \quad . \quad (3)$$

3.2 Rotational contribution.

The methyl-pyridines contain a methyl group, which is attached to the planar pyridine ring. The direction of the bond between the methyl group and the pyridine ring is perpendicular to the proton triangle. This line is at least a threefold rotational symmetry axis, since a rotation of $2\pi/3$ radians around this axis transforms the proton triangle into itself. The rotation around this axis will be energetically favourable above rotations about other symmetry axes. The eigenfunctions ψ of the threefold rotations will be only dependent on the angular coordinate ϕ . If a hindrance occurs to a freely rotating motion around the threefold axis, we can describe this by a potential barrier $V(\phi)$, which can be expanded in a Fourier series with a periodicity of $2\pi/3$ radians, due to the methyl group symmetry.

$$V(\phi) = \sum_{n=1}^{\infty} (V_{3n}/2)(1-(-1)^{p_n}) \cos 3n\phi; \quad p_n = 0 \text{ or } 1.$$

The energies, belonging to eigenfunctions $\psi_m(\phi)$, are calculated by solving the Schrödinger equation:

$$-\frac{\hbar^2}{2I} \frac{d^2 \psi(\phi)}{d\phi^2} + V(\phi)\psi(\phi) = E\psi(\phi) \quad , \quad (4)$$

I denotes the inertial moment of the planar rotating methyl group, and is slightly dependent on the environment. Its numerical value¹¹⁾ amounts to $5.3 \times 10^{-47} \text{ kgm}^2$. The energies can be labelled by index m , which is the free rotor quantum number. The eigenfunctions ψ_m are divided into three classes, characterized by the irreducible representations of group C_{3v} . For $m \equiv 0 \pmod{3}$ ψ_m is non-degenerate (type A species). In the other cases ψ_m is twofold

degenerate (E species). The total degeneracy, including proton spin degeneracy, of all levels is fourfold ¹²⁾. The partition function can be easily calculated, from which the specific heat is derived. Transitions between eigenstates possessing different types of ψ are in first order prohibited. In general the associated conversion time τ_c will be strongly temperature dependent ¹³⁾. We can consider two extreme situations: the conversion time τ_c is small compared to the time t_m , needed for a measurement, or τ_c is large compared to t_m . In the first case the theoretical specific heat must be calculated from all possible transitions, which is denoted as the equilibrium specific heat, and in the second case only transitions between the same symmetry type of energy levels have to be taken into account, called the normal specific heat.

In general the potential barrier to internal rotation of methyl groups will be threefold. For 4MP, the twofold symmetry of the pyridine ring combined with the threefold symmetry of the methyl group favours a sixfold symmetry as is also seen in microwave experiments in the vapour phase. In the solid state, intermolecular forces contribute to the potential barrier. INS data ⁵⁾ on 4MP show that the main symmetry of the potential barrier remains sixfold.

3.3 *Trunk rotation and rocking methyl groups.*

The final contribution to the specific heat arises from torsional motions of the pyridine ring and rocking modes of the methyl group. Since the corresponding energies ¹⁴⁾ are rather large compared to the temperature region of our experiment, only the low-temperature onset is observed, hence the specific heat is fitted by Einstein functions.

3.4 *Conversion.*

By the rotor-phonon interaction internal Boltzmann equilibrium in the A and E subsystems of the rotor can be established in first order. To bring the combined rotor system into equilibrium with the lattice, a part of the methyl groups must be converted from A to E symmetry (conversion process). The perturbation, that generates these transitions, is given by the sum of the (non-secular part of the) dipolar hamiltonian and the rotor-phonon interaction. Let us consider the high field case i.e. the external field exceeds the dipolar fields. Furthermore, for the moment, we will simplify the rotor system to a system consisting of one (effective) A level with a total nuclear spin value $\tilde{I} = 3/2$, split up by the magnetic field into 4 levels, and one E_a

and E_b level with $\tilde{I} = \frac{1}{2}$, split up into 2 levels each. The energy gap between A and (E_a, E_b) states is given by the effective tunnelling splitting $\hbar\omega_t$. In this way the rotational system has become an eight-level spin system, with one constraint: the conservation of the number of particles. So it has seven degrees of freedom and as a consequence the occupation number operator, ρ , can be expressed as a function of a complete set of seven mutually orthogonal, traceless diagonal operators O_k and the unit operator¹⁵⁾. It can be shown (see eq.(5)) that the tunnelling system, corresponding to operator O_6 , and the dipolar system, corresponding to operator O_5 , are coupled together. While in NMR experiments the conversion process is studied by observing the time development of the dipolar signal (corresponding to the temperature of the dipolar system), specific-heat experiments probe the evolution of the temperature of the tunnelling system, as will be clarified below.

We will introduce the parameter $x = z\langle O_5 \rangle$, in which the expectation value of $\langle O_5 \rangle$ is multiplied by $z = (3\cos^2\beta - 1)$, β being the angle between the normal to the CH_3 -rotor plane and the direction of the magnetic field; for polycrystalline samples, one has to average all possible orientations. The out-of-equilibrium value of the tunnelling system is denoted by $y = \langle O_6 \rangle - \langle O_6 \rangle^0$. Here $\langle O_6 \rangle^0$ corresponds to the equilibrium population difference of A and E levels:

$$\langle O_6 \rangle^0 = (\exp(\epsilon^0) - \exp(-\epsilon^0)) / 8(\exp(\epsilon^0) + \exp(-\epsilon^0)) ,$$

with $\epsilon^0 = \hbar\omega_t / 2kT_L$.

When a heat pulse is supplied to the system, the population of the levels will change, only transitions between the same symmetry type of levels being allowed. Therefore the ratio of the population of the A levels and of the E levels is no longer in Boltzmann equilibrium with the lattice temperature. By the in first order forbidden A-E transitions, the population approaches the new equilibrium value. Mathematically this process is described by the following equations, starting with the time behaviour of dipolar and tunnelling systems³⁾:

$$\begin{aligned} \dot{x} &= D_{55} x + D_{56} y \\ \dot{y} &= D_{65} x + D_{66} y \end{aligned} \quad (5)$$

The D_{ij} are given by:

$$D_{55} = -8D \exp(-\epsilon) \quad D_{56} = (16D/5\sqrt{2})\{\exp(\epsilon) + \exp(-\epsilon)\} \quad (6)$$

$$D_{65} = (8D/\sqrt{2}) \exp(-\epsilon) \quad D_{66} = -8D\{\exp(\epsilon) + \exp(-\epsilon)\}; \quad \epsilon = \hbar\omega_t/2kT_L \quad ,$$

$\hbar\omega_t$ is the effective tunnelling energy, T_L the lattice temperature, while D is related to the transition probability, see eq.(10). The general solution of eq.(5) becomes for y :

$$y = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t) \quad ,$$

C_1 , C_2 , λ_1 and λ_2 are found by solving the eigenvector and eigenvalue problem of the D matrix; in general they are complex quantities.

The eigenvalues λ_i normalized to D are:

$$\lambda_1/4D = -(\exp(\epsilon)+2\exp(-\epsilon)) + \sqrt{\exp(2\epsilon)+0.8+0.8\exp(-2\epsilon)} \quad , \quad (8)$$

$$\lambda_2/4D = -(\exp(\epsilon)+2\exp(-\epsilon)) - \sqrt{\exp(2\epsilon)+0.8+0.8\exp(-2\epsilon)} \quad ,$$

$$C_1 = D_{65} x(0)/(\lambda_1 - \lambda_2) - D_{66} y(0)/(\lambda_1 - \lambda_2) \quad , \quad (9)$$

$$C_2 = y(0) - C_1 \quad .$$

D is given by:

$$D = 2(27/256) \delta^2 \gamma^4 \hbar^2 r^{-6} R(T_L) \quad , \quad (10)$$

δ^2 is an efficiency factor ($\lesssim 1$), γ is the nuclear gyromagnetic ratio, r denotes the distance between the protons in a methyl group and R is a function of the temperature-dependent correlation times in the A and E subsystems¹³⁾ (to be discussed in the next subsections):

$$R = \tau^A P(A)/(1+(\Delta_A \tau^A/\hbar)^2) + \tau^E P(E)/(1+(\Delta_E \tau^E/\hbar)^2) + 1/(\tau_{01}(\Delta_{01}/\hbar)^2) \quad ; \quad (11)$$

$P(A)$ is the normalized population of the system having A symmetry. At low temperatures - below 15 K - the effective tunnelling splitting $\hbar\omega_t$ becomes equal to the real tunnelling splitting Δ_{01} , because only the lowest A and E levels contribute significantly to R; the highest A level is scarcely populated. τ^A and τ^E are the correlation times of the A and E states, mainly determined by the transitions between the two lower A and E levels respectively, separated in energy by an amount of Δ_A and Δ_E . The correlation time τ is given in eq.(12) for A levels (for τ^E one has to replace Δ_A by Δ_E):

$$(1/\tau^A) = (1/Q)(V/k)^2(\Delta_A/k)^3(2 \sinh(\Delta_A/kT_L))^{-1}; \quad (12)$$

V is the potential barrier. At low temperatures Q is found to be ¹³⁾:

$$1/Q = 27 k^5 C_{\text{rot}} / (8\pi\rho v^5 h^4) \quad , \quad (13)$$

ρ is the density, v is the velocity of sound and C_{rot} a coefficient of about unity. The third term in eq.(11) follows from the time-dependent second-order perturbation theory and it is in most cases negligible. At very low temperatures its contribution to R predominates. The direct conversion rate between the two ground state levels τ_{01}^{-1} is given by:

$$\tau_{01}^{-1} = (27C_{\text{rot}}/(8\pi\rho v^5 h^4))(V^2 \Delta_{01}^3)(2 \sinh(\Delta_{01}/2kT_L))^{-1} \quad . \quad (14)$$

In zero field the tunnelling system remains the same. The dipolar system now corresponds to the total rather than the truncated dipolar hamiltonian. Also the process, which establishes the internal equilibrium of the tunnelling system can be described as above. In the zero-field case C_{rot} and δ^2 will be considered as fitting parameters.

3.5 Heat capacity in a converting system.

For the analysis of the heat-capacity data in a converting system, we consider two subsystems 1 and 2, each characterized by its own heat capacity K and temperature T . System 1 consists of the lattice and rotor system in which only symmetry conserving transitions occur. System 2 is the rotor system where the temperature is brought into equilibrium with the lattice (system 1) temperature by the conversion process. The response to a heat current $\dot{Q}$ applied to system 1, is given by eq.(15), where $\beta = 1/kT$ and q is a

parameter which is simply related to the heat capacity.

$$\dot{Q} = q_1 \dot{\beta}_1 + q_2 \dot{\beta}_2 \quad . \quad (15)$$

The temperature response of system 2 is given by:

$$\dot{\beta}_2 = (\beta_2 - \beta_1) / \tau_c \quad , \quad (16)$$

where τ_c is the relaxation time for heat exchange between system 1 and 2. We will describe two situations: (a) $\dot{Q} = 0$ and (b) $\dot{Q} = P$, where P is the applied heat current. The general solution of case (a) is given by:

$$\beta_1(t) = f \exp(t/\tau) + u \quad ; \quad (17)$$

f and u are integration constants, determined by the starting conditions and $\tau = \tau_c(q_1/(q_1+q_2))$. The general solution of case (b) is given by:

$$\beta_1(t) = \eta_1 \exp(-t/\tau) + Pt/(q_1+q_2) + \eta_2 \quad ; \quad (18)$$

η_1 and η_2 are integration constants. If we demand that at $t=0$, $\beta_1(0)=\beta_2(0)$, it directly follows from eq.(14) that $\dot{\beta}_2(0) = 0$; so we derive from eq.(15) that:

$$P = q_1 \dot{\beta}_1 = K_1 \dot{T}_1 \quad \text{and thus} \quad q_1 = -kT_1^2 K_1.$$

The analytical solution of (b) in this special case is given by:

$$\beta_1(t) - \beta_1(0) = \left(-P/(q_1+q_2) \right) \times \left(t + (q_2/q_1)\tau(1-\exp(-t/\tau)) \right) \quad . \quad (19)$$

This special case, $\beta_1(0) = \beta_2(0)$, is chosen since the corresponding physical state of the two systems (in equilibrium) is easy to realize.

4. *Experimental data.*

The specific heat is displayed in the figures 1, 2 and 3 for 2MP, 3MP and 4MP. Fig. 3, 4MP, needs an explanation. The lower row of points for temper-

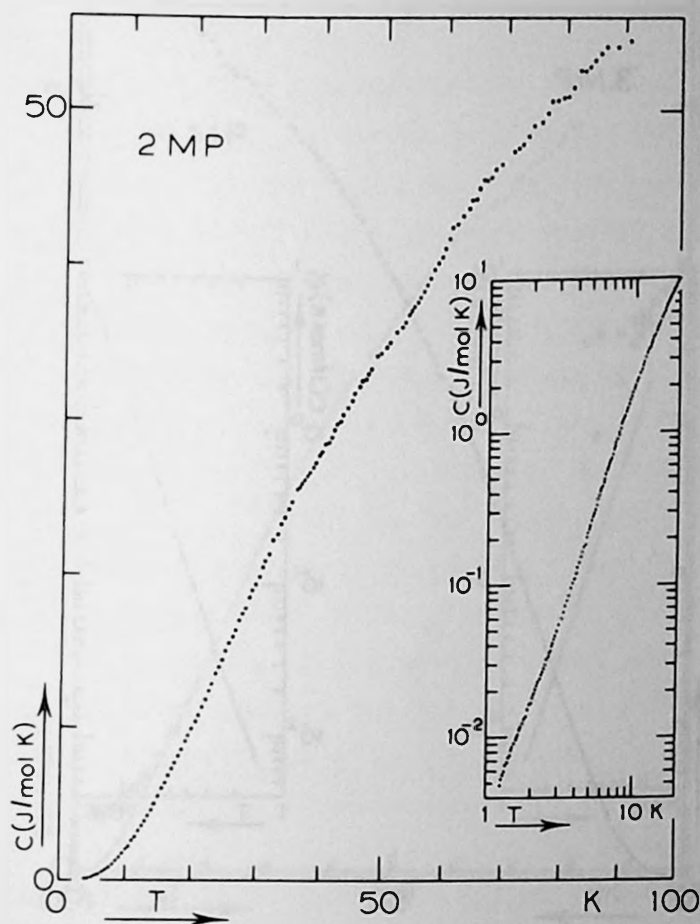


Fig. 1 The specific heat, C , of 2MP vs. temperature. The insert displays the experimental data below 20 K on a logarithmic scale. 2MP stands for 2-methyl-pyridine.

atures below 15 K was obtained without a heat shield. In the logarithmically scaled insert the results of the experiment with the shield are displayed. In our first experiment (no shield) serious problems were encountered in the interpretation of the recorded temperature data. We had to deal with two relaxation processes: thermal relaxation to the bath temperature (non-

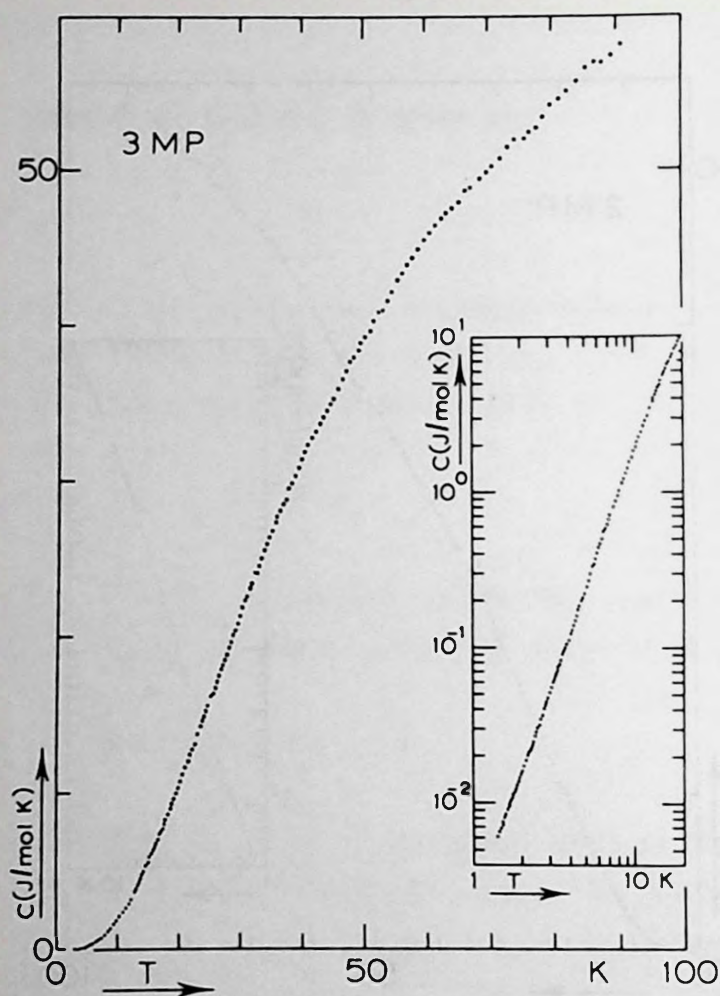


Fig. 2 The specific heat of 3MP vs. temperature.

adiabaticity) with a characteristic time τ_n and the methyl group conversion, described by τ_c , which appeared to be of the same order of magnitude as τ_n . The change in temperature of the sample, caused by a heat pulse, is two orders of magnitude smaller than the temperature difference between the sample and the bath. So the change of the sample temperature per second, caused by the thermal relaxation, is at least equal to or larger than the conversion rate of the methyl group. The non-adiabatic conditions prevented us from reaching

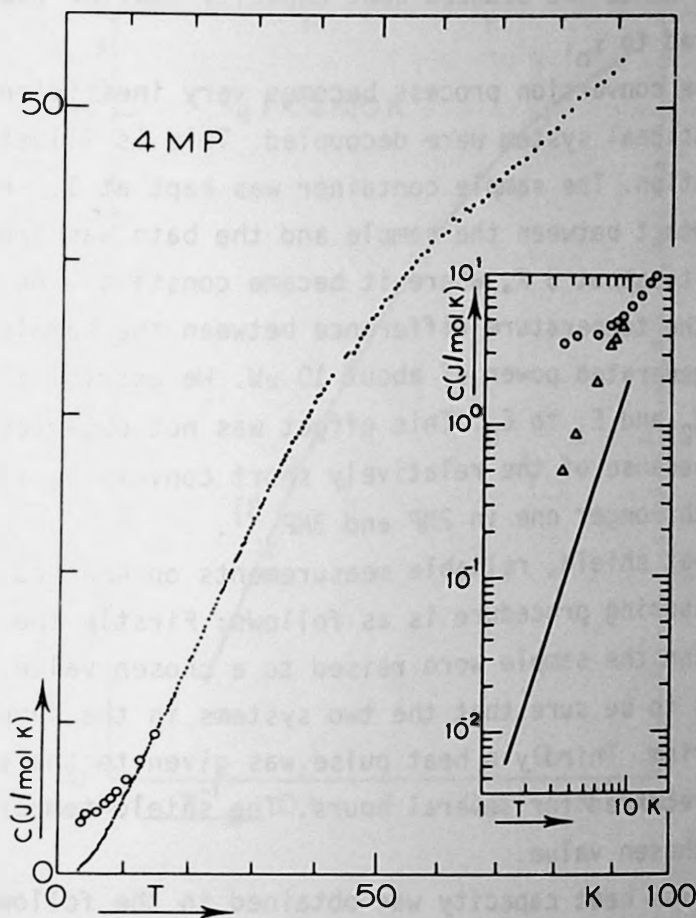


Fig. 3 The specific heat of 4MP vs. temperature. Below 15 K the data, obtained without the use of the heat shield (dotted) and the data from the experiment with the heat shield (equilibrium, circles) are shown. The normal specific heat (triangles) is displayed in the insert; the solid line represents the approximated values of the specific heat of 2MP and 3MP.

a state of internal equilibrium at a temperature higher than bath temperature. Since the contribution of the conversion process was included in the leak to the bath, the extrapolated temperature change due to the heat pulse was too large and hence the deduced heat capacity smaller than if τ_c is negligible compared to τ_n .

Below 3 K the conversion process becomes very inefficient, so that the lattice- and rotational system were decoupled. This is illustrated by the following observation. The sample container was kept at 1.2 K during 18 hours. When the heat contact between the sample and the bath was broken, the sample temperature rose to about 3 K, where it became constant. The heat production, responsible for the temperature difference between the sample and the bath, corresponded to a generated power of about 10 μ W. We ascribe it to the slow depopulation of E_2 and E_1 to E_0 . This effect was not observed in 2MP and 3MP, presumably because of the relatively short conversion time in 4MP, compared to a much longer one in 2MP and 3MP³⁾.

Using the heat shield, reliable measurements on 4MP could be made down to 3.5 K. The measuring procedure is as follows: Firstly the temperature of the heat shield and the sample were raised to a chosen value. Secondly we waited some hours to be sure that the two systems in the sample were in internal equilibrium. Thirdly a heat pulse was given to the sample and its temperature was recorded for several hours. The shield temperature was kept constant on the chosen value.

The equilibrium heat capacity was obtained in the following way. The temperature behaviour after the applied heat pulse was approximated by two exponentials, the first one originating from the heat leak between the sample and the shield and the second one from the conversion process, described by eq.(8). By the subtraction of both exponentials from the observed temperature decay, the total heat capacity of the sample, $K_1 + K_2$, was derived. τ is simply the time constant of the second exponential. The substitution of $\beta_1(t)$ and t_n in eq.(19) gives us the value of q_1 and since $q_1 + q_2$ and τ are already known, the conversion time τ_c can now be calculated. $q_1 + q_2$ is proportional to the equilibrium rotational and lattice specific heat. The parameters obtained from the experiment using the heat shield are, in a sequence of descending accuracy: τ , $q_1 + q_2$, q_1 and τ_c . The values of K_1 and C_{normal} , being K_1 normalized to 1 mol, are tabulated in table 1. τ_c is plotted in fig. 4 where also the fit of τ_c based on eq.(7) is given.

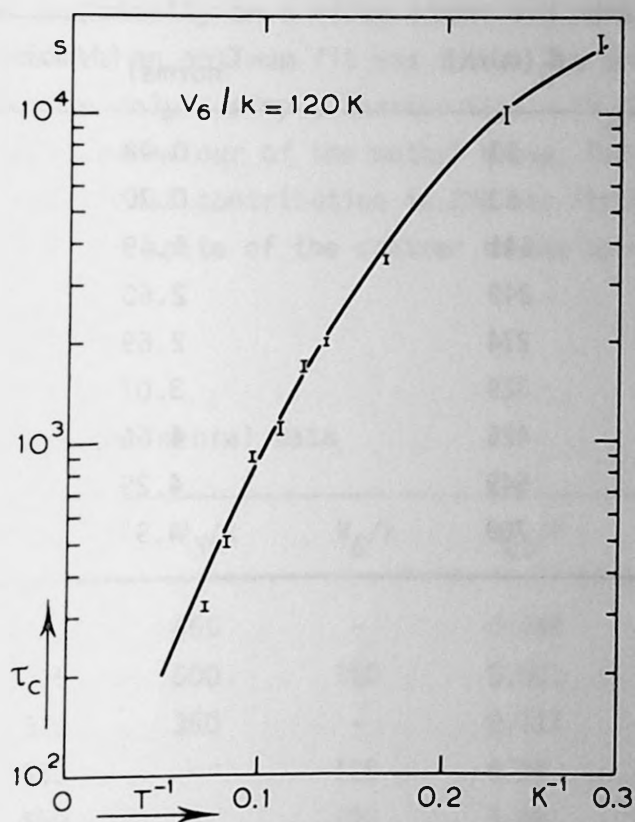


Fig. 4 A semilogarithmic plot of the experimentally obtained conversion times, τ_c , vs. reciprocal temperature, T^{-1} . The solid line represents the calculated conversion times for $V_6/k = 120 \text{ K}$ as described in section 3.

Table 1

The value of K_1 and C_{normal} .

T(K)	K_1 (mJ/K)	C_{normal} (J/mol K)
3.48	37	0.42
4.30	63	0.70
6.02	141	1.49
7.44	249	2.60
8.19	274	2.69
9.10	329	3.07
10.48	425	4.66
12.16	549	4.29
14.18	709	4.91

5. Interpretation.

We have interpreted our specific-heat data by four mechanisms i.e. two lattice vibrations, one internal rotation and one torsional vibration. The 2MP and the 3MP are most useful to determine the low-temperature Debye thetas. At temperatures below 10 K transitions violating symmetry rules do not occur anymore. The normal specific heat is very low compared to the lattice contribution. If we plot the specific heat of both compounds against T^3 , two straight lines are found of nearly the same slope. The corresponding low-temperature Debye thetas are 99.0 K and 102.5 K respectively for 2MP and 3MP. At temperatures above 10 K we need another Debye contribution to describe the lattice. This can be done as follows: one three-dimensional Debye function, characterized by θ_D , describes the molecular vibrations and another three-dimensional Debye function describes the torsional oscillations. In order to fit the experimental data at temperatures above 60 K also a three-dimensional Einstein function was introduced with a corresponding temperature θ_E . Using the low-

temperature value of Θ_D , the parameters needed to fit the experimental data are: one of the two Θ_D 's, the potential barrier V of the methyl-group rotation and Θ_E . The computer-calculated results and the experimental specific-heat data were displayed graphically on a video screen and were compared visually. By varying the parameters an optimum fit was found. The parameters are listed in table 2. First we use only a simple barrier $V(\phi) = (V_3/2)(1-\cos 3\phi)$ to describe the rotational behaviour of the methyl group. For 3MP $V_3/k = 350 \pm 5$ K was found. The rotational contribution in 2MP was firstly approximated with $V_3/k = 450 \pm 10$ K. In spite of the scatter in the specific-heat data,

Table 2

Parameters to fit the experimental data

compound	Θ_D	Θ_E	V_3/k	V_6/k	Δ_{01}/k	Δ_{02}/k
2MP	99	375	450	-	0.049	155
	99	375	500	100	0.051	138
3MP	102	375	350	-	0.117	133
4MP equil.	100	450	-	120	6.84	31
normal	100	450	-	190	5.92	24

All values are given in K.

this fit is not the optimum which can be reached. If we extend the barrier with a sixfold contribution to $V(\phi) = (V_3/2)(1+\cos 3\phi) + (V_6/2)(1+\cos 6\phi)$ better results are obtained with $V_3/k = 500 \pm 10$ K and $V_6/k = 100 \pm 20$ K.

4MP is more difficult to analyze. Since the methyl group exhibits already below 6 K a considerable specific heat, a low-temperature Debye theta could not be established. However this theta value will not differ much from the values of 2MP and 3MP, since densities and structures are very much alike. Using the same procedure for fitting these equilibrium data, substituting the values of 2MP and 3MP for the low-temperature Debye theta, an optimum fit was found, labelled equil. in table 2. The rotational part was characterized by $V_6/k = 120 \pm 10$ K. From the numerical analysis it is found that this value is insensitive for a variation of 5% in Θ_D .

Also the experimental normal specific heat of 4MP derived from q_1 in eq.(19) allows us to determine the potential barrier. This calculation is slightly different from the preceding one. Substituting a value V_6 into the Schrödinger equation, energies and eigenfunctions are determined. Since there are two symmetry species, A and E, we calculate the normalized population of these species, $P(A)$ and $P(E)$ at a given temperature. From the specific heats, with transition between A type or E type levels only, C_A and C_E , the normal specific heat C_N is calculated as follows:

$$C_N = C_A P(A) + C_E P(E) \quad . \quad (20)$$

We can fit the normal specific heat only below 10 K. Above this temperature, τ_c becomes comparable to the heating time t_h and furthermore the difference between the normal and the equilibrium specific heat decreases. Consequently the determination of the normal heat capacity will be too inaccurate to be useful for the determination of the potential barrier. Below 10 K the normal specific heat is described by a purely sixfold barrier $V_6/k = 190 \pm 10$ K.

As we have indicated it is not only possible to calculate the barrier but also - within a simple model - to deduce the conversion time τ_c from the experiment, see e.g. fig. 4. In section 3.4 it is shown that in general one may expect the conversion process to be determined by two exponents, the weights depending on the initial conditions. In specific-heat experiments a heat pulse is applied to the sample, and as a consequence the tunnelling system is no longer in equilibrium with the lattice: $x(0) = 0$ and $y(0) \neq 0$. So $C_1 = -(D_{66} + \lambda_2) y(0) / (\lambda_1 - \lambda_2)$ and $C_2 = +(D_{66} + \lambda_1) y(0) / (\lambda_1 - \lambda_2)$. Because $\lambda_1 \gg \lambda_2$ one has $C_2 \gg C_1$ and the conversion time will be determined by λ_2 .

In figs. 4 and 5 we show a fit based on the expression for λ_2 as given in eq.(8). As fitting parameters we have used the strength of the "normal" process and the strength of the direct conversion process. In the normal process through phonon interactions within the A and E level systems the levels are sufficiently broadened, that the proton-dipolar interaction can change the rotor symmetry.

In the direct conversion process ¹³⁾ the rotor-dipolar and rotor-phonon interaction give the possibility of a direct conversion in a second order process, which leads to an expression for τ_c^{-1} (see eq.(14)) which is analogous to a direct process relaxation-rate equation for electron spins.

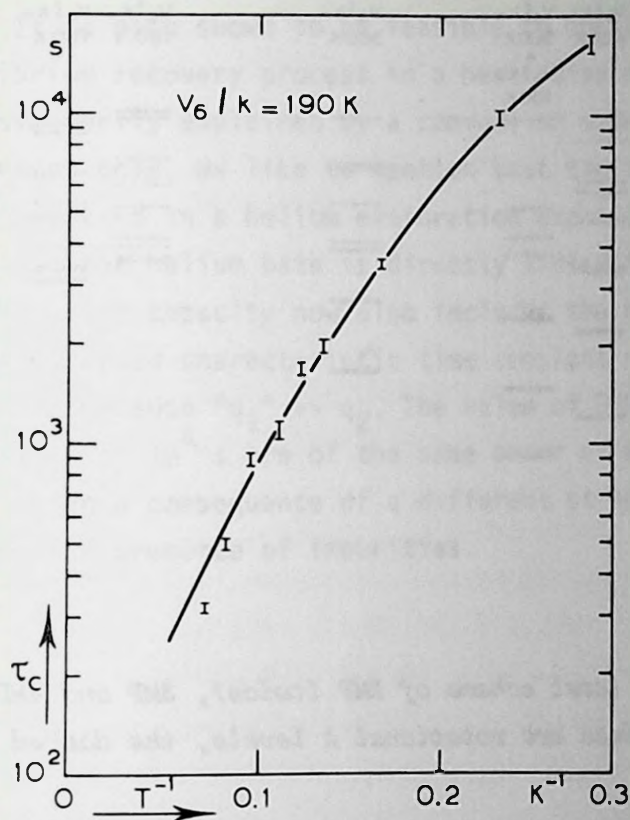


Fig. 5 The experimentally deduced and calculated ($V_6/k = 190$ K) τ_c vs. T^{-1} .

It appeared that the reduction factor for the "normal" conversion process, expressed by C_{rot} and δ^2 , is about 0.06 while the efficiency factor of the direct conversion process is about 0.02. The lowest energy levels as deduced from the calorimetric measurements on the mono-methyl-pyridines are given in fig. 6.

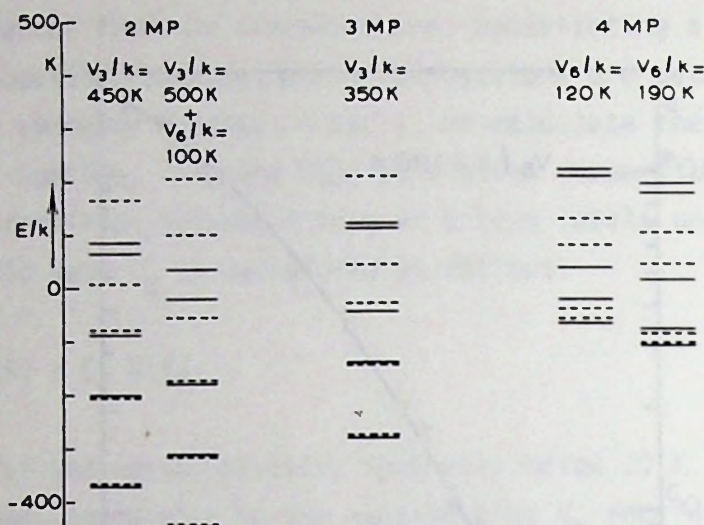


Fig. 6 The energy level scheme of 2MP (twice), 3MP and 4MP (twice).
The full lines are rotational A levels, the dashed lines are the E levels.

6. Comparison.

As to our knowledge, there are no other data available about the rotational barrier in the solid state of 2MP. In 3MP the INS ⁴⁾ data for the tunnelling splitting agree well with the tunnelling splitting, calculated from our model. However, the peak observed with INS techniques at 8.9 meV cannot be assigned to an energy splitting of the rotational system. If so, its contribution to the specific heat would already be considerable at 15 K, where no significant deviations from the lattice specific heat were observed. Possibly there is a relation with the low-temperature Debye theta ($\theta_D = 102$ K) which is very close to 8.9 meV (103 K).

For 4MP the barrier as derived from the normal specific heat ($V_6/k = 190 \pm 10$ K) is within its experimental error the same ($V_6/k = 180$ K) as deduced from INS ⁵⁾ measurements. However, $V_6/k = 180$ K (or 190 K) leads to a predicted specific heat between 10 K and 20 K, which is lower than the experimental value. It is also shown to be feasible to derive the conversion rate from the equilibrium recovery process in a heat-pulse experiment. The results can be satisfactorily explained by a conversion model based on intramolecular processes only. We like to mention that the conversion time of γ -picoline was also measured in a helium evaporation experiment by Beckmann et al ¹⁶⁾. In this case the helium bath is directly linked to the picoline sample, and the normal heat capacity now also includes the heat capacity of the helium bath. The observed characteristic time constant $\tau = \tau_c(q_1/(q_1+q_2))$ becomes now equal to τ_c because " q_1 " $\gg$ q_2 . The value of 3800 s found in this experiment and our value of 10^4 s are of the same order of magnitude, the difference possibly being a consequence of a different strength of the direct conversion process or the presence of impurities.

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CHAPTER 5

CH₂D GROUP ROTATION IN 4-METHYL-PYRIDINE

Synopsis.

The specific heat of 4-CH₂D-pyridine was measured between 0.2 and 90 K. A second order transition occurs around 5.4 ± 0.05 K. The transition is not observed in dielectric measurements. Furthermore 4-CH₂D-pyridine displays internal rotation down to below 10 K. From the data the barrier against internal rotation of the CH₂D group above the transition temperature is deduced, a phenomenological model is proposed for the data below the transition temperature and energy levels, combined with their relative degeneracies are given.

1. Introduction.

Since the first observation ¹⁾ of nuclear dipolar polarization in 4-methyl-pyridine (γ -picoline) upon a sudden temperature variation of the lattice, many studies, such as nuclear magnetic resonance ^{2,3)} (NMR), inelastic neutron scattering ^{3,4)} (INS) and specific heat ⁵⁾ (SH) were performed on several members of the methyl-pyridine family. We have restricted ourselves to mono-methyl-pyridines. For 4-methyl-pyridine the first SH results were not in agreement with NMR and INS data, because of long conversion times, a direct result of the symmetry properties of the methyl group. In order to avoid these difficulties, we lowered the symmetry by the partial deuteration of the CH₃ group. Since the barrier against internal rotation is low, its

contribution to the specific heat will dominate the lattice contribution at low temperatures, which allows a reliable determination of this barrier, rather independent of the lattice contribution. Because the specific heat is not only a function of the mutual energy differences, as imposed by the barrier, but also depends on the degeneracy of the energy levels, it is also a suitable method to probe the nuclear spin assignment ($I = 1$ or 0) to the levels with different rotational symmetry.

2. Apparatus and sample.

The specific heat was measured between 0.95 K and 90 K in an adiabatic set-up, using the heat pulse method. Because also measurements had to be performed below 1 K, we designed a calorimeter - see fig. 1 -, compatible with one of the adiabatic demagnetization set-ups, present in this laboratory. It was cylindrically shaped, 20 mm long, it had a diameter of 15 mm and its weight was 7 g. The case and its lid were made of 0.2 mm thick copper. The bottom, consisting of 0.2 mm thick german silver, was provided with a feed-through for the thermometer. A bundle of about 50 copper wires, 0.1 mm thick and 15 cm long, were silver soldered at one end and were inserted in the feedthrough. The thermometer was soldered outside the calorimeter to this brush. Another copper brush was attached to the lid of the shell. A vane was attached to a copper rod which was silver soldered to the shell. The vane could be clamped between the jaws of a mechanical heat switch, providing a heat link to the bath, or it was soldered to the copper cooling rod of the demagnetization set-up⁶⁾. A 200 Ω Evanohm resistance wire was wound around the shell. The carbon thermometer (25 k Ω at 0.95 K, 9k Ω at 4 K and 2.7 k Ω at 90 K) was calibrated against the saturated vapour pressure of ^3He , ^4He , n- H_2 and O_2 . The heat capacity of the empty cell was measured between 1 K and 90 K in a separate run beforehand. Below 1 K, we extrapolated these heat-capacity data, using a C/T vs. T^2 fit.

The dielectric measurements were performed in the high-temperature specific-heat set-up. The capacitance meter, using a RC method at 850 Hz, is described elsewhere⁷⁾. The cylindrically shaped measuring capacitor, see fig. 2, consisted of two coaxial pyrex tubes, each 1 mm thick. The outer one had an outside diameter of 24 mm, the inner one 20 mm. At both ends they were sealed off. The useful volume amounts to 2 cm³. At the top a 3 cm long

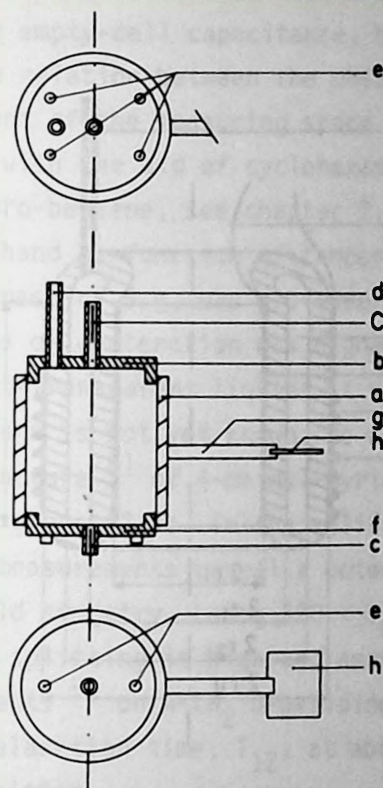


Fig. 1 The calorimeter used in this experiment. The thermometer and the copper brushes are not shown.

- | | |
|---------------|------------------------|
| a case | e attachment stub |
| b lid | f german-silver bottom |
| c feedthrough | g copper rod |
| d capillary | h vane |

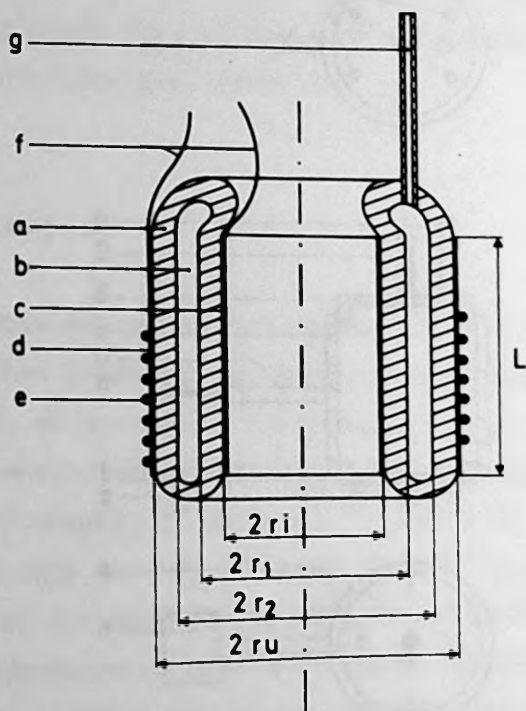


Fig. 2 The measuring capacitor. The thermometer is not shown. The radii, r , are the same as mentioned in section 4.

- | | |
|------------------------|---------------------------|
| a glass wall | d silver paint (grounded) |
| b sample volume | e resistance heater |
| c plate (silver paint) | f electrodes |
| | g capillary |

capillary was attached, through which the cell was filled and sealed. The capacitor plates were realized by a silver layer, painted on the glass walls of the cell. The outer plate was electrically grounded. A $100\ \Omega$ Evanohm resistance wire was wound around this plate. Below 80 K we employed a carbon

thermometer, similar to the one used for the specific-heat measurements; above 80 K it was replaced by a platinum thermometer. Both were mounted at the top of the capacitor. The cell could be cooled by helium gas. It appeared difficult to calculate the empty-cell capacitance, being about 15 pF at room temperature. Therefore the relation between the observed capacitance and the relative dielectric constant of the measuring space was determined experimentally at room temperature with the aid of cyclohexane, carbon tetrachloride, m-xylene, benzene and chloro-benzene, see chapter 2. The empty cell and its leads were measured beforehand as function of temperature.

The sample, having a mass of 5 g, was provided by Merck, Sharp and Dohme, (Canada). The degree of deuteration was higher than 98%. The sample is at room temperature a light-transparent liquid; it solidifies at $\approx 3^\circ\text{C}$. Because the crystal structure is not yet known, we will assume that it will be comparable with the structure ⁸⁾ of 4-methyl-pyridine, which is monoclinic, characterized by the space group $P2_1/c$. In the solid state of 4-methyl-pyridine, INS, NMR and SH measurements reveal a potential barrier against internal rotation of sixfold symmetry, being $120 < V_6/k < 200$ K. The observed low-temperature tunnelling splitting is high and amounts in temperature units to about 6 K. NMR measurements ⁹⁾ on 4-CH₂ D-pyridine display an anomaly in the nuclear spin-lattice relaxation time, T_{12} , at about 6 K, indicating the occurrence of a phase transition.

3. Theory.

There are several contributions to our observed specific-heat data. Since they are additive, we will deal with each of them separately.

3.1 Collective lattice vibrations.

This kind of contribution is described by the Debye model. In the low-temperature range ($T < \Theta_D/10$), Θ_D being the Debye temperature, the lattice specific heat, C_L , is proportional to the temperature cubed, $C_L \propto T^3$. The compound considered here is a molecular crystal. It consists of two rigid groups, the CH₂D top and the pyridine ring. We describe the lattice specific heat with two Debye functions, each characterized by their Debye thetas, Θ_1 and Θ_2 :

$$C_L(T)/R = 3D(\Theta_1/T) + 3D(\Theta_2/T) \quad , \quad (1)$$

where $D(T)$ is the Debye function. In the low-temperature region eq.(1) leads to:

$$C_L(T)/R = (12\pi^4/5)((T/\Theta_1)^3 + (T/\Theta_2)^3) \quad . \quad (2)$$

If the coefficient of T^3 is known, we can determine the value of Θ_2 by means of eq.(2), if we fix a value for Θ_1 .

3.2 Rotational contribution.

We assume that the pyridine ring is fixed in the crystal lattice at least at low temperatures. At high temperatures the motion of the pyridine ring will be limited to torsional vibrations, as described in section 3.3. The CH_2D group is an asymmetric top. Its principal moments of inertia are not known experimentally in this configuration, but they can be easily calculated as follows. We assume that a CH_2D group is characterized by the same dimensions and bond angles as a CH_3 group. A non-diagonal inertia tensor, $\tilde{I}$, is derived with respect to the 4-C atom of the pyridine ring. By the application of a similarity transformation, the tensor is diagonalized, and the rotational axes with their corresponding moments of inertia are determined. The rotational axis of the smallest principal moment of inertia, I_s , does not coincide with the corresponding axis in a CH_3 group, the trigonal symmetry axis; the angle between both axes amounts to $4^\circ 14'$. A rotation of the CH_2D group around this I_s axis would induce a bending of the bond between the pyridine trunk and the CH_2D top. This bending is not likely to occur as may also be inferred from the $\hbar^2/2Ik$ value found in other compounds with CH_2D groups: $\hbar^2/2Ik = 5.70 \text{ K}^{10,11}$; the value of $\hbar^2/2I_s k$ amounts to 5.85 K. So we conclude that the rotation occurs along an axis through the 4-C atom of the trunk and the C atom of the top.

The rotational motion of the top will be hindered by both intramolecular and intermolecular interactions. In 4-methyl-pyridine we have seen that the symmetry of the barrier, hindering the rotation, is mainly the same as the symmetry of the intramolecular forces. If we assume, that this is still true for the partly deuterated compound, the spatial symmetry of the potential barrier for rotation of the top is C_{2v}^{12} . So the barrier can be expanded in a Fourier series, with a periodicity of π radians:

$$V(\phi) = \sum_{n=1}^{\infty} (V_{2n}/2)(1-(-1)^{P_{2n}}\cos 2n\phi) \quad , \quad (3)$$

with $P_{2n} = 0$ or 1 . For the calculation of the thermodynamic properties, we have to solve the Schrödinger equation:

$$-(\hbar^2/2I)d^2\psi/d\phi^2 + V(\phi)\psi = E\psi \quad , \quad (4)$$

where I is the moment of inertia, already discussed. After substitution of eq.(3) in eq.(4), the latter is invariant under C_{2v} . Then the eigenfunctions can be divided into four classes, according to the four irreducible representations of the group C_{2v} , i.e. A_1 , A_2 , B_1 and B_2 . In general the eigenfunctions are given by:

$$\psi_{s,m}(\phi) = \sum_{k=-\infty}^{+\infty} a_{k,s} \exp(i\phi(2k+m)) \quad , \quad (5)$$

where s is a binary variable expressing whether ψ is symmetric or anti-symmetric with respect to ϕ , and m is the free rotor quantum number. The calculations are simplified by the introduction of functions $\omega_{s,k,m}(\phi)$, which are (anti)symmetric functions of ϕ , depending on s, k and m :

$$\omega_{s,k,m}(\phi) = \exp(i\phi(2k+m)) - (-1)^s \exp(-i\phi(2k+m)) \quad . \quad (6)$$

So eq.(5) reduces to:

$$\psi_{s,m}(\phi) = \sum_{k=k_0}^{\infty} b_k \omega_{s,k,m}(\phi) \quad , \quad (7)$$

where k_0 is dependent on s and m . The representations of the eigenfunctions are given in table 1. The group C_{2v} has only one-dimensional representations so there is no rotational degeneracy.

Table 1

The types of rotational eigenfunctions.

ψ	m	even	odd
symmetric		A_1	B_1
anti-symmetric		A_2	B_2

The nuclear spin of the two protons in the top can lead to different degeneracies of the energy levels. The Pauli principle states that the total eigenfunction of the system must be antisymmetric for a permutation of two protons (fermions). We confine ourselves to those permutations, which are equivalent to rotations¹³⁾. A single permutation, being equivalent to a mirror operation, is not compatible with a rotation, because it changes the frame¹³⁾ of the CH_2D group. Two successive permutations of the protons correspond in case of CH_2D to the identity transformation. They form a group, isomorphous to C_1 ; this group only contains the identity transformation. As a result any nuclear spin value of the proton, $I = 1$ or $I = 0$, will occur in combination with a given level. There is only one D-atom in the top: its spin, $I = 1$, will introduce an extra degeneracy, being the same for each type of energy level, so, the total degeneracy is the same for all levels, both as regards the proton spin and the deuteron spin degeneracy.

3.3 *Non-collective lattice contributions.*

Finally we will consider for the specific-heat contribution, the torsional motion of the pyridine ring and the rocking modes of the top. The associated energies¹⁴⁾ are high compared to the temperature region of our experiment. We approximate the onset of these contributions by Einstein functions.

3.4 *Neutron scattering.*

If monochromatic neutrons are scattered by a solid sample, containing tunnelling molecules or molecular groups, the energy differences of the tunnelling states can be transferred to the neutrons; (energy loss and energy gain). If the energy uncertainty of the monochromatic neutrons, which is also called energy resolution, is smaller than the transferred energies, the tunnelling levels can be determined by measuring the energy distribution of the scattered neutrons. In the past this method has contributed a lot of information to the tunnelling of light molecules and molecular groups in the solid state. One of the first samples, where this method was successfully employed⁴⁾, was 4-methyl-pyridine in the undeuterated form.

4. Experimental data.

The measurements have been performed on two different samples. The experimental specific heat of the first sample is displayed in fig. 3 and fig. 4. In the first sample a second-order phase transition was found at 5.42 ± 0.02 K. The transition temperature, T_p , was independent of the circumstance, whether the measurements were performed at increasing or decreasing temperature. No thermal relaxation at low temperatures was observed after a heat pulse to the sample, even below 1 K, so the conversion time between different symmetry species must be short, compared to the heating time, the latter being about 20 s. The small peak at 63 K is originated by air, present in the calorimeter. After these measurements, the cell was opened and the 4-CH₂D-pyridine removed was found to be dark coloured. The second sample was measured in a calorimeter of which all parts were now gold plated.

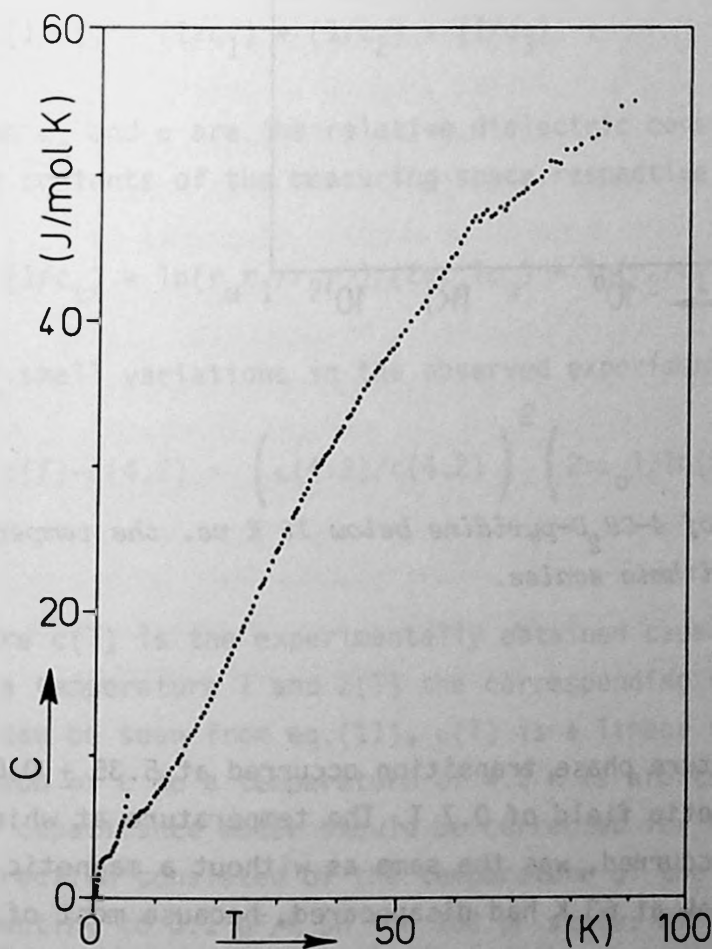


Fig. 3 The specific heat, C , of 4-CH₂D-pyridine vs. the temperature T .

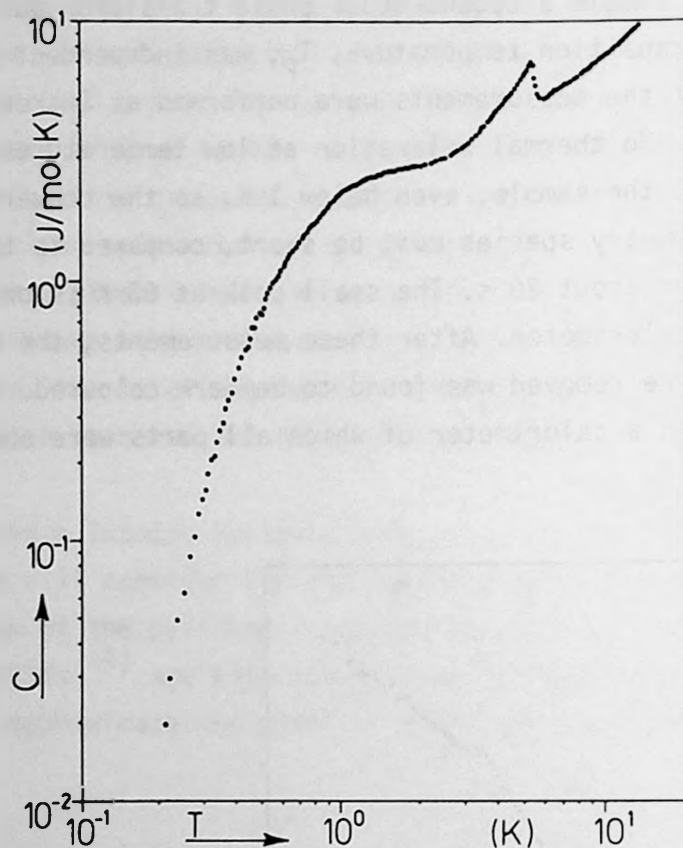


Fig. 4 The specific heat, C , of 4-CH₂D-pyridine below 15 K vs. the temperature, T , both on logarithmic scales.

In this sample the low-temperature phase transition occurred at 5.35 ± 0.02 K. It was also measured in a magnetic field of 0.7 T. The temperature at which the maximum in specific heat occurred, was the same as without a magnetic field. The high-temperature peak at 63 K had disappeared, because most of the air in the container was removed.

The dielectric measurements were performed between 1 K and 300 K. In order to keep the construction of the measuring capacitor simple, the 4-CH₂D-pyridine was not in direct contact with the capacitor plates (see fig. 2). This introduces a difficulty in obtaining the relative dielectric constant ϵ of the 4-CH₂D-pyridine. The capacitance, c , of a cylindrically shaped vacuum capacitor is given by:

$$c = 2\pi\epsilon_0 l / \ln(r_u/r_i) \quad , \quad (8)$$

where l is the length of the plates, r_u the inner radius of the outer plate, r_i the outer radius of the inner plate and ϵ_0 the absolute dielectric constant of the vacuum. Our measuring cell consisted of three capacitors, switched in series; see fig. 2. The first capacitor is the inner glass wall of the cylinder, the second the useful measuring space and the third the outer glass wall of the cylinder. The total capacitance, c_t , is calculated from:

$$(1/c_t) = (1/c_1) + (1/c_2) + (1/c_3) \quad . \quad (9)$$

When ϵ_g and ϵ are the relative dielectric constants of the glass used and the contents of the measuring space respectively, c_t is given by:

$$(1/c_t) = \ln(r_u r_1 / r_2 r_i) / (2\pi\epsilon_0 l \epsilon_g) + \ln(r_2 / r_1) / (2\pi\epsilon_0 l \epsilon) \quad . \quad (10)$$

For small variations in the observed experimental capacitance, ϵ is given by:

$$\epsilon(T) - \epsilon(4.2) = \left(\epsilon(4.2) / c(4.2) \right)^2 \left(2\pi\epsilon_0 l / \ln(r_2 / r_1) \right) \left(c(T) - c(4.2) \right) \quad , \quad (11)$$

where $c(T)$ is the experimentally obtained capacitance of the filled capacitor at a temperature T and $\epsilon(T)$ the corresponding relative dielectric constant. As can be seen from eq.(11), $\epsilon(T)$ is a linear function of $c(T)$. The normalization of ϵ to a temperature of 4.2 K is arbitrary. The recorded reading of the capacitance meter should be corrected for the measuring cell. The first correction consisted of the temperature of the electronic parts of the meter, amounting to 0.1 pF/K on the 100 pF scale. All readings were normalized to 25 °C. The second correction was the capacitance of the leads, its thermal

variation and the dependence of the empty-cell capacitance on temperature. These corrections were determined experimentally in a separate run beforehand. The third correction originates from the leads passing through a cryogenic liquid, which has a dielectric constant different from the gas phase. This contribution, being proportional to the length of the wires submerged, was also determined by the experiment for liquid oxygen and helium. The theoretical and measured values are for oxygen 3.0 pF/m and 7.3 pF/m and for helium 0.3 pF/m and 0.72 pF/m respectively. The absolute accuracy of the measured capacitance amounted to 1 pF. Because of the large scatter in the determination of the relation between the total capacitance and the relative dielectric constant of the useful volume of the capacitor, the absolute value of ϵ is accurate to about 5%. However the scatter in the observed readings at low temperatures was much smaller i.e. 0.05%. The experimental results, see fig. 5, are displayed in arbitrary units. Obviously no change in the reading was found at T_p , it remained constant between 1 K and 15 K, see the insert of fig. 5.

The neutron-scattering results were obtained at the triple axis spectrometer Hadas at the Dido Reactor in Jülich, using graphite crystals as monochromator and analyzer. The sample temperature was kept fixed at 2.5 K. With exactly the same experimental conditions, we performed two measurements, one on 4-CH₃-pyridine, which gave the same results as already discussed in ref. 4 (the dots in fig. 6) and one on 4-CH₂D-pyridine, which is shown as the open circles in fig. 6. Within the statistical accuracy, the intensity of the elastic line is the same for both samples. However, the inelastic line of the rotating methyl group at 0.52 meV shifts to 0.41 meV for the partly deuterated methyl group. The intensity of the inelastic line is different by a factor of about six. An indication of a second inelastic line was observed at an energy transfer of 0.72 meV. However the half width of this line is too small; it is not clear, whether this line is true or spurious. It is necessary to repeat this part of the measurements with a better statistical accuracy.

5. Interpretation.

To explain the observed specific heat, we will use the mechanisms described in section 3. If we assume the same type of lattice specific heat, as observed in the mono-methyl-pyridine family, then, after its subtraction, the remaining

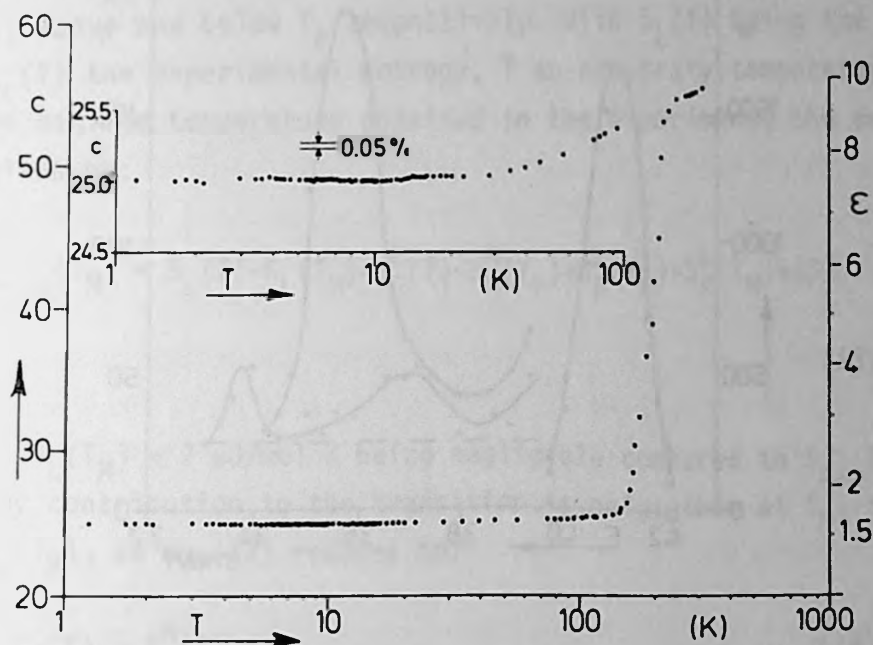


Fig. 5 The capacitance, c , of the measuring cell (left) vs. temperature, on a logarithmic scale. The scale at the right side gives the relative dielectric constant ϵ . The insert displays the data between 1 K and 100 K on a ten times expanded vertical scale. The error bar indicates a relative error in the observed total capacitance of 0.05%.

specific heat must be of the rotational type. We use two three-dimensional Debye functions and one three-dimensional Einstein function to approximate the lattice contribution. The specific heat of pyridine can be described also by two three-dimensional Debye functions, but one only two-dimensional Einstein function. The wagging motion of the CH_2D group is not present in pyridine, leading to one Einstein function less. In our opinion the phase transition has its origin in the asymmetry of the CH_2D group; this might also

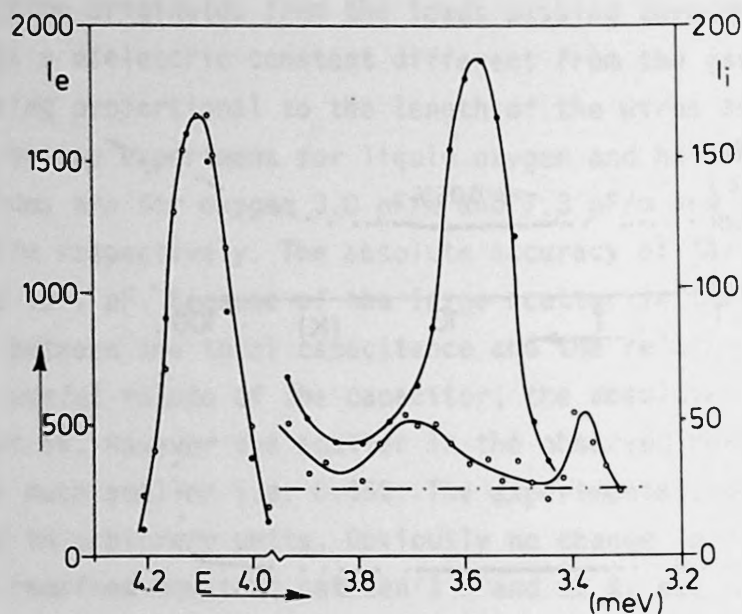


Fig. 6 The neutron scattering intensity vs. energy in the time of flight experiment. At the left side the elastic intensity, I_e , and at the right side the inelastic intensity, I_i , is given in counts per 20 minutes. The dots display the data of 4-CH₃-pyridine, the circles of 4-CH₂D-pyridine. The back ground level is indicated by the dash-dot line.

be inferred from the 4-CH₃-pyridine data, where no such transition is found. At high temperatures ($T > T_p$), the asymmetry of the top is obscured by averaging effects. At sufficiently low temperatures the rotation of the top is restricted to a torsional vibration along a principal axis; the free energy and entropy are lower than in the high-temperature phase. If this change in rotational motion is collective in character, it leads to a peak in the specific heat. In this phase transition the role of the lattice entropy will be neglected, because the transition entropy, ΔS_p , being roughly 0.6 J/mol K (see below), is six times larger than the lattice entropy itself at T_p , assuming equal lattice entropies for 4-CH₃-pyridine and 4-CH₂D-pyridine. So,

$$\Delta S_p = S_R^H(T_p) - S_R^L(T_p) , \quad (12)$$

where $S_R^H(T_p)$ and $S_R^L(T_p)$ are the rotational entropies at T_p , characterized by the barriers, above and below T_p respectively. With $S_L(T)$ being the lattice entropy, $S_{\text{exp}}(T)$ the experimental entropy, T an arbitrary temperature above T_p and T_M the minimum temperature obtained in the experiment, the entropy balance is given by:

$$S_{\text{exp}}(T) - S_{\text{exp}}(T_M) = S_L(T) - S_L(T_M) + S_R^H(T) - S_R^H(T_p) + S_R^L(T_p) - S_R^L(T_M) + \Delta S_p , \quad (13)$$

$T_M = 0.211$ K, $S_L(T_M) = 7$ $\mu\text{J/mol K}$ being negligible compared to $S_{\text{exp}}(T_M)$. If the entropy contribution to the transition is negligible at T_M , then $S_R^L(T_M) \approx S_{\text{exp}}(T_M)$, so eq.(13) reduces to:

$$S_{\text{exp}}(T) - S_L(T) - S_R^H(T) = 0 . \quad (14)$$

Table 2

The entropy differences above T_p .

$T(\text{K})$	$S_{\text{exp}} - S_L - S_R^H$ (J/mol K)
10.01	0.03
15.01	0.06
20.05	0.09
25.18	0.07
30.21	0.04
35.09	0.02
40.35	+0.01
45.45	-0.02
50.58	-0.04

First we will try to fit the data above 6 K, using the same barriers as found for 4-methyl-pyridine from SH, INS and NMR measurements ^{5,2,4)} ($120 \text{ K} < V_6/k < 200 \text{ K}$). It turns out, however, that these barriers do not sufficiently approximate our data.

In analogy to CH_2DOH ¹⁵⁾, where in absence of a twofold symmetric trunk, a term with a periodicity of 2π radians was added to the threefold symmetric barrier, as found for CH_3OH , we will add an extra twofold symmetric term to our original sixfold potential. In first approximation the contribution with fourfold symmetry (see eq.(3)) is neglected. Using this potential, we can fit ¹⁶⁾ our data above 6 K by $V_2/k = 26.5 \pm 1 \text{ K}$ with $P_2 = 1$ and $V_6/k = 70 \pm 10 \text{ K}$ with $P_6 = 1$. If we use in our calculations equal degeneracies for both the A and B type levels, $g = 1$ (see section 3.2 and appendix A) eq.(14) is fulfilled within 0.1 J/mol K , as is demonstrated in table 2. The correspondence between the experimental and calculated rotational specific heat is displayed in fig. 7. The energies and degeneracies are listed in table 3.

Table 3

The rotational energy levels above T_p

E/k (K)	g
0	1
1.3	1
15.4	1
25.2	1
27.2	1
41.2	1

Our specific-heat data can also be fitted with other ratios between the degeneracies than one to one; however, the deviations from zero in eq.(14) for temperatures between 6 K and 50 K amount to at least 2 J/mol K , being twenty times larger than for the ratio one to one.

We can describe the experimental data above T_p with a barrier, being the sum of a mainly sixfold- and less dominant twofold symmetric contribution. The

entropy above T_p deduced from the data, obtained in the entire measured temperature region, can be satisfactorily explained - assuming model 1 (see chapter 3) to be valid - if we demand that the degeneracies of the levels are equal. This result is also predicted by the application of group theory (see section 3.2)

The description of the data below T_p is less straightforward. The first

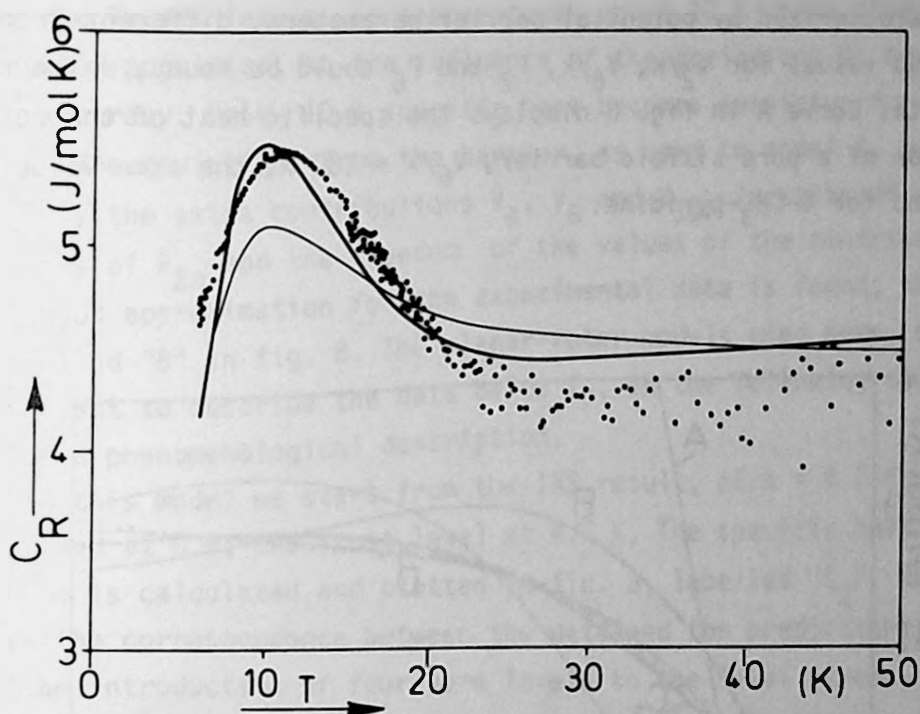


Fig. 7 The experimental rotational specific heat, C_R , (dots) after subtraction of the lattice contribution vs. temperature, above T_P . The solid curve is the best fit to the data for the specific heat of a rotor, hindered by a potential barrier of the form $(V_2/2)(1+\cos 2\phi) + (V_6/2)(1+\cos 6\phi)$ with $V_2/k = 26.5$ K and $V_6/k = 70$ K. The lower curve is obtained using a barrier of the shape $(V_2/2)(1+\cos 2\phi) + (V_6/2)(1-\cos 6\phi)$ with $V_2/k = 27$ K and $V_6/k = 60$ K.

problem, we face, is the occurrence of the peak. In our model it originates from the CH_2D group, which can lower its rotational entropy and free energy due to a rise in barrier height. Considering the shape of the observed peak, we assume that for $T < 0.4 T_P$ the contribution of the phase transition to the specific heat becomes negligible. Therefore we have only tried to fit the data

below 2.5 K. We will discuss four models, A, B, C and D, for the description of these data.

Model A. We use a barrier, composed of both a twofold and a sixfold contribution, characterized by potential-barrier parameters, different from those above T_p . No values for V_2/k , V_6/k , P_2 and P_6 could be found, which reasonably fit the data. Curve A in fig. 8 displays the specific heat of the rotational contribution of a pure sixfold barrier, $V_6/k = 180$ K, the same value and shape, as was found for 4-CH₃-pyridine.

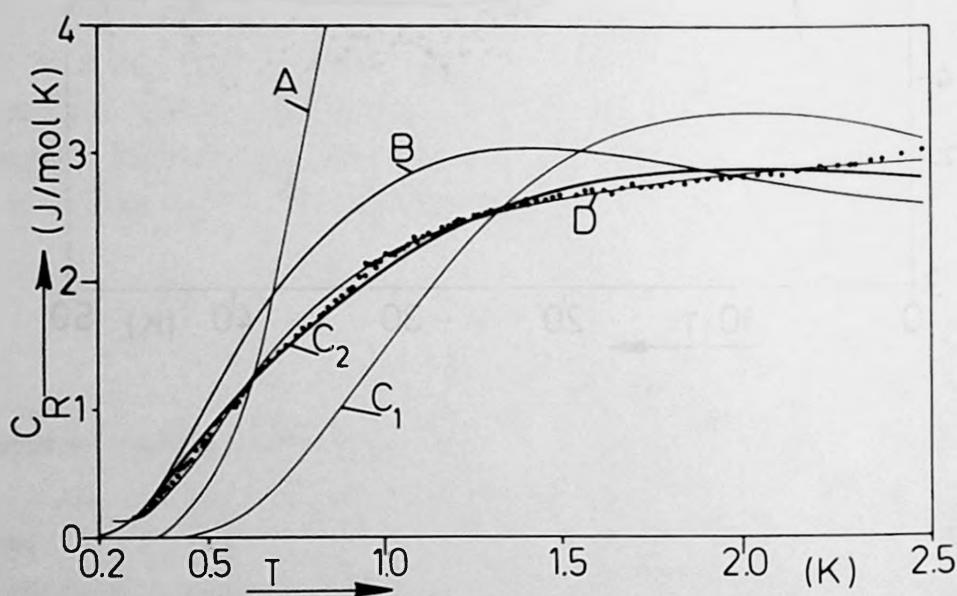


Fig. 8 The experimental rotational specific heat, C_R , after subtraction of the lattice contribution vs. temperature below 2.5 K. Curve A is calculated for a pure sixfold rotational barrier, $V_6/k = 180$ K with equal spin degeneracies for all levels. Curve B is described in section 5, model B. Curve C_1 is obtained from an equally degenerate two level system, separated in energy ΔE with $\Delta E/k = 4.7$ K. Curve C_2 is found via the use of a six level scheme, as described in table 4, model C. The line D is generated by a free model, using six equally degenerate levels, as listed in table 4 under model D.

Model B. In this model we use a barrier, as described by eq.(3). The infinite Fourier expansion is cut after the fifth term. Small deviations of the shape of this barrier reflect themselves in small changes in the energy levels, mainly in the lowest levels. At temperatures above 10 K these levels are almost equally populated, so the influence of the deviations is beyond the measuring accuracy. Below 10 K specific heat becomes sensitive for these deviations. The deviations from the barrier, as used in model A, are approximated here by the extra contributions V_4 , V_8 and V_{10} . In spite of all the possibilities of P_{2n} and the freedom of the values of the contributions V_{2n}/k , no good approximation for the experimental data is found; the best fit is labelled "B" in fig. 8. The planar-rotor models used here, seem to be insufficient to describe the data below T_p . In the following two models, we will use a phenomenological description.

Model C. In this model we start from the INS result, $\Delta E/k = 4.7$ K. The ground level is fixed at 0 K, the first level at 4.7 K. The specific heat of this level scheme is calculated and plotted in fig. 8, labelled " C_1 ". When we try to improve the correspondence between the data and the predictions of the model by the introduction of four more levels to the level scheme, and when we vary the energy differences of those extra levels with respect to the ground level, even the best fit obtained is not satisfactory. We consider four additional levels (making a total of six) because the sixfold barrier in 4-CH₃-pyridine leads to six lower levels, of which two are rotational doublets. By the lowering to a twofold symmetry, the levels will all be singlets, but they remain well separated from the higher sextets.

A substantial improvement is found, if we assume that the degeneracy of the ground level is three times as large as that of the other levels. The curve calculated in this way is labelled " C_2 " in fig. 8. The levels with their corresponding degeneracies are listed in table 4. This ground-level degeneracy may be accidental; a combination of three levels, separated in energy less than 20 mK (expressed in temperature units), and the three non-zero levels from table 4 also reproduce curve " C_2 ". As mentioned in the previous section also the INS data give an indication of an additional higher level at $\Delta E/k \approx 8$ K. However, the accuracy is too small to draw further conclusions.

Model D. This is a free model, in the sense that the ground level is fixed at 0 K and the other levels are varied arbitrarily in order to get minimal deviations from the observed specific-heat data. The degeneracies of the levels are equal. A reasonable fit between 0.3 K and 2.5 K is found, see curve

Table 4

The energy levels below T_p

Model C		Model D	
E/k (K)	g	E/k (K)	g
0	3	0	1
4.7	1	0.054	1
2.0	1	2.5	1
6.2	1	6.8	1
		13.5	1
		> 20	1

"D" in fig. 8; the energy levels are listed in table 4. This fit leads to a doubly degenerate ground level.

Summarizing we can say, that it is possible to fit the experimental specific-heat data below 2.5 K, using six non-degenerate levels. If the energy difference between the ground state and one of the other levels is set equal to ΔE , as found by INS, a fit to the specific-heat data remains possible. In this case the ground state has to be almost threefold degenerate.

6. Conclusion.

By lowering of the symmetry of the methyl groups by partly deuteration, the selection rules of the transitions between the various rotational levels are released. The conversion times between levels, belonging to different (rotational)symmetry classes, are considerably reduced. In the specific-heat data a second-order phase transition is seen at $T_p = 5.4 \pm 0.05$ K. The specific-heat data above T_p are described by the rotation of the CH_2D group, hindered by a potential barrier with a twofold and sixfold symmetric contribution, $V_2/k = 26.5 \pm 1$ K, $V_6/k = 70 \pm 10$ K and $P_2 = P_6$. It has to be assumed that all rotational levels have equal nuclear-spin degeneracies. The phase transition likely has its origin in the asymmetry of the CH_2D group. The accompanying change in entropy is found in the rotational system. At $T = 2.5$ K one,

possibly two, inelastic peaks are observed in inelastic neutron-scattering measurements, with energies $\Delta E/k = 4.7$ K (and $\Delta E/k = 8.3$ K). Although it is possible to fit the experimental specific-heat curve for $T < T_p$ by a level scheme, using the INS level(s), further INS measurements are needed to get an unambiguous description of the CH_2D system below T_p .

APPENDIX A

We summarize the formulae for the free energy, entropy and specific heat of a system of discrete energy levels. The system to be described consists of N levels, the i^{th} level being characterized by the energy E_i and the degeneracy g_i . The partition function Z is given by:

$$Z(T) = \sum_{i=1}^N g_i \exp(-E_i/kT) \quad . \quad (\text{A.1})$$

The free energy F is found by:

$$F(T)/R = -T \ln Z(T) \quad . \quad (\text{A.2})$$

The entropy S is deduced from $-(\partial F/\partial T)$, so:

$$S(T)/R = \ln Z(T) + Y(T)/Z(T) \quad , \quad (\text{A.3})$$

with

$$Y(T) = \sum_{i=1}^N g_i (E_i/kT) \exp(-E_i/kT) \quad . \quad (\text{A.4})$$

The specific heat C is calculated by $T(\partial S/\partial T)$, which leads to

$$C(T)/R = X(T)/Z(T) - (Y(T)/Z(T))^2 \quad , \quad (\text{A.5})$$

with

$$X(T) = \sum_{i=1}^N g_i (E_i/kT)^2 \exp(-E_i/kT) . \quad (A.6)$$

The free energy depends both on the absolute values of the energies and degeneracies, as can directly be seen from eq.(A.1). Apart from the temperature scaling, the entropy and specific heat are independent of the absolute values of the energies; the entropy is a function of the level degeneracies, while the specific heat only depends on their ratio (see eqs.(A.3) and (A.5)).

The levels are labelled in ascending order of energy magnitude; we consider a temperature T , $T > 0$ K and $kT \ll E_1 - E_0$. As a consequence:

$$Z(T) \approx g_0 \exp(-E_0/kT) , \quad (A.7)$$

and

$$Y(T) \approx g_0 (E_0/kT) \exp(-E_0/kT) , \quad (A.8)$$

so:

$$S(T)/R \approx \ln g_0 . \quad (A.9)$$

We calculated the rotational entropy in eq.(14), assuming all levels to be non-degenerate. Since no data are available below T_M , $S_{\text{exp}}(T_M)$ (eq.(13)) was chosen to be zero. However, if the degeneracy of the ground level is g_0 , an additional entropy contribution, $R \ln g_0$, has to be gained, when the initial temperature would have been $T = 0$ K. So $S_{\text{exp}}(T_M)$ should be at least $R \ln g_0$. $S_{\text{exp}}(T)$, calculated from the data by numerical integration from T_M to T , should also be larger by an amount of $R \ln g_0$. For the correct determination of the entropy balance, we have to add $R \ln g_0$ at the left side of eq.(14). In this way the result remains the same if all degeneracies are multiplied with the same factor.

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SAMENVATTING

Het onderzoek, in dit proefschrift beschreven, betreft het gedrag van roterende methylgroepen in de vaste aggregatietoestand. Alhoewel er in het verleden reeds veel over rotoren gepubliceerd is, is in het laatste decennium de belangstelling voor dit onderwerp verder toegenomen. Enerzijds groeit het gebruik van organische liganden in het onderzoek naar zwakke magnetische wisselwerkingen, anderzijds worden grote organische moleculen gebruikt bij organische (super)geleiders. Indien deze bouwstenen, methyl-, ethyl- of ammoniakgroepen bevatten, kunnen deze een aanzienlijke bijdrage leveren tot bijvoorbeeld de soortelijke warmte en kernspinrelaxatie processen. Een goede kennis van de beweging van roterende moleculen kan in beide onderzoeksgebieden bijdragen tot een duidelijke interpretatie van de waargenomen verschijnselen.

In het inleidende hoofdstuk 2 wordt ingegaan op enige van de experimentele technieken en op de verwerking van de meetgegevens. Daarnaast is beschreven, hoe men op elegante wijze de Schrödingervergelijking kan oplossen voor een vlakke rotor, waarvan de rotatie om zijn traagheidsas gehinderd wordt door een superpositie van cosinusvormige potentiaalbarrières met een willekeurige symmetrie. Tevens is aangegeven (in appendix - C), hoe men met behulp van eenvoudige groepentheorie de algemene machtreeksontwikkeling van de golf-functies vereenvoudigt en de matrices opstelt, waaruit men de energieën en de bijbehorende golffuncties bepaalt.

Hoofdstuk 3 behandelt de soortelijke warmte, kernspinresonantie en dielectrische metingen aan dimethyl-tin-difluoride, $(\text{CH}_3)_2 \text{Sn F}_2$. Deze verbinding vertoont een tweede orde faseovergang bij 70.4 K; de hinderende methylgroepen verandert in een temperatuurgebied rond 70 K, hetgeen in deze overgang een grote rol speelt; beneden 70 K is de barriere tweemaal zo hoog als boven de overgangstemperatuur. Uit de entropie beschouwingen boven 70 K volgt direct de hoogte van de potentiaalbarriere: $V_3/k = 165 \pm 10$ K. Beneden de overgangstemperatuur kunnen we slechts de ondergrens voor de hoogte van de barriere vaststellen, te weten $V_3/k = 330 \pm 10$ K. Beide waarden stemmen overeen met die, verkregen door middel van quasi-elastische- en inelastische neutronenverstrooiingsexperimenten. De kernspinresonantiemetingen leveren weliswaar niet zulke scherpe grenzen voor de barrierehoogten op, maar ze stemmen ermee overeen. De dielectrische metingen bevestigen slechts de faseovergang bij 70 K.

De calorimetrische experimenten aan de drie mono-methyl-pyridines (picolines) worden beschreven in hoofdstuk 4. De analyse van de soortelijke warmte metingen aan 3-methyl-pyridine leveren een potentiaalbarriere op van $V_3/k = 350 \pm 10$ K. De hieruit berekende waarde voor de tunnelopsplitsing van de grondtoestand komt uitstekend overeen met de waarde bepaald uit inelastische neutronenverstrooiingsmetingen; de hoogte en de vorm van de potentiaalbarriere die uit neutronen- en kernspinresonantie metingen wordt afgeleid, stemt echter niet overeen met de resultaten van onze soortelijke warmtemetingen in het temperatuurgebied van 10 tot 40 K. De metingen aan 2-methyl-pyridine kunnen niet in hun totaliteit verklaard worden met één enkele cosinusterm in de barriere, dit ondanks de spreiding in de soortelijke warmte gegevens. De potentiaalbarriere, die de rotatiebijdrage het best beschrijft, is een superpositie van een drievoudige bijdrage van 500 K en een zesvoudige bijdrage van ongeveer 100 K. Er zijn tot nu toe geen resultaten ter vergelijking bekend. In het laatste preparaat uit deze serie, 4-methyl-pyridine, treden problemen op, die hun oorsprong hebben in (observeerbare) overgangen tussen quantummechanische toestanden met verschillende symmetrie. Dit proces noemt men conversie. De hiermee verbonden relaxatietijden variëren tussen enige uren bij 3.5 K tot enkele minuten bij 15 K. Gebruikmakend van de soortelijke warmte bepaald uit de overgangen tussen energieniveaus van het zelfde type, leiden we uit de metingen beneden 10 K een barriere af van $V_6/k = 190 \pm 10$ K, in overeenstemming met de resultaten van inelastische neutronenverstrooiing en kernspinresonantie. Indien we naast bovengenoemde overgangen ook die meenemen, waarbij het type van de energieniveaus *wel* ver-

andert, kunnen we de gemeten soortelijke warmte in het gehele temperatuur-gebied beschrijven met een barrierehoogte, $V_6/k = 120 \pm 10$ K. Een barrierehoogte van 190 K levert een te geringe bijdrage op, om de metingen tussen 10 en 25 K te kunnen beschrijven. Het model ter verklaring van de experimenteel bepaalde conversietijden sluit geen van beide barrierehoogten uit.

In het vijfde en laatste hoofdstuk worden de resultaten van soortelijke warmte en inelastische neutronenverstrooiingsmetingen aan het gedeeltelijk gedeutereerde 4-methyl-pyridine besproken. Ook in deze stof treedt een tweede orde faseovergang op, bij 5.4 K. De drievoudige symmetrie van de methylgroep is opzettelijk verstoord door het gedeeltelijke deutereren, ten einde meer informatie te verkrijgen over de ligging van de energieniveaus, nu hierbij niet gehinderd door de conversie. De resterende symmetrie van de methylgroep is die van de romp van het molecuul, te weten tweevoudig. Deze symmetriebeschouwingen leiden tot gelijke ontaarding voor de rotatie energieniveaus, hetgeen ook volgt uit de experimenteel bepaalde waarde van de entropie boven de overgangstemperatuur. De soortelijke warmte kunnen we beschrijven met een samengestelde barriere met $V_2/k = 26.5 \pm 1$ K en $V_6/k = 70 \pm 10$ K. Beneden de overgangstemperatuur kan de soortelijke warmte niet meer met een dergelijk simpele barriere beschreven worden. Een fenomenologisch model, gebruikmakend van de met inelastische neutronenverstrooiing gemeten opsplitsing, beschrijft het meetresultaat onder aanname van nog niet met neutronentechnieken waargenomen energieniveaus.

De hoofdstukken 3, 4 en 5 zijn ter publikatie in Physica B aangeboden.

CURRICULUM VITAE

Op verzoek van de faculteit der wiskunde en natuurwetenschappen volgt hier een overzicht van mijn studie.

Nadat ik in 1969 geslaagd was voor het eindexamen gymnasium- β aan het Libanon Lyceum te Rotterdam, startte ik in hetzelfde jaar aan de Rijks-universiteit te Leiden met de studie natuurkunde en wiskunde, met als bijvak sterrenkunde (N1). Na het candidaatsexamen in het voorjaar van 1972 trad ik toe tot de werkgroep van prof.dr. W.J. Huiskamp, waar ik begon met het meten van soortelijke warmte van vaste stoffen, onder de dagelijkse leiding van dr. Z. Dokoupil. Achtereenvolgens assisteerde ik dr. F.W. Klaaijsen, die mij experimentele technieken bij lage temperaturen bijbracht, en drs. G.M. Nap. In het najaar van 1975 deed ik doctoraal examen experimentele natuurkunde met als bijvak numerieke wiskunde. In januari 1976 werd ik in tijdelijke dienst aangesteld als wetenschappelijk assistent, tot september 1980. Bij mijn onderzoek ondervond ik nu ook de steun van dr. H.B. Brom.

Sedert 1973 was ik verbonden aan het practicum voor hoofdvak precandidaten. Verder ben ik sinds de zomer 1977 in tijdelijke dienst aangesteld bij de Haagse Leergangen te 's Gravenhage.

SLOTOPMERKINGEN

Gedurende de tijd die ik op het Kamerlingh Onnes Laboratorium heb doorgebracht, ondervond ik de hulp van zeer veel medewerkers. Diepgaande besprekingen met dr. Z. Dokoupil en met dr. H.B. Brom hebben veel bijgedragen tot het onderzoek. Daarnaast dient te worden vermeld de samenwerking met de kernspinresonantiegroep van de Technische Hogeschool Delft, in het bijzonder dr. R.A. Wind en dr. D.J. Ligthelm en met dr. B. Alefeld van het Institut für Festkörperforschung te Jülich. Bij mijn metingen en de bijbehorende uitwerking werd ik achtereenvolgens geassisteerd door drs. F.G. Ras, drs. P. van Liempt, drs. M. van Dijk en de heren R. van Tuyl en P. Schaminee.

Op het technische vlak heb ik nooit tevergeefs aangeklopt bij de heer T. Nieboer voor preparaathoudertjes of voor ander fijnmechanisch constructiewerk, terwijl mijn, soms buitenissige, wensen op het gebied van glazen apparaten gerealiseerd werden door de heren C.J. van Klink en L. van As. De heren J.D. Sprong, J.A.Th. van Schooten en J. de Vink hebben zich altijd bijzonder ingespannen om mij de benodigde cryogene vloeistoffen te verstrekken.

De mini-computergroepen van het Centraal Reken Instituut en dit laboratorium waren altijd bereid mij de nodige rekenfaciliteiten te verlenen, die het mij mogelijk maakten berekeningen en analyses in een kort tijdbestek uit te voeren. De tekeningen werden door de heren W.F. Tegelaar, J. Bult en L. Gijsman gemaakt, terwijl het manuscript met voortvarendheid door mevr. B.M.E. Cats getypt werd.

STELLINGEN

1. Het blijkt dat structurele fase overgangen in veel organische stoffen gepaard gaan met anomalieën in de diëlectrische constante. Deze overgangen kunnen op eenvoudiger wijze met diëlectrische metingen dan met de gebruikelijke soortelijke warmte metingen worden gevonden.

Dit proefschrift, hoofdstuk 3.

2. De bewering van Tomala en anderen dat in metallische gadolinium verbindingen voor de geleidingselectronen meestal de configuratie $5d^1 6s^2$ wordt aangenomen, is in tegenspraak zowel met experimentele resultaten alsook met theoretische berekeningen.

*K. Tomala, G. Czjzek, J. Fink en H. Schmidt,
Solid State Communications 24(1977)857.*

3. De in hun artikel over warmtegeleiding in He II in zeer nauwe kanalen door Helvensteijn en anderen veronderstelde uitdrukking voor de drukgradient is onjuist.

*B.P.M. Helvensteijn, S.R. Breon en S.W. Sciver,
Proc. Cryogenic Engineering Conference, San Diego 1981,
Plenum Press, in druk.*

4. Het verdient aanbeveling met inelastische en quasiëlastische neutronenverstrooiingsmetingen de vorm en de hoogte van de potentiaalbarriere in 2-methyl-pyridine verder te ontrafelen.

Dit proefschrift, hoofdstuk 4.

5. De correcties, die door Kugel en anderen op het gemeten hyperfijnveld H_{hf} van zeldzame aardionen in ijzer en nikkel zijn toegepast teneinde de 4f bijdrage aan H_{hf} te bepalen, zijn onjuist.

*H.W. Kugel, L. Eytel, G. Hubler en D.E. Murnick
Phys. Rev. B13(1976)3697.*

6. Reeksontwikkelingen voor de thermodynamische grootheden in het Debye model zijn efficiënter en doorzichtiger bij berekeningen dan de gebruikelijke formules in integraal-vorm.

Dit proefschrift, hoofdstuk 2.

7. De door zenders van openbare en andere diensten veroorzaakte opwarming van preparaten bij lage temperatuur, kan op eenvoudige wijze voorkomen worden.

Dit proefschrift, hoofdstuk 2.

8. De bewering van Trammell, dat de magnetische susceptibiliteit in lage velden anisotroop is in kubische verbindingen met een r_3 doublet grondtoestand, is onjuist.

G.T. Trammell, Phys. Rev. 131(1963)932

B. Bleaney, Proc. Roy. Soc. A376(1981)217.

9. Nu het rijk en de gemeenten drastisch moeten bezuinigen, verdient het aanbeveling het principe van de financiële gelijkstelling van het bijzonder onderwijs met het openbaar onderwijs niet tot meer schooltypen uit te breiden, maar dit principe vanuit het kostenvraagstuk voor de overheid, opnieuw ter discussie te stellen.
10. Goede ontvangst van sateliet TV signalen in het frequentie bereik rond 12 GHz zal de komende vijf jaren technisch voorbehouden blijven aan de firma's die de TV signalen via het huidige kabelnet distribueren.
11. De algemeen gebezigde Nederlandse vertaling van LPG, te weten "vloeibaar petroleum gas", is nog onzinniger dan het gebruik van "vloeibare stoom", als men water bedoelt.

Gezien de beperkte ruimte in de Senaatskamer, kan slechts toegang tot de promotie worden verleend op vertoon van een toegangskaartje.

De receptie na afloop van de promotie wordt gehouden in het Academiegebouw, Rapenburg 73.

Men dient rekening te houden met zeer tijdrovende parkeerproblemen in de omgeving van het Academiegebouw.