PHYSICAL REVIEW B VOLUME 44, NUMBER 22 1 DECEMBER 1991-II

Inelastic-neutron-scattering study at low temperature of the quantum sine-Gordon breather in 4-methyl-pyridine with partially deuterated methyl groups

F. Fillaux
Laboratoire de Spectrochimie Infrarouge et Raman, Centre National de la Recherche Scientifique,
2 rue Henri-Dunant, 94320 Thiais, France

C. J. Carlile
ISIS Pulsed Neutron Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 OQX, United Kingdom

G. J. Kearley
Institut Laue-Langevin, 156X, 38042 Grenoble CEDEX, France

(Received 3 December 1990)

Inelastic-neutron-scattering spectra of 4-methyl-pyridine (4MP) molecules with partially deuterated methyl groups, referred to as 4MP-*ch*$_2$*d* and 4MP-*chd*$_2$, are reported. At 1.6 K, the observed frequencies for the CH_2D and CHD_2 derivatives are 388 μeV (3.13 cm^{-1}) and 337 μeV (2.72 cm^{-1}), respectively. 4MP-*ch*$_2$*d* shows an additional band at 436 μeV (3.51 cm^{-1}). Between 1.6 and 5.0 K, the band at 3.13 cm^{-1} progressively merges into the band at 3.51 cm^{-1}. At a higher temperature, 7.5 K, the frequency shifts upwards to 477 μeV (3.84 cm^{-1}). Three different models for the methyl-group dynamics are considered: single-particle model, coupled-pair model, and an infinite chain of coupled methyl groups. All the data strongly support the quantum sine-Gordon theory used to describe the dynamics of an infinite chain of coupled methyl groups. At low temperature the bands are assigned to transitions between the quantized traveling states of the sine-Gordon breather mode. The potential for 4MP-*ch*$_2$*d* is the same (to first order) as that previously proposed for the fully hydrogenated material. However, small perturbations are introduced, which account for the break of threefold symmetry in the partially deuterated systems. In this case, the breather band splitting at very low temperature corresponds to the coexistence of different chain conformations, or phase correlations, with respect to the methyl-group torsional coordinates. Between 1.6 and 5.0 K, one of the chain conformations is progressively converted into the other. This conversion is monitored by the tunneling states of the chains. It corresponds to the recovery of the threefold symmetry for the on-site potential. Finally, the breather-frequency shift above about 5K, which is in marked contrast to the fully hydrogenated compound, is attributed to the "imbalance" character of the partially deuterated methyl group. Therefore, there is a coupling of the methyl-group torsion coordinate with other librational modes in the crystal. Above about 5 K this coupling averages out the on-site potential. A part of the breather rest energy (mass) is converted into kinetic energy and the traveling frequency increases. The breather is progressively converted into rotons in an almost freely rotating chain of coupled methyl groups.

I. INTRODUCTION

The rotational dynamics of the methyl groups in 4-methyl-pyridine (4MP or γ-picoline) have been thoroughly investigated using many techniques.[1-21] Inelastic-neutron-scattering (INS) experiments on 4MP showed a single band near 520 μeV (4.19 cm^{-1}) (Ref. 5) which was assigned to the methyl-group tunneling transition. This is one of the highest frequencies ever observed for this kind of transition and a sixfold potential with a low barrier was proposed. With higher resolution ($\sim$15 μeV), this band was found to be split into several components.[19] As well as the main band at 510 μeV (4.11 cm^{-1}), weaker bands at 468 μeV (3.77 cm^{-1}) and 535 μeV (4.31 cm^{-1}) were partially resolved. This splitting was attributed to coupled pairs of methyl groups, as in lithium acetate ($CH_3COOLi{\cdot}2H_2O$, or LiAc).[22-24] However, further studies on mixtures of fully hydrogenated with fully deuterated molecules (referred to as 4MP-*h*$_7$ and 4MP-*d*$_7$, respectively) revealed spectacular frequency shifts, depending on concentration and temperature,[20,21] which cannot be explained by coupled pairs. However, when the sine-Gordon theory[25-36] is applied to an infinite chain of coupled methyl groups, a remarkably good agreement with the experimental observations is obtained. The main band at 510 μeV is then interpreted as arising from the transition to the first-excited traveling state of the massive quantum particle referred to as a sine-Gordon breather mode. The weaker sidebands correspond to in-phase (535 μeV) and out-of-phase (468 μeV) tunneling transitions for the chain.[20,21]

It is widely accepted that partial deuteration of the methyl group lowers the symmetry of the effective potential. However, the traveling states of the sine-Gordon breather mode are not expected to be destroyed by a weak perturbation of the local symmetry caused by partial deuteration. The frequency should be affected mainly by the change of the particle mass. Therefore, partial deuteration should provide a useful distinction between single-particle and collective rotations of methyl groups.

Some measurements on partially deuterated 4MP-ch_2d (INS, heat-capacity, dielectric relaxation) have already been reported.[9,14] Heat-capacity measurements[9] indicate a second-order phase transition at 5.4 K for the partially deuterated sample which is absent for the fully hydrogenated molecule.[8] For pure 4MP-ch_2d at 2.5 K, the INS frequency is shifted downwards to 410 μeV (3.30 cm^{-1}) but no temperature effect has been reported. Other INS experiments on a mixture of 4MP-ch_2d and 4MP-h_7, with a concentration ratio $[\text{4MP-}ch_2d]/[\text{4MP-}h_7]=\frac{88}{12}$, have shown a distinct upward frequency shift with temperature, from 405 μeV (3.26 cm^{-1}) at 1.4 K to 457 μeV (3.68 cm^{-1}) above 6 K.[14] This effect, which is in marked contrast to pure 4MP-h_7 for which there is no frequency shift with temperature,[19–21] was attributed to fast exchange between two nonequivalent conformations of the CH_2D group with respect to the molecular frame. However, this interpretation should be treated with caution since it was assumed that the INS band arose entirely from fully hydrogenated molecules, and it is not clear that the band at 410 μeV is representative of the partially deuterated molecules.[8] Further, the temperature effect could be due to isotopic mixing, as in the case of mixtures of 4MP-h_7 and 4MP-d_7,[20,21] rather than fast exchange between nonequivalent conformations.

In the present paper we present INS data of pure 4MP-ch_2d and pure 4MP-chd_2 which show frequency shifts which are consistent with the sine-Gordon theory. The observed temperature effects are then discussed in this context.

II. EXPERIMENTAL DATA AND SPECTRA

A. Experiment

The 4MP-ch_2d derivative was obtained by hydrolysis with D_2O of 4-methyl-pyridine-lithium prepared according to Ref. 37. NMR shows a deuteration of 97 atom % in 4MP-ch_2d. The 4MP-chd_2 derivative was obtained in three steps. Methylisonicotinate was reduced with $LiAlD_4$ into the carbinol product[38] which was then converted into 4-chloromethyl-d_2-pyridine-hydrochloride. This compound was finally reduced with Zn in acetic acid.[39]

The neutron-scattering experiments were carried out on the IRIS time-of-flight spectrometer[40] at the ISIS pulsed neutron facility (Rutherford Appleton laboratory, UK) and on the IN5 time-of-flight spectrometer at the Institut Laue-Langevin (Grenoble, France).

IRIS is an inverted-geometry inelastic-neutron spectrometer which uses a long incident flight path and an array of pyrolytic-graphite analyzers close to backscattering to define both the incident and scattered neutron energies to a high precision. The elastic resolution of the spectrometer is 15 μeV and the energy-transfer range available with good resolution is quite large. The low final energy reflected by the crystal analyzers (1.82 meV) provides a spectrometer which is particularly well suited for neutron energy-loss spectroscopy from cold samples.

IN5 is a direct-geometry spectrometer which was operated with an incident neutron energy of 0.72 meV so as to provide an elastic resolution of 9 μeV and a maximum energy transfer of 500 μeV.

4MP-ch_2d and 4MP-chd_2 are liquid at room temperature. They were loaded into aluminum containers of dimension $40\times40\times1$ mm^3. These were mounted into a standard liquid-helium cryostat with temperature control better than ±0.5 K.

B. Crystal structure

The crystal structure of 4-methyl-pyridine at 4 K (Fig. 1) is tetragonal, $I4_1/a$ (C_{4h}^6), with four molecules in the primitive cell.[17] The structure is unchanged up to 120 K (Ref. 11) and is identical with that of the fully deuterated analog.[17] (The monoclinic structure at 90 K proposed by Biswas[18] was not confirmed.) The site symmetry is $C2$ and the methyl groups are disordered. The dominant dipole-dipole interaction leads to an antiparallel ordering of the molecules along the c axis. Intermolecular distances perpendicular to c are typical van der Waals distances for aromatic molecules. The shortest methyl-methyl contact is 3.46 Å (parallel to the c axis) which is significantly shorter than the sum of van der Waals radii for two methyl groups of about 4 Å (see, for instance, molecules labeled 1 and 2, or 3 and 4 on Fig. 1). Ohms

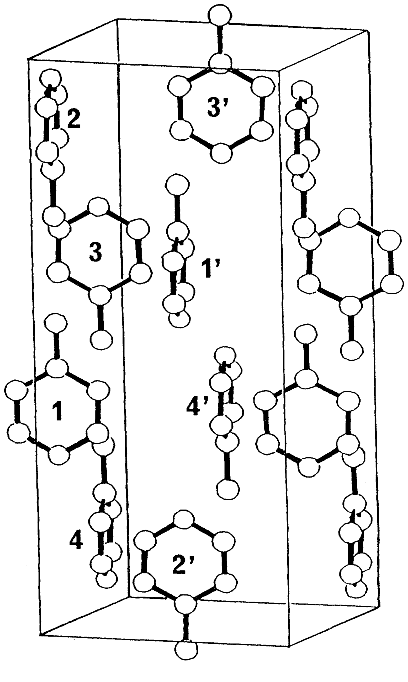

FIG. 1. Crystal structure of 4-methyl-pyridine at 4 K after Ref. 17.

and co-workers[11] state that this short CH_3-CH_3 distance is only possible when a strong correlation between the mutual orientation of adjacent methyl groups of different molecules exists. The methyl groups would be rotated by 60° with respect to each other and perform combined hindered rotations. This conclusion has been confirmed by the Rietveld analysis refinement of the neutron-diffraction data at 4 K.[17]

Besides these close-contact pairs, the next shortest methyl-methyl distances ($\sim$4 Å for molecules labeled 1 and 3, or 4 and 4′ in Fig. 1) occur perpendicular to the crystallographic *c* axis. They form two different sets of equivalent infinite chains of equidistant methyl groups in a zigzag formation with their mean directions parallel to the *a* or *b* axes, respectively. Chains in the *a* or the *b* directions are not located in the same (a,b) plane. All other methyl-methyl distances are greater than 6 Å.

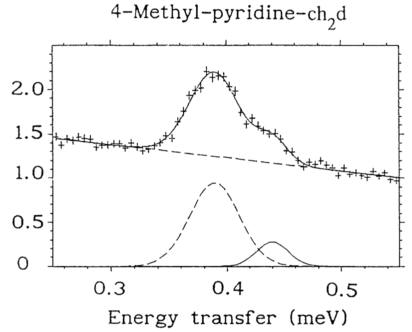

FIG. 3. Band decomposition into Gaussian components for the spectrum at 1.6 K.

C. INS spectra

The IRIS spectra of 4MP-ch_2d at various temperatures are shown in Fig. 2. At the lowest temperature (1.6 K) the maximum intensity is at 388 μeV (3.13 cm^{-1}). The band is rather asymmetric and band decomposition into Gaussian components suggests a second component at 436 μeV (3.51 cm^{-1}) (Fig. 3) with an integrated intensity ratio $I_{388\,\mu eV}/I_{436\,\mu eV} \sim 3.9$. As the temperature is increased the main maximum shifts upwards to 477 μeV (3.84 cm^{-1}) at 7.5 K and, simultaneously, the bands broaden and merge into a rather symmetric single band. It then becomes impossible to distinguish subbands in the spectra. The Arrhenius plot shown in Fig. 4 suggests a first-order law and an activation energy of 4.5 ± 0.5 cm^{-1}.

The IN5 spectra (Fig. 5) provide more details of the two components in the 450-μeV (3.60 cm^{-1}) region. At 2 K they are well resolved, but at higher temperatures the band at 388 μeV (3.13 cm^{-1}) merges progressively into the band at 436 μeV (3.51 cm^{-1}). This latter band is almost unshifted between 2 and 5 K. In addition, there is a weak band at 74 μeV (0.59 cm^{-1}) whose intensity increases with temperature.

Owing to the high purity of the samples, these bands are known to be due to the CH_2D group which is in conflict with the conclusion of Brom and co-workers[14] that there is no spectral contribution from the partially

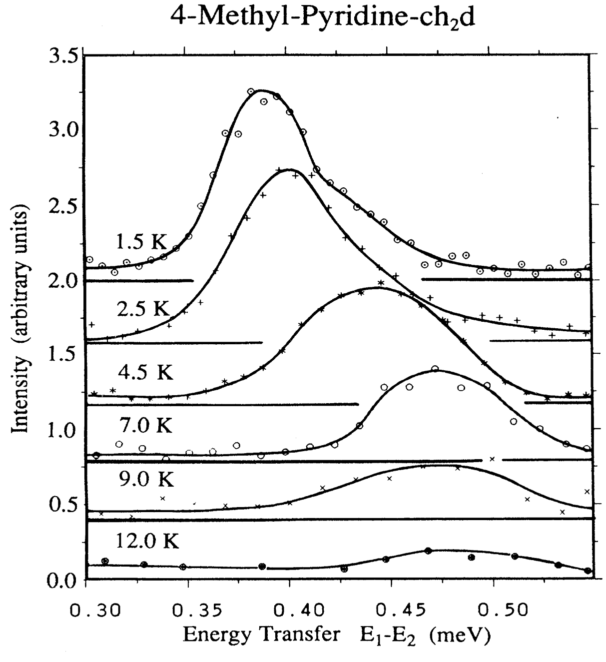

FIG. 2. Inelastic-neutron-scattering spectra of partially deuterated 4-methyl-pyridine ch_2d at various temperatures. IRIS spectrometer.

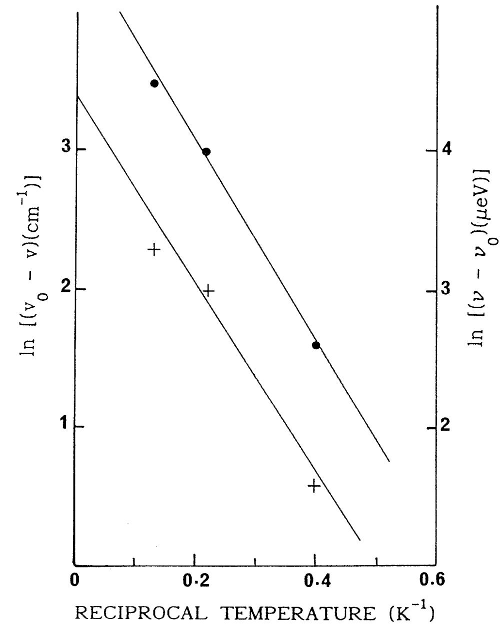

FIG. 4. Arrhenius plots. +, observed frequencies. ●, calculated on-site potentials V_0.

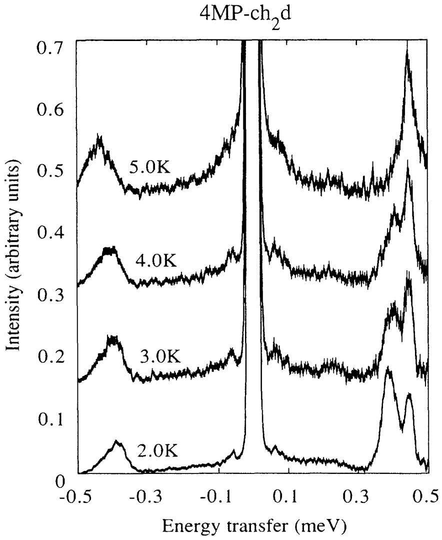

FIG. 5. Inelastic-neutron-scattering spectra of partially deuterated 4-methyl-pyridine *ch*$_2$*d* at various temperatures. IN5 spectrometer.

deuterated methyl groups in the 400-μeV region.

The INS spectrum of 4MP-*chd*$_2$ is rather weak even with a sample thickness of about 2 mm. Above this limit, multiple scattering becomes non-negligible. Nevertheless, a peak at 338 μeV (2.72 cm^{-1}) is observed at 2.5 K, with, in addition, a weak ill-defined band around 250 μeV (2.02 cm^{-1}).

III. INTERPRETATION

At present, three different approaches have been proposed for the tunneling spectra of methyl groups with low hindering barriers: single-particle model, pairs of coupled methyl groups, and infinite chains. Although previous works on 4-methyl-pyridine strongly support the chain model,[20,21] partial deuteration could change the symmetry and effective potential of the methyl groups in such a way that different dynamics may appear. We therefore reconsider all three models in our interpretation of the data presented in Sec. II. The spectra at the lowest temperatures (Figs. 2 and 5) where two components are resolved are analyzed in Sec. III A and the temperature effects are discussed in Sec. III B.

A. Methyl dynamics at low temperature

1. Single particle

The simplest approach to methyl rotation is the isolated internal top experiencing a periodic potential. The corresponding Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta^2} + V(3\theta) \ . \tag{1}$$

I_r is the reduced moment of inertia of the internal top, θ is the angular coordinate and $V(3\theta)$ is a periodic potential consistent with the threefold symmetry of the methyl group. In this equation the kinetic coupling with the molecular frame is neglected. Usually one of the terms (V_3 or V_6) is dominant in the Fourier series expansion for the potential and the eigenproblem associated with the torsional motion may then be transformed into the well-established Mathieu equation.[41] The observed band corresponds to the tunneling transition and the frequency gives an estimate of the barrier height, either threefold or sixfold.[5,16]

The values in Table I for various isotopic derivatives of 4MP were obtained with potential functions, scaled with respect to the observed frequencies, for either the fully hydrogenated or the fully deuterated material. This is to allow for changes of the effective potential due to complete deuteration. Inspection of Table I reveals an important difference between observed and calculated frequencies for the partially deuterated samples and it follows that the frequency shifts cannot be assigned simply to the mass effect.

If we adjust the potentials to the observed frequencies (Table II), we obtain a large reduction of the barrier height for the partially deuterated methyl groups ($\sim$30% for 4MP-*ch*$_2$*d* and $\sim$40% 4MP-*chd*$_2$). This would be in marked contrast with the small increase of the barrier resulting from complete deuteration. Moreover, even if we accept large erratic variations of the effective potential with partial deuteration, the simple Hamiltonian [Eq. (1)]

TABLE I. Single-particle potential barriers and tunneling transitions for various isotopic derivatives of 4-methyl-pyridine at low temperatures.

		ν_{cal} (cm^{-1})			
	ν_{obs} (cm^{-1})	$V_3=32$ cm$^{-1\,\text{a}}$	$V_3=38$ cm$^{-1\,\text{b}}$	$V_6=160$ cm$^{-1\,\text{a}}$	$V_6=176$ cm$^{-1\,\text{b}}$
$C_6H_4NCH_3$	4.16$^{\text{c}}$	4.14	3.75	4.10	3.87
$C_6H_4NCH_2D$	3.13	2.59	2.24	2.51	2.30
$C_6H_4NCHD_2$	2.72	1.98	1.66	1.89	1.70
$C_6D_4NCD_3$	0.80$^{\text{c}}$	1.03	0.80	0.93	0.80

[a] Potential function scaled to the CH_3 frequency.
[b] Potential function scaled to the CD_3 frequency.
[c] From Ref. 21.

TABLE II. The single-particle model: potential barriers and tunneling transitions for isotopic derivatives of 4-methyl-pyridine at low temperatures.

	ν_{obs} (cm^{-1})	V_3 (cm^{-1})	ν_{cal} (cm^{-1})	V_6 (cm^{-1})	ν_{cal} (cm^{-1})
$C_6H_4NCH_3$	4.16[a]	32	4.14	160	4.10
$C_6H_4NCH_2D$	3.13	23	3.17	116	3.13
$C_6H_4NCHD_2$	2.72	20	2.74	100	2.71
$C_6D_4NCD_3$	0.80[a]	38	0.80	176	0.80

[a] From Ref. 21.

cannot account for the two bands in the spectra (Figs. 2, 3, and 5). Additional terms due to partial deuteration must be admitted.

For partially deuterated methyl groups, the symmetry is no longer exactly threefold or sixfold and different energies are expected for inequivalent methyl-group conformations. An appropriate potential representing the dynamics of partially deuterated methyl groups is

$$H'=H_0+V'(\theta) \ . \tag{2}$$

If $V(\theta)$ is threefold, the periodicity of $V'(\theta)$ is 2π and one methyl-group conformation is distinct from the two others with an energy difference of $\frac{3}{2}V'$. [If $V(3\theta)$ is sixfold, $V'(\theta)$ is twofold.] In the high-barrier limit, the tunnel splitting in the unperturbed potential is smaller than the energy difference between the nonequivalent conformations. Wave functions are then localized within each well and tunneling disappears. In the low-barrier case, which is relevant for 4MP, the tunnel splitting in $V(3\theta)$ can be larger than $\frac{3}{2}V'$. Then the wave functions are partially delocalized and tunneling transitions may survive, although with weaker intensities. The effect of $V'(\theta)$ is then to remove the degeneracy of the E level and two transitions can be observed. The splitting is of the order of $\frac{3}{2}V'$.

A potential function consistent with the spectrum of 4MP-ch_2d at ~2 K is illustrated in Fig. 6 (energy levels are given in Table III). The transition at lower frequency [388 μeV (3.13 cm^{-1})] corresponds to the most probable conformation (see the wave functions in Fig. 6) and is more intense than the transition at 436 μeV (3.51 cm^{-1}), in agreement with observation (Figs. 2, 3, and 5). The weak transition at 0.6 cm^{-1} may correspond to the hot transition between the two excited states at 3.13 and 3.51 cm^{-1}. However, the energy difference (0.38 cm^{-1}) between these levels is rather far from the observation (0.6 cm^{-1}).

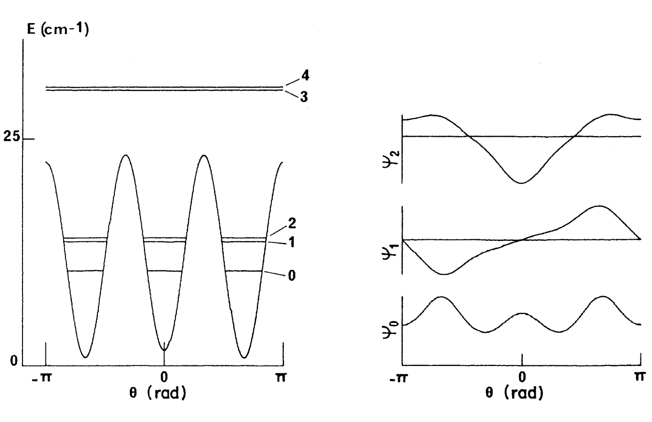

FIG. 6. Potential function, energy levels, and wave functions for $V=(-1.1/2)(1-\cos\theta)+(21.8/2)[1-\cos(3\theta)]$. V and θ are in cm^{-1} and rad units, respectively.

2. *Pair of coupled methyl groups*

Pairs of coupled methyl groups with their axes parallel to the crystallographic c axis are suggested by the crystal structure (Fig. 1). The appropriate Hamiltonian is

$$H_{12}=-\frac{\hbar^2}{2I_r}\left[\frac{\partial^2}{\partial\theta_1^2}+\frac{\partial^2}{\partial\theta_2^2}\right]+V_0(3\theta_1)+V_0(3\theta_2)+V_{12}(3(\theta_1-\theta_2)) \ , \tag{3}$$

where θ_1 and θ_2 are the angular coordinates of the methyl groups. The two groups rotate in a static field V_0, around a common axis and are coupled together via an interaction potential V_{12}. This model was proposed for lithium acetate.[22–24] In the case of 4MP, it was further suggested that a dynamical coupling (represented by a term proportional to $\partial^2/\partial\theta_1\partial\theta_2$) should be added to the Hamiltonian in order to account for the observed intensities.[19]

Figure 7 shows the corresponding energy-level dia-

TABLE III. The single-particle model: observed and calculated frequencies for partially deuterated 4-methyl-pyridine (4MP-ch_2d). $V=(-1.1/2)(1-\cos\theta)+(21.8/2)[1-\cos(3\theta)]$. V and θ are in cm^{-1} and rad units, respectively.

Transition	Obs.	Calc.
0→1	3.13	3.11
0→2	3.51	3.51
0→3		19.84
0→4		20.19
0→5		39.10
0→6		40.62

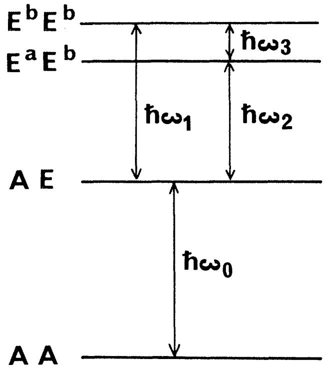

FIG. 7. Energy-level diagram for a pair of coupled methyl groups, after Ref. 23.

gram. There are four levels denoted as AA, AE, E^aE^b, and E^bE^b.[22] Three transitions (namely, $AA \rightarrow AE$, $AE \rightarrow E^aE^b$, and $AE \rightarrow E^bE^b$) are predicted in the 400 μeV (3.2 cm^{-1}) region but only two bands are visible in the low-temperature spectra (Figs. 2 and 5). However, the third may be hidden beneath one of the other bands and it is possible to adjust V_0 and V_{12} to account for the actual observation. As with the single-particle model (Sec. III A 1), the band observed at $\sim 0.6\ \text{cm}^{-1}$ would then correspond to the transition between excited tunneling states ($E^aE^b \rightarrow E^bE^b$) expected at 0.4 cm^{-1}.

For coupled pairs of partially deuterated methyl groups, the Hamiltonian becomes

$$H'_{12} = H_{12} + V'_0(\theta_1) + V'_0(\theta_2) + V'_{12}\left[\theta_1 - \theta_2 + p\frac{2\pi}{3}\right], \quad p = 0, \pm 1\ , \tag{4}$$

V'_0 accounts for the break of the static-field symmetry while V'_{12} represents the difference of potential energy for the various nonbonded pairs (H-H, H-D, and D-D). The in-phase ($\theta_1 - \theta_2 = 0$) or out-of-phase ($\theta_1 - \theta_2 = \pm 2\pi/3$) conformations are either stabilized or destabilized with respect to the fully hydrogenated system. If $p = 0$, the H-H or D-D pairs are either favored or disfavored, while, if $p = \pm 1$, the H-D pairs are either more stable ($V'_c > 0$) or less stable ($V'_c < 0$) than the other pairs.

V'_0 removes the degeneracy of the AE state (Fig. 7) and the most intense band splits into two components. Since this splitting is not observed in the spectra it must be less than $\sim 10-15$ μeV. Therefore, all the methyl-group conformations should be virtually equivalent in this case.

3. *Infinite chain*

The third approach to the dynamics of the methyl groups in 4MP is that of an infinite chain of coupled rotors.[20,21] The Hamiltonian is

$$H_c = \sum_j \left[-\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}[1-\cos(3\theta_j)] + \frac{V_c}{2}\{1-\cos[3(\theta_{j+1}-\theta_j)]\} \right]\ , \tag{5}$$

where θ_j is the angular coordinate of the jth rotor in the one-dimensional chain with parameter L. V_0 is the on-site potential, which does not depend on lattice position, and V_c is the coupling ("strain" energy) between neighboring rotors. When $\theta_{j+1} - \theta_j$ is sufficiently small, Eq. (5) is equivalent to the sine-Gordon equation[25–36]

$$H_c \sim \sum_j \left[-\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}[1-\cos(3\theta_j)] + \frac{9V_c}{4}(\theta_{j+1}-\theta_j)^2 \right]\ . \tag{6}$$

The dynamics of this system are quite different and much richer than those of the single-particle or coupled pair. The relevant mathematical formulas are given in Table IV.

The rotational motions of the single particle (i.e., small oscillations about the equilibrium position) become a continuum of roton states in the infinite chain. This is the familiar correspondence between isolated vibrations and collective excitations in crystals. Tunneling for the single particle gives an analogous collective tunneling for the whole chain. However, in contrast to rotons, there is no continuum of states. Only in-phase and out-of-phase permutations of the protons are allowed by the translational symmetry of the chain.

In addition to these collective excitations, spatially localized excitations may occur in the chain. Analytical formulas are known for the kink, or soliton, and for the breather mode, or doublet, in the sine-Gordon equation.[28–34] In the ideal case (i.e., in the continuous chain), these excitations have infinite lifetimes and behave as massive pseudoparticles traveling along the chain. Solitons carry the mean position of the methyl groups from one minimum of the local potential (say $\theta = 0$) to another minimum (say $\theta = 2\pi/3$) and vice versa for antisolitons. This is analogous to jumping over the potential barrier in the classical picture of the single rotor. In both cases, these processes are thermally activated and disappear at low temperatures. The breather mode, on the other hand, has no counterpart with single rotors. As a soliton-antisoliton bound pair (or doublet), it can be visualized as a preliminary step for the creation of a free soliton and a free antisoliton. Alternatively, it may be visualized as a superposition of roton states corresponding to spatially localized oscillations of the methyl groups around their equilibrium positions. At very low temperatures, only breather modes survive while the density of solitons and antisolitons vanishes.

Quantization of the sine-Gordon equation gives mass renormalization for the particles,[26,29] which accounts for the soliton or breather interactions with rotons which modify the zero-point energy. The renormalized mass is interpreted as the observable mass, as opposed to the bare

TABLE IV. Soliton and breather modes in the sine-Gordon potential: $V(\theta_j)=29.5/2[1-\cos(3\theta_j)]+44/2[1-\cos3(\theta_{j+1}-\theta_j)]$. V and θ are in cm^{-1} and rad units, respectively. L is the lattice parameter.

$C_6H_4NCH_3$	$C_6H_4NCH_2D$ (12%h_7)	$C_6H_4NCH_2D$	$C_6H_4NCHD_2$	$C_6D_4NCD_3$	
5.6	4.4	4.2	3.36	2.66	Rotational constant F/cm^{-1}=$h^2/8\pi^2 I_r$
38.56	34.18	33.39	29.88	26.57	$\hbar\omega_0$/cm^{-1}=$(9FV_0)^{1/2}$ (1)
47.09	41.74	40.78	36.48	32.46	$\hbar\omega_c$/cm^{-1}=$(9FV_c)^{1/2}$
25.33	24.30	24.08	22.93	21.55	$\hbar\omega_0'$/cm^{-1}=$2E^0_{0A}$ (2)
35.08	33.08	32.66	30.56	28.21	$\hbar\omega_c'$/cm^{-1}=$2E^c_{0A}$
26.74	22.81	22.18	19.67	17.75	$\hbar\omega_0'$/cm^{-1}=$E^0_{1A}-E^0_{0A}$ (3)
33.71	27.63	27.09	24.91	23.16	$\hbar\omega_c'$/cm^{-1}=$E^c_{1A}-E^3_{0A}$
		1.22			d/L: particle-width parameter
		144.11			E_0/cm^{-1}=$4(V_0V_c)^{1/2}$: rest energy of the classical soliton
		92.5			E_K/cm^{-1}=$E_0(1-9/8\pi)$: renormalized rest energy of the semiclassical soliton
		142.16			$E_B(1)$/cm^{-1}=$2E_K\sin[9/16(1-9/8\pi)]$: renormalized rest energy of the semiclassical breather
4.31(4.31)^a	2.93	2.75	2.13(2.03)	1.14(0.8)^a	Calculated (observed) in-phase tunneling frequencies
3.77(3.77)^a	2.31	2.11(2.16)	1.49	0.60(0.8)^a	Calculated (observed) out-of-phase tunneling frequencies
7.50 (4.15)^a	5.92 (3.26)^b	5.66 (3.13)	4.55 (2.74)	3.61 (1.8)^a	(1) Calculated (observed) frequencies for the 0→1 transitions of the semiclassical breather traveling in an infinite chain
4.21	3.80	3.65	3.20	2.74	(2)
3.89	2.66	2.52	2.13	1.85	(3)

[a] After Ref. 21.

[b] After Ref. 14.

mass of the classical theory.[32] In addition, the continuum of mass (or rest energy) states for the classical breather mode turns into a discrete spectrum $E_B(l)$ characterized by the quantum number l. The number of states depends on the potential periodicity: in the threefold case there is only one mass state ($l=1$), which is the ground state, while in a sixfold potential there is no breather state at all.

The breather mode behaves like a free quantum particle in a periodic medium. Because of the translational symmetry of the chain, steady propagation can occur only for discrete values of the energy:[20,21,26]

$$E_{n,l}=[E_B^2(l)+n^2\hbar^2\omega_c^2]^{1/2}, \quad n=0,\pm1,\pm2,\cdots \ . \tag{7}$$

For low potential barriers the harmonic frequency $\hbar\omega_c$ is not relevant (see Table IV, case 1). The effective value $\hbar\omega_c'$ depends on the mean-square amplitude for the internal oscillation of the breather mode. If this amplitude is small $\hbar\omega_c'$ is close to the frequency in the ground state labeled 0_A (see Table IV, case 2 with $\hbar\omega_c'=2E_{0A}^c$). For greater amplitudes $\hbar\omega_c'=E_{1A}^c-E_{0A}^c$ (see Table IV, case 3). As the deuteration increases, the agreement between calculated and observed traveling frequencies shifts smoothly from case 2 to case 3. This is because of the increasing of the mean-square amplitude for the internal oscillation as $\sim\omega_0^{-1}$. These results suggest strongly that the effective potentials for partially deuterated and fully hydrogenated methyl groups are very close to each other, both being amenable to interpretation as sine-Gordon systems.

The in-phase and out-of-phase tunneling transitions are calculated at 341 μeV (2.75 cm^{-1}) and 262 μeV (2.1 cm^{-1}), respectively. (In contrast to 4MP-h_7,[21] these transitions are expected far from the breather mode.) Thus, the simple sine-Gordon Hamiltonian [Eq. (6)] does not account for the existence of an additional band at very low temperatures in the breather mode region (at 436 μeV, Figs. 2 and 5). Two different effects may cause the observed band splitting: long-range ordering of the methyl-group conformations or changes of the potential barriers in Eq. (5) due to partial deuteration.

(a) Long-range ordering of the methyl groups. The splitting of the breather band can be due to the removal of the threefold symmetry in partially deuterated methyl groups. The Hamiltonian for an infinite chain of such particles is

$$H_c'=H_c+\frac{V_0'}{2}(1-\cos\theta_j)+\frac{V_c'}{2}\left[1-\cos\left[\theta_{j+1}-\theta_j+p\frac{2\pi}{3}\right]\right], \quad p=0,\pm1 \ . \tag{8}$$

As for the single particle (Sec. III A 1), V_0' destroys the on-site potential symmetry. This term probably has two distinct physical origins: the mean crystal field including long-range atom-atom interactions, and the local coupling with librations of the whole molecule. It follows that the minimum (or maximum) of V_0' [i.e., the origin of the angular coordinate ($\theta_j=0$)] may have different orientations with respect to the crystal axes for methyl groups at different sites. We therefore distinguish the "local" and the "absolute" angular coordinates as θ_j and Θ_j, respectively.

V_c' is due to different potential energies for the nonbonded pairs (H-H, H-D, and D-D), as in the model of coupled pairs (Sec. III A 2). However, in the sine-Gordon system this term may induce order for the methyl-group conformations along the chain which can be either in phase ($\theta_{j+1}-\theta_j=0$) or out of phase ($\theta_{j+1}-\theta_j=\pm2\pi/3$) with respect to the local angular coordinate.

Since V_0' and V_c' are small compared to V_0 and V_c, the change of the rest mass of the breather is negligible and different traveling frequencies are mainly due to different ω_c values in Eq. (7). Depending on the sign of V_c', the corresponding values are

$$\begin{aligned}
&\omega_{ci}=\omega_c\pm(FV_c')^{1/2}, \quad \theta_{j+1}=\theta_j, \ p=0 \ ;\\
&\omega_{co}=\omega_c\mp\left[\frac{FV_c'}{2}\right]^{1/2}, \quad \theta_{j+1}=\theta_j\pm\frac{2\pi}{3}, \ p=0 \ ;\\
&\omega_{ci}=\omega_c\mp\left[\frac{FV_c'}{2}\right]^{1/2}, \quad \theta_{j+1}=\theta_j, \ p=\pm1 \ ;\\
&\omega_{co}=\omega_c\pm(FV_c')^{1/2}, \quad \theta_{j+1}=\theta_j\pm\frac{2\pi}{3}, \ p=\pm1 \ .
\end{aligned} \tag{9}$$

$V_c'=0.25$ cm^{-1} gives a breather mode splitting of 0.38 cm^{-1} (47 μeV) in agreement with the observation. The chains can thus be described as a series of two different types of ordered domains at very low temperatures (Fig. 8): one of the two bands corresponds to a dephasing of

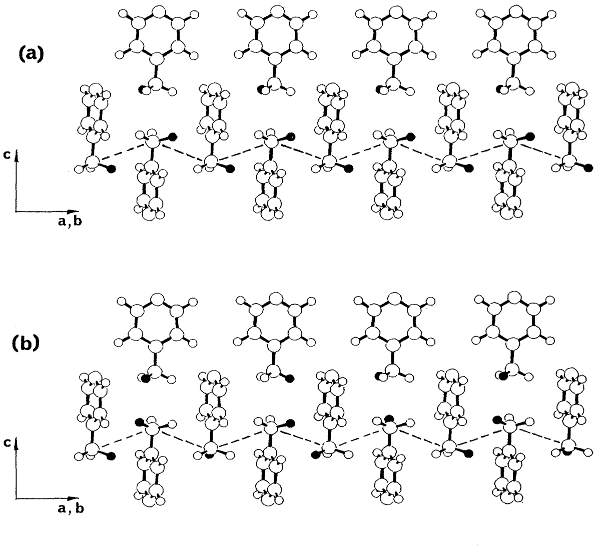

FIG. 8. Schematic view of chains of methyl groups in 4-methyl-pyridine ch_2d. Solid circles represent deuterium atoms. (a) In-phase conformation. (b) Out-of-phase conformation.

$\pm 2\pi/3$ for the methyl groups, while the domains where all the methyl groups are in phase with respect to the local coordinates correspond to the other band. Since the two bands are well resolved, breathers are presumably trapped in each domain and cannot readily cross the border between two adjacent domains.

Although partial deuteration reduces the threefold symmetry of the on-site potential, tunneling is still possible for an infinite chain if the energy difference between inequivalent local conformations is sufficiently small. Since tunneling of the whole chain converts randomly distributed methyl-group conformations into statistically equivalent distributions, such transitions can be observed. In contrast, if there is a long-range ordering of the methyl groups, then permuting the atoms of methly groups yields a nonequivalent chain conformation and tunneling should disappear.

Tunneling transitions calculated at 2.75 and 2.11 cm^{-1} (Table IV) are not readily observed (see Figs. 2 and 5). These bands may be lost in the background noise since they are much weaker than the breather mode[21] and their intensities are further decreased by the partial localization of the wave functions. Moreover, they would be split into several components in the different domains of the partially deuterated system.

In ordered domains the potential functions for in-phase and out-of-phase tunneling are

$$V_i(\theta_j)=\frac{V_0}{2}+\frac{V_0'}{2}(1-\cos\theta_j)\ , \tag{10}$$

$$\begin{aligned} V_o=&\frac{V_0}{2}[1-\cos(3\theta_j)]+\frac{V_0'}{2}(1-\cos\theta_j)\\ &+\frac{V_c}{2}[1-\cos(6\theta_j)]\\ &+\frac{V_c'}{2}\left[1-\cos\left[2\theta_j+p'\frac{2\pi}{3}\right]\right]\ . \end{aligned} \tag{11}$$

Here $p'=0$ or ± 1 for the two different domains, respectively. In all events, the band splits into two components for each tunneling mode.

In disordered domains V_0' averages out for the in-phase tunneling [Eq. (10)] and the band is single. Alternatively, there is an infinity of different averaged values for V_0' and V_c' for out-of-phase tunneling and the band should be broad.

Although it is not possible to propose a direct estimate of V_0' from the tunneling bands, the intensity ratio of the two breather modes in 4MP-ch_2d at very low temperatures ($I_{3.13\ \text{cm}^{-1}}/I_{3.51\ \text{cm}^{-1}}$) is proportional to the probability ratio for the two different domains of methyl-group conformations and, therefore, it is related to V_0' and V_c'. ($V_0'\sim 2$–$3\ \text{cm}^{-1}$ is consistent with the observation.) The relative stability of the two domains is a balance between two conflicting effects. Whereas V_0' stabilizes domains for which all local coordinates are in phase ($\theta_j=0$), V_c' favors the dephasing of the methyl groups. The two different domains can thus coexist even at very low temperatures.

(b) Change of the effective potential. An alternative approach to the spectra of 4MP-ch_2d within the sine-Gordon theory is to assume that an important change of the effective potential results from partial deuteration. Then, the bands at 3.13 and 3.51 cm^{-1} are assigned to the breather mode and to the in-phase tunneling transition, respectively. The corresponding potential parameters are $V_0=18\ \text{cm}^{-1}$ and $V_c=33\ \text{cm}^{-1}$. The relative decrease with respect to 4MP-h_7 is about 30%. Since the calculated out-of-phase tunneling frequency of 3.15 cm^{-1} is so close to the transition of the breather mode, the corresponding band would not be resolved. Again, the band at 0.6 cm^{-1} could correspond to the hot transition between the tunneling states.

In this approach there is no evidence of additional band splitting indicating significant V_0' and V_c' terms. However, if $V_0'=0$ and $V_c'\neq 0$, there is only one type of chain with constant dephasing of the methyl-group orientation. Since the on-site potential is purely threefold, in-phase tunneling is possible. In contrast, out-of-phase tunneling should be destroyed by a large V_c' term which may account for the absence of a band at 3.15 cm^{-1}. Alternatively, if $V_0'\neq 0$, then the distribution of methyl-group conformations along the chain should be random ($V_c'=0$) to allow for tunneling transitions. In this case the two tunneling transitions would be split.

4. *Discussion*

There is no unique interpretation of the spectra of 4MP-ch_2d at very low temperatures for the methyl-group dynamics. If rather large changes for the effective potential, due to partial deuteration, are accepted, then the spectra are well represented by different models: either coupled pairs (Sec. III A 2) or sine-Gordon infinite chains [Sec. III A 3 (b)]. Alternatively, if it is supposed that partial deuteration should remove the threefold symmetry of the methyl groups, then either the single-particle approach (Sec. III A 1) or the sine-Gordon theory [Sec. III A 3 (a)] are relevant. However, only the sine-Gordon theory is consistent with negligible changes of the main potential terms and small perturbations due to partial deuteration [Sec. III A 3 (a)]. In Sec. III B it is shown that temperature effects provide additional information which further supports the sine-Gordon interpretation.

B. Temperature effect

In methyl-group tunneling spectroscopy, two mechanisms are supposed to contribute to frequency shifts with temperature: mixing of tunneling states[42–47] or coupling with phonons in the crystal.[24,48] However, both mechanisms are negligible in pure 4MP-h_7 for which no frequency shift is observed for the breather mode between 2 and 15 K.[15,19,21] Therefore, the observed temperature effects (Figs. 2 and 5) are related to the partial deuteration of the methyl group.

The spectra in Figs. 2 and 5 suggest two different manifestations of the temperature effects. One of them is revealed by the spectra in Fig. 5 which shows that the band at 3.13 cm^{-1} merges progressively into the band at 3.51 cm^{-1} between 2 and 5 K, the conversion being almost completed at 5 K. This indicates a thermal equilibrium between different states, or conformations, with a slow exchange rate. The spectra in Fig. 3, on the other hand, show a continuous upward frequency shift to 3.84 cm^{-1} above 7 K which may be due to a fast exchange between different states. The two possible behaviors are discussed separately below.

1. The low-resolution limit

In this model the band splitting is neglected (Fig. 2) and only the temperature effect on the mean frequency can be considered. In contrast to the CH_3 or CD_3 groups, the rotor axis of the partially deuterated methyl group is different from that of the $C2$ axis of the pyridine ring. The center of mass of the H_2D group is at about 0.25 Å from the $C2$ axis and the angle between the effective axis of rotation and the pyridine $C2$ axis is about 5°. Consequently, the rotation of the CH_2D group induces fluctuations for the mean orientation of the molecule and the internal rotation becomes coupled to the rotational librations of the whole molecule. Clearly, this is different from the fully hydrogenated material. This is referred to as the "imbalance" effect.

The Hamiltonian describing methyl groups coupled with phonons has been extensively discussed.[21,23,24,28] If coupling with a particular phonon is dominant, then the variation with temperature of the effective potential is close to a first-order law with an activation energy corresponding to that phonon frequency. However, in the case of 4MP-ch_2d, the estimated activation energy (4.5±0.5 cm^{-1}, see Fig. 4) is too low to be representative of rotational librations in the crystal.[13] Rather, it is close to the frequency of the main band itself and the population of the excited state may be an important factor in the mechanism of the temperature effect.

A possible interpretation is that the mean rotational amplitude of the methyl groups is greater in the excited state. Then, because of the imbalance effect, the effective on-site potential for the methyl groups is averaged out. This explanation is relevant only for the breather mode while, for the single particle, there is no change of the mean amplitude in the excited tunneling states.

In the sine-Gordon theory, changing V_0 or V_c has opposing effects on the traveling frequency of the breather mode. The frequency increases as the on-site potential decreases due to the decreasing of the rest energy in Eq. (7). In contrast, the frequency decreases with V_c and it is very unlikely that this term could increase at high temperature. [It is assumed that intermolecular mean distances do not vary with temperature for 4MP-ch_2d as for 4MP-d_7 or 4MP-h_7 (Ref. 17).] Therefore, the observed upward frequency shift is mainly due to the decreasing of V_0 at high temperatures. An eventual decreasing of V_c is much less important and can be neglected.

Within the assumption that the frequency shift is due only to changes of the on-site potential, the calculated rest energy of the breather and the local potential at the temperatures corresponding to the experiments are collected in Table V. The variation of V_0 with temperature is consistent with a first-order law and an activation energy of 4.5±0.5 cm^{-1} (see Fig. 4).

TABLE V. Effective rest energy, E_B, and local potential V_0 for the breather in 4MP-ch_2d at various temperatures. The coupling potential is $V_c=44$ cm^{-1}.

T (K)	Freq. (cm^{-1})	E_B (cm^{-1})	V_0 (cm^{-1})
1.6	3.13	133	29.5
2.5	3.26	126	27.7
4.5	3.59	114	22.7
7.5	3.84	106	19.6

For a more quantitative approach it is assumed that, at very low temperatures (~0 K), only the ground traveling state of the breather is populated and the on-site potential V_0 is a maximum (i.e., 29.5 cm^{-1}, see Tables IV and V). At higher temperatures, the first-excited state is populated and V_0 decreases. Since higher excited states are above 2 meV (16 cm^{-1}) (Ref. 21), their populations can be neglected below 15 K. Therefore, the population of the first-excited state is

$$P_1(T)=\frac{2e^{-E_{01}(T)/kT}}{1+2e^{-E_{01}(T)/kT}} . \qquad (12)$$

The factor 2 accounts for the degeneracy of the traveling states [Eq. (7)]. In the excited state, the local potential becomes $V_1 < V_0$ and the averaged potential experienced by the methyl groups becomes

$$V(T)=\frac{V_0+2V_1e^{-E_{01}(T)/kT}}{1+2e^{-E_{01}(T)/kT}} . \qquad (13)$$

The solid line in Fig. 9 was obtained with $V_1=5$ cm^{-1} with the rest energy of the breather in the ground state being adjusted to 137 cm^{-1}. It appears that the local po-

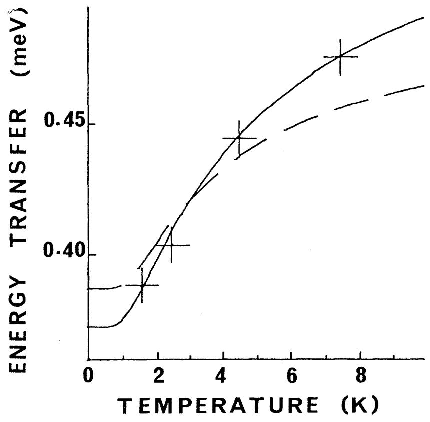

FIG. 9. Variation of the frequency at maximum intensity in the partially deuterated 4-methyl-pyridine ch_2d. +, experimental measurements. Solid line, calculated for the pure sample. Dashed line, calculated for a mixture of the partially deuterated molecules containing 12% of fully hydrogenated derivative.

tential is strongly decreased when the breather travels along the chains. As the temperature increases, the breather width, which is about $4V_c/V_0$, increases while the rest mass decreases. The breather mode at low temperatures is progressively converted into a superposition of rotons in an almost freely rotating chain of coupled methyl groups.

The change of the breather dynamics with the density of traveling breathers in the system implies breather-breather interactions. This is in marked contrast to the fully hydrogenated 4-methyl-pyridine which demonstrates the ideal sine-Gordon case in which there is no such interaction. This interaction is therefore a consequence of the partial deuteration.

Because of the imbalance effect, when two traveling breathers associate to form a pair, a part of the potential energy (particle mass) is converted into kinetic energy and the pair velocity is greater than that of the single pseudoparticle. The amplitude for the envelope oscillation is larger for the pair and the effective on-site potential decreases. Presumably, this decrease accounts for the stability of the pair. Moreover, as the density of traveling breathers increases, more than two breathers can associate to form larger aggregates which decreases the effective potential still further.

2. *The very low-temperature regime*

The better resolved spectra (Fig. 5) reveal two bands at 3.13 and 3.51 cm^{-1} which show different temperature effects which are inconsistent with a simple decreasing of the on-site potential. The band at 3.13 cm^{-1} merges progressively into the band at 3.51 cm^{-1} which itself shows no significant frequency shift below 5 K. Simultaneously, the intensity of the band at 74 μeV (0.6 cm^{-1}) increases.

Three of the four models discussed in Sec. III A are inconsistent with these observations: the single particle (Sec. III A 1), the coupled pair (Sec. III A 2) and the large change of the effective sine-Gordon potential due to partial deuteration [Sec. III A 3 (b)].

In the single-particle model (Sec. III A 1) and the coupled pair (Sec. III A 2), the band at 0.6 cm^{-1} is due to a hot transition between the two levels at 3.13 and 3.51 cm^{-1}. It should diminish in frequency and then disappear as the band at 3.13 cm^{-1} increases in frequency. In contrast, however, the two bands show opposite temperature effects: the intensity of the band at 0.6 cm^{-1} is greater at high temperature.

In the simple sine-Gordon model, which assumes large changes of the effective potential with deuteration [Sec. III A 3 (b)], the bands at 3.13 and 3.51 cm^{-1} are assigned to the breather and the in-phase tunneling transitions, respectively. Both should show similar upward frequency shifts when V_0 decreases at high temperature. One interpretation of the observation is that V_0 does not change while V_c increases with temperature, but this is unlikely according to previous observation on 4MP-h_7.[21] Further, the out-of-phase tunneling band should be shifted downwards, away from the breather band and it should have a similar intensity to the band at 3.51 cm^{-1}. However, this band is not observed.

In contrast, the interpretation in terms of different domains corresponding to different methyl-group conformations [Sec. III A 3 (a)] provides a consistent account of the temperature effect. As the temperature increases, the tunneling states at 2.11 and 2.75 cm^{-1} are progressively populated. The probability distribution for the local coordinate θ_j can be then described by a superposition of the three states and the resulting wave function is very similar to that of a true threefold potential (see Fig. 6 for a qualitative picture of the wave functions). The corresponding phenomenological picture is that V_0' vanishes when the tunneling excited states become populated. In contrast, V_c' is little affected because the coherence of the chain is retained when the tunneling states are populated. Owing to the conflicting effects of V_0' and V_c' [see Sec. III A 3 (a)], when V_0' decreases the chain domains stabilized by this term (where all the methyl groups are in phase with respect to the local coordinate θ_j) progressively convert into chains characterized by a $\pm 2\pi/3$ dephasing of the methyl-group conformations. These domains are stabilized by V_c' and the breather frequency is 3.51 cm^{-1}. This conversion is almost complete at 5 K. The methyl-group chains are then homogeneous regarding the sine-Gordon dynamics. Breathers can propagate freely and may interact with each other such that the averaging mechanism for V_0 becomes effective. Simultaneously, out-of-phase tunneling levels calculated near 2.11 cm^{-1} are populated and the intensity of the hot transition to the in-phase tunneling levels near 2.75 cm^{-1} is enhanced. In this case, the expected frequency (0.64 cm^{-1}) is in close agreement with the observed peak (0.6 cm^{-1}).

In the fully hydrogenated material the tunneling frequencies are at 3.77 (out of phase) and 4.31 cm^{-1} (in phase, see Table IV). Therefore, the hot transition between the two tunneling states should appear at 0.54 cm^{-1}. Despite considerable effort, it has never been observed. The population of the state at 3.77 cm^{-1} in 4MP-h_7 is lower than that of the state at 2.11 cm^{-1} in 4MP-ch_2d at the same temperature. But the difference is rather tiny and additional effects are likely. The partial localization of the wave functions in the partially deuterated sample seems to be an important factor. A thorough calculation of the transition matrix elements should be necessary to account for the observation.

IV. DISCUSSION

The analysis of the INS spectra of 4MP-ch_2d presented in Sec. III strongly supports the sine-Gordon model already proposed for fully hydrogenated 4-methyl-pyridine. The other possible approaches (single-particle or pair of coupled methyl groups) can be eliminated. Moreover, the effective potential at very low temperatures is unaffected (to first order) by partial deuteration. However, small perturbation terms need to be added to account for the loss of the threefold symmetry of the partially deuterated methyl group. These terms produce a splitting of the breather band.

In this section (Sec. IV A), it is shown that additional support for these conclusions is provided by the spectra of an isotopic mixture containing partially deuterated and fully hydrogenated molecules.[14] Then a detailed picture of the methyl-group dynamics and crystal phase transitions in 4-methyl-pyridine is presented (Sec. IV B).

A. Isotopic mixture

Brom and co-workers have studied a mixture of 4MP-*ch*$_2$*d* doped with fully hydrogenated 4MP-*h*$_7$ (12%).[14] At 1.4 K they observed a single band at 405 μeV (3.26 cm^{-1}). This frequency progressively increased to 457 μeV (3.68 cm^{-1}) above 10 K. The curve representing the variation of the frequency with temperature has a sigmoidal shape consistent with the existence of a second-order phase transition at 5.4 K.[8] Our data (Fig. 2) show a much larger frequency shift for pure 4MP-*ch*$_2$*d*. This discrepancy is not surprising since the breather is a collective mode. Previous experiments have shown that the isotopic concentration in 4-methyl-pyridine has important effects on the frequency.

In the mixture of 4MP-*ch*$_2$*d* and 4MP-*h*$_7$, molecules are randomly distributed at the crystal sites. If the fully hydrogenated molecules introduce only small perturbations for the breather mode, the crystal behaves like a homogeneous medium characterized by an effective moment of inertia (I_e) which is the average value:

$$I_e = pI_{4\text{MP-}h_7} + (1-p)I_{4\text{MP-}ch_2d} \,. \tag{14}$$

Here, p is the concentration for 4MP-*h*$_7$ molecules. The calculated frequency for the traveling breather (Table IV) is then close to that observed. At first sight, this seems to confirm the collective behavior of the methyl-group dynamics in 4-methyl-pyridine and a slight sensitivity of the effective potential to isotopic substitutions.

However, the agreement between the calculated and observed frequencies may be misleading. According to Eq. (7) and using the relevant formulas given in Table IV, the frequency (ν_{01}) for the breather transition can be rewritten as:

$$\nu_{01} = (16V_0V_c + 9FV_c)^{1/2} - 4(V_0V_c)^{1/2} \,. \tag{15}$$

Therefore

$$\frac{\Delta\nu_{01}}{\nu_{01}} \cong -\frac{\Delta I_e}{I_e} + \frac{1}{2}\left[\frac{\Delta V_c}{V_c} - \frac{\Delta V_0}{V_0}\right] . \tag{16}$$

The frequency difference between pure 4MP-*ch*$_2$*d* and the isotopic mixture is consistent with

$$\frac{\Delta\nu_{01}}{\nu_{01}} = -\frac{\Delta I_e}{I_e} \,. \tag{17}$$

Therefore, either V_0 and V_c are constant or they are correlated such that

$$\frac{\Delta V_c}{V_c} = \frac{\Delta V_0}{V_0} \,. \tag{18}$$

This latter possibility seems unlikely since the two potentials have quite different physical origins.

The frequency shift with temperature in the isotopic mixture can be represented by the same mechanism as pure 4MP-*ch*$_2$*d* (Sec. III B 1). The dashed line on Fig. 9 was obtained with $V_1 = 12$ cm^{-1} [Eq. (13)], in agreement with the observation.[14]

Comparison with the values obtained for 4MP-*h*$_7$ ($V_1 = V_0 = 29.5$ cm^{-1}) and 4MP-*ch*$_2$*d* ($V_1 = 5$ cm^{-1}) shows that V_1 in the mixture is much larger than the value of ~ 8 cm^{-1} obtained by averaging the relative concentrations for each species. Fully hydrogenated molecules stabilize the on-site potential relatively to the imbalance effect of partially deuterated methyl groups. They limit the size of breather aggregates and, therefore, the decrease of V_0.

It was shown[21] that the breather dynamics in mixtures of 4MP-*h*$_7$ and 4MP-*d*$_7$ at very low temperatures are determined by the cluster size distribution of either hydrogenated or deuterated molecules. This is due to the relatively large difference for the zero-point energies of both species (4.2 cm^{-1}=6.3 K). For very diluted mixtures (below 20% in 4MP-*h*$_7$), the breathers due to hydrogenated methyl groups are trapped in very small clusters (boxes) and the traveling frequency is low (3.06 cm^{-1}). On the contrary, mixtures of 4MP-*ch*$_2$*d* and 4MP-*h*$_7$ molecules behave as a continuous medium. Breathers in 4MP-*h*$_7$ and 4MP-*ch*$_2$*d* clusters are not trapped. This is consistent with the much smaller difference for their zero-point energies (1.8 cm^{-1}=2.7 K). Even at the lowest temperature reported for the mixture (1.4 K),[14] this difference remains similar to the thermal-bath fluctuations and breather-roton states can travel across the clusters.

In contrast to pure 4MP-*ch*$_2$*d* (Fig. 5), the spectra of Brom and co-workers[14] show no band splitting for the breather in the isotopic mixture. This may be due to insufficient resolution and more accurate data would be necessary to analyze the effect of the isotopic dilution on the ordering of the partially deuterated methyl groups.

B. Methyl-group dynamics and crystal phase transitions

The spectra obtained for partially deuterated molecules and previous Raman[13] and INS (Refs. 20 and 21) data provide a more comprehensive picture of the physics determining the methyl-group dynamics in 4-methyl-pyridine. In 4MP-*h*$_7$ below $\sim$100 K, Raman bands due to methyl-group rotation are in good agreement with the traveling states calculated for the breather.[21] Above 100 K free rotation occurs in 4MP-*h*$_7$, indicating that V_0 and V_c have completely averaged. This transition is monitored by a rotational libration mode at 61 cm^{-1}.[13] Between 1.6 and 15 K, the INS spectra of 4MP-*h*$_7$ show no frequency shift for the breather mode in the 500-μeV region. There is no change of the effective potential in this temperature range and no observable breather-breather interaction. This is entirely consistent with negligible population of the phonon state at 61 cm^{-1} at such temperatures and with the absence of coupling to other phonons at lower energy.

In contrast, the partially deuterated molecule shows a decrease of the on-site potential V_0 already below 10 K.

Because V_c seems to be unaffected, the averaging mechanisms are different for the on-site and for the coupling potential.

The on-site potential is due to the mean crystal field including long-range interactions with all the atoms. Its averaging by thermal excitation depends on the mean amplitude of the coupled phonon. A spectacular consequence of partial deuteration is the reduction of the activation energy for the averaging process of V_0 by a factor ~ 15. This arises from the coupling of the rotational and librational modes induced by the imbalanced methyl groups.

The coupling potential V_c, on the other hand, is due to methyl-methyl interaction along the chains and both the amplitude and the wave vector of the coupled phonon play a role in averaging out V_c. Only phonons with short spatial wavelength (i.e., large k vectors) can create large fluctuations for the methyl-methyl distances along the chain. Temperature effects on 4MP-ch_2d suggest that neither excitation of the collective tunneling states nor traveling breathers can change V_c.

The crystal structure of 4MP-ch_2d is not known, but presumably, the cell parameters are similar to those measured for 4MP-h_7 and 4MP-d_7 which are identical to each other.[17] According to these structures, the fully hydrogenated or fully deuterated methyl groups are crystallographically disordered, even at liquid-helium temperature. In contrast, the breather band splitting at ~ 2 K shows that partial deuteration introduces a new order parameter related to the relative angular phase of the methyl groups. Different ordered domains can be distinguished at low temperatures. The very small energy difference is related to the perturbation terms V_0' and V_c' in Eq. (8).

As temperature is increased, one type of domain is converted into the other one, this conversion being monitored by the tunneling states near 2.5 cm^{-1}. The conversion is complete by ~ 5 K and may, therefore, correspond to the second-order phase transition found at 5.4 K by calorimetric measurements.[9] It is noticeable that, in the low-temperature phase, two different domains of methyl-group conformations coexist, whereas only one conformation survives above the transition. However, the increasing order with respect to the relative phase $(\theta_{j+1}-\theta_j)$ of the methyl groups along the chains is achieved at the expense of an increasing disorder for the torsional coordinate (θ_j). The transition corresponds to the recovery of the averaged threefold symmetry for the on-site potential above 5 K.

So far the methyl-group dynamics and conformation have been described in terms of the local torsional coordinates (θ_j). In order to propose some correspondence with the absolute coordinate (Θ_j), it is necessary to understand the physical origin of the different terms of the sine-Gordon potential. The methyl-group dynamics in 4-methyl-pyridine suggest that three different types of interaction can be distinguished.

Firstly, the interaction of the methyl groups with the pyridine rings of the surrounding molecules in the crystal. This is the main source of the on-site potential. Because all molecules are equivalent, all on-site potentials are equivalent with respect to the local coordinate θ_j. However, in terms of the absolute coordinate, Θ_j, the potentials are different for chains parallel to the a or b crystal axes (see Figs. 1 and 8). Further, in partially deuterated molecules, interactions are slightly different for hydrogen and deuterium atoms, but owing to the rather high site symmetry for the molecular environment, such small differences cannot produce any contribution to V_0'.

Secondly, the coupling of the methyl-group rotation to the molecular librational modes is a key factor in the methyl-group dynamics. In the partially deuterated materials, the potential V_0' is mainly due to the imbalance effect. This potential has thus a definite orientation with respect to the molecular referential. Inspection of the crystal structure (Figs. 1 and 8) reveals that, for a given chain, all pyridine rings are parallel. Therefore, the V_0' potential functions are identical with respect to the absolute coordinate. However, these potentials are different with respect to the crystal referential for chains along the a or the b directions.

Thirdly, the pair interactions (H-H, H-D, and D-D) between methyl groups are responsible for the coupling potentials V_c and V_c'. However, the physical origin of these terms is unclear. In principle, the most important interaction should be the closest-contact pairs of methyl groups along the c direction. In contrast, the dynamics appear to be governed by interactions along the a or b crystal axes which correspond to greater atom-atom distances. This suggests that simple van der Waals pair interactions do not represent the real potential adequately. Alternatively, the picture of infinite chains along well-defined directions may be questioned. In all events, the sine-Gordon theory is successful in providing a consistent representation of the physics within the crystal.

V. CONCLUSION

The inelastic-neutron-scattering spectra of 4-methyl-pyridine with partially deuterated methyl groups can distinguish between the different theoretical approaches proposed so far to describe the methyl-group dynamics: isolated methyl groups, pairs of coupled rotors, and infinite chains of coupled methyl groups. Single-particle and coupled pairs of methyl groups can be rejected. In contrast, all the INS data obtained so far on a large set of different isotopic derivatives of 4-methyl-pyridine and their mixtures are consistent with the existence of traveling breathers as predicted by the quantum sine-Gordon theory.

Moreover, the INS spectra of the partially deuterated derivatives illustrate some properties of the sine-Gordon model extended to asymmetric particles. The sine-Gordon potentials for 4MP-h_7 and 4MP-ch_2d are identical to first order (V_0 and V_c), but for 4MP-ch_2d, small perturbation terms (V_0' and V_c') must be considered. The first term removes the on-site threefold symmetry of the methyl groups, while the second term accounts for different potential energies for the nonbonded pairs H-H, H-D, and D-D.

At low temperatures (~ 2 K), different chain domains regarding methyl-group conformations are distinguished on the basis of different breather velocities. This is directly related to V_c'. The estimated value ($V_c'=0.25$ cm^{-1}) is very small compared to the first-order term ($V_c=44$ cm^{-1}).

The probabilities for each chain conformation are determined by V_0' and V_c'. As the temperature increases, the threefold symmetry of the on-site potential is recovered and only one chain conformation survives at 5 K. The conversion is monitored by the tunneling states of the chain near 2.5 cm^{-1}. This may correspond to the second-order phase transition shown by calorimetric measurements.[9]

The main consequence of the imbalance effect for partially deuterated methyl groups is a mixing of the rotational coordinate with molecular librations in the crystal. The effective on-site potential then depends on the amplitude of the methyl-group rotation itself. Traveling breathers may then associate to form dimers, trimers, etc., in which a part of the potential energy (mass) is converted into kinetic energy. The velocity increases with the density of excited breathers. Simultaneously, because of the mixing with librations, V_0 is averaged out and breathers progressively transform into rotons. This is in marked contrast to the fully hydrogenated material for which there is no evidence of breather self-association.

ACKNOWLEDGMENTS

We would like to thank Dr. M. F. Lautié from LASIR-CNRS, Thiais, for her careful preparation of the deuterated samples and S. T. Robertson for his help in the neutron-scattering experiments.

---

[1] H. D. Rudolph, H. Dreizler, and H. Seiler, Z. Naturforsch. Teil A **22**, 1738 (1967).

[2] J. Haupt, Phys. Lett. **38A**, 389 (1972).

[3] J. Haupt, Z. Naturforsch. Teil A **28**, 98 (1973).

[4] A. Péneau, Thèse de Doctorat d'Etat, Université Paris-Sud, Orsay, 1975.

[5] B. Alefeld, A. Kollmar, and B. A. Dasannacharya, J. Chem. Phys. **63**, 4415 (1975).

[6] J. B. Moffat, J. Mol. Struct. **32**, 67 (1976).

[7] W. Press, *Single Particle Rotation in Molecular Crystals*, Vol. 92 of *Springer Tracts in Modern Physics* (Springer-Verlag, Berlin, 1981).

[8] H. den Adel, H. B. Brom, Z. Dokoupil, and W. J. Huiskamp, Physica B **111**, 160 (1981).

[9] H. den Adel, H. B. Brom, W. J. Huiskamp, and B. Alefeld, Physica B **112**, 309 (1982).

[10] A. Péneau, M. Gourdji, and L. Guibé, J. Mol. Struct. **111**, 227 (1983).

[11] U. Ohms, H. Guth, W. Treutmann, H. Dannohl, A. Schweig, and G. Heger, J. Chem. Phys. **83**, 273 (1985).

[12] L. Soulard, F. Fillaux, G. Braathen, N. Le Calvé, and B. Pasquier, Chem. Phys. Lett. **125**, 41 (1986).

[13] N. le Calvé, B. Pasquier, G. Braathen, L. Soulard, and F. Fillaux, J. Phys. C **19**, 6695 (1986).

[14] H. B. Brom, H. den Adel, and B. Alefeld, in *Quantum Aspects of Molecular Motions in Solids*, edited by A. Heidemann, A. Magerl, M. Prager, D. Richter, and T. Springer (Springer-Verlag, Berlin, 1987), p. 113.

[15] K. J. Abed, S. Clough, C. J. Carlile, B. Rosi, and R. C. Ward, Chem. Phys. Lett. **141**, 215 (1987).

[16] N. Le Calvé, D. Cavagnat, and F. Fillaux, Chem. Phys. Lett. **146**, 549 (1988).

[17] C. J. Carlile, R. M. Ibberson, F. Fillaux, and B. T. M. Willis, Z. Kristallogr. **193**, 243 (1990).

[18] S. G. Biswas, Ind. J. Phys. **35**, 261 (1961).

[19] C. J. Carlile, S. Clough, A. J. Horsewill, and A. Smith, Chem. Phys. **134**, 437 (1989).

[20] F. Fillaux and C. J. Carlile, Chem. Phys. Lett. **162**, 188 (1989).

[21] F. Fillaux and C. J. Carlile, Phys. Rev. B **42**, 5990 (1990).

[22] S. Clough, A. Heidemann, A. J. Horsewill, and M. N. J. Paley, Z. Phys. B **55**, 1 (1984).

[23] A. Heidemann, K. J. Abed, C. J. Barker, and S. Clough, Z. Phys. B **66**, 355 (1987).

[24] A. Heidemann, H. Friedrich, E. Gunther, and W. Hausler, Z. Phys. B **76**, 335 (1989).

[25] A. Scott, F. Chu, and D. McLaughlin, Proc. IEEE **61**, 1443 (1973).

[26] R. F. Dashen, B. Hasslacher, and A. Neveu, Phys. Rev. D **11**, 3424 (1975).

[27] S. Coleman, Phys. Rev. D **11**, 2088 (1975).

[28] M. J. Rice, A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Phys. Rev. Lett. **36**, 432 (1976).

[29] R. Jackiw, Rev. Mod. Phys. **49**, 681 (1977).

[30] M. B. Fogel, S. E. Trullinger, A. R. Bishop, and J. A. Krumhansl, Phys. Rev. B **15**, 1578 (1977).

[31] J. F. Currie, S. E. Trullinger, A. R. Bishop, and J. A. Krumhansl, Phys. Rev. B **15**, 5567 (1977).

[32] S. E. Trullinger, Solid State Commun. **29**, 27 (1979).

[33] E. Stoll, T. Schneider, and A. R. Bishop, Phys. Rev. Lett. **42**, 937 (1979).

[34] J. F. Currie, J. A. Krumhansl, A. R. Bishop, and S. E. Trullinger, Phys. Rev. B **22**, 477 (1980).

[35] M. Altenbokum, U. Kaulfuss, and J. J. M. Verbaarschot, Phys. Rev. D **34**, 1840 (1986).

[36] R. D. Carlitz and P. A. Millard, Phys. Rev. D **37**, 2269 (1988).

[37] O. F. Beumel, Jr., W. N. Smith, and B. Rybalka, Synthesis **43**, (1974).

[38] V. M. Micovic and H. Lj. Mihailovic, Recl. Trav. Chim. Pays-Bas **71**, 970 (1952).

[39] H. C. Brownand and G. J. McDonald, J. Amer. Chem. Soc. **85**, 2514 (1966).

[40] C. J. Carlile, Nucl. Instrum. Methods (to be published).

[41] J. R. Durig, S. M. Craven, and W. C. Harris, *Vibrational Spectra and Structure* (Marcel Dekker, New York, 1972), Vol. I, p. 73.

[42] P. S. Allen, J. Phys. C **7**, L22 (1974).

[43] S. Clough, J. Phys. C **9**, L523 (1976).

[44] S. Clough and A. Heidemann, J. Phys. C **12**, 761 (1979).

[45] S. Clough, J. Phys. C **14**, 1009 (1981).

[46] A. C. Hewson, J. Phys. C **15**, 3841 (1982).

[47] K. D. Moller and H. G. Andresen, J. Chem. Phys. **37**, 1800 (1962).

[48] M. Prager, J. Stanislawski, and W. Hausler, J. Chem. Phys. **86**, 2563 (1987).