

**PROCEEDINGS OF THE THIRD CONFERENCE
LOCALIZATION & ENERGY TRANSFER IN NONLINEAR
SYSTEMS**

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COLLECTIVE ROTATIONAL TUNNELLING AND QUANTUM SINE-GORDON SOLITONS

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The collective rotational dynamics in 1-D of methyl groups in the 4-methylpyridine crystal are analyzed. In the quantum sine-Gordon theory, heavy pseudo particles corresponding to coherent translation of large numbers of kinks or antikinks account for collective rotation. We speculate these excitations are also solutions of the fully periodical Hamiltonian for an isolated infinite chain of coupled methyl groups. In the quantum regime these spatially extended particles are not diffracted by the chain lattice and free translation takes place if the kinetic energy is within the tunnelling energy band. The periodicity of the eigenstates imposes quantization of the kinetic momentum p of the particles to be an integer number of \hbar/r , where r is the radius of the tops. The calculated spectrum is in accordance with previously reported transitions for collective tunnelling.

1. INTRODUCTION

Nonlinear dynamics giving rise to spatially localized non-dissipative waves in an extended lattice are a source of new phenomena and technological principles in advanced materials research.¹ They are also supposed to be key elements in complex events on the molecular level of life functioning. Among nonlinear models, the sine-Gordon equation covers a vast area of applications: dislocations in solids, long Josephson junctions, ferromagnets, charge-density waves, liquid crystals, methyl rotation, field theory, *etc.* Nonlinear waves such as kinks, antikinks and breathers are exact solutions of this integrable system in the continuous limit. In the classical regime, the stability and dynamics of these excitations are rather well documented but theoretical and experimental studies of the quantum regime are rather scarce. The 4-methylpyridine crystal (4MP or γ -picoline, C_6H_7N) is a unique example where the rotational dynamics of infinite chains of coupled methyl groups can be represented with the quantum sine-Gordon theory.^{2,3,4,5,6} This theory accounts for a long list of experimental data. However, it was built with different pieces that could be mutually in conflict: the fully periodical Hamiltonian for an infinite chain of coupled rotors

–see below Eq. (1)– and the sine-Gordon Hamiltonian –see below Eq. (5)– that is an approximation, in the strong coupling limit, of the fully periodical case. This gives extended tunnelling states in an energy band structure, on the one hand, and discrete travelling states of the breather pseudo particle, on the other. However, previously reported measurements of the decay of the tunnelling band intensity on a rather long timescale of $\approx 70 \text{ h}^4$ is not consistent with tunnelling transitions arising from the ground state. In this talk, we consider an alternative representation of the tunnelling transitions with thermally activated pseudo particles composed of a large number of kinks or antikinks.

2. Theoretical model

The Hamiltonian for an isolated infinite chain of coupled rotors can be written as

$$H = \sum_j -\frac{\hbar^2}{2I_r} \frac{\partial^2}{\partial \theta_j^2} + \frac{V_0}{2} (1 - \cos 3i\theta_j) + \frac{V_c}{2} [1 - \cos 3i(\theta_{j+1} - \theta_j)], \quad (1)$$

where θ_j is the angular coordinate of the j th 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. The index $i = 1, 2 \dots$ determines the potential periodicity compatible with the C_{3v} symmetry of the methyl-groups.

In a previous work, rotational tunnelling was regarded as a one-dimensional band-structure problem.² The tunnel splitting varies continuously between two extremes (E_{ip} and E_{op}) located at the zone center, where methyl groups are tunnelling in-phase, and at the zone boundary, where tunnelling occurs out-of-phase:

$$\begin{aligned} H_{ip} &= -\frac{\hbar^2}{2I_r} \frac{\partial^2}{\partial \theta_j^2} + \frac{V_0}{2} (1 - \cos 3i\theta) \\ H_{op} &= -\frac{\hbar^2}{2I_r} \frac{\partial^2}{\partial \theta_j^2} + \frac{V_0}{2} (1 - \cos 3i\theta) + \frac{V_c}{2} (1 - \cos 6i\theta). \end{aligned} \quad (2)$$

These extremes correspond to the maxima of the density-of-states and transitions observed with the INS technique at (539 ± 4) and $(472 \pm 4) \mu\text{eV}$ in pure 4-methylpyridine were attributed to in-phase and out-of-phase (E_{op}) tunnelling transitions of the chain, respectively. The potential terms V_0 and V_c were determined accordingly. Apart from a phase factor, the wave functions for the tunnelling states can be represented with the basis set for

free rotors as

$$\begin{aligned}
\varphi_{0A}(\theta) &= (2\pi)^{-1/2} a_{0A0} + \pi^{-1/2} \sum_{n=1}^{\infty} a_{0A3n} \cos(3n\theta) \\
\varphi_{0E+}(\theta) &= \pi^{-1/2} \sum_{n=1}^{\infty} a_{0E+n} \cos(n\theta) + a_{0E+2n} \cos(2n\theta) \\
\varphi_{0E-}(\theta) &= \pi^{-1/2} \sum_{n=1}^{\infty} a_{0E-n} \sin(n\theta) - a_{0E-2n} \sin(2n\theta).
\end{aligned} \tag{3}$$

The tunnel splitting is $E_{0E\pm} - E_{0A}$. The wave function for the lowest state is φ_{0A} , whilst φ_{0E+} (symmetrical) and φ_{0E-} (anti-symmetrical) correspond to the degenerate tunnelling states. The inelastic neutron scattering function is

$$S_{0A0E\pm}(Q_r, \omega) = |\langle \varphi_{0E\pm}(\theta) | \exp(iQ_r \times r\theta) | \varphi_{0A}(\theta) \rangle|^2 \delta(E_{0A0E\pm} - \hbar\omega). \tag{4}$$

The momentum transfer vector $\mathbf{Q} = \mathbf{k}_0 - \mathbf{k}_f$ with $|\mathbf{k}_0| = 2\pi/\lambda_0$ and $|\mathbf{k}_f| = 2\pi/\lambda_f$, where λ_0 and λ_f are the incident and scattered wavelengths, respectively. Q_r is the component of the momentum transfer vector perpendicular to the axis of rotation. $S_{0A0E\pm}(Q_r, \omega)$ is non-zero if $Q_r \times r$ is an integer number, say t .

In the strong coupling (or displacive) limit, $\theta_{j+1} - \theta_j$ is small and Eq. (1) can be expanded into the sine-Gordon equation

$$H \approx \sum_j -\frac{\hbar^2}{2I_r} \frac{\partial^2}{\partial \theta_j^2} + \frac{V_0}{2} (1 - \cos 3i\theta_j) + \frac{(3i)^2 V_c}{4} (\theta_{j+1} - \theta_j)^2. \tag{5}$$

In the continuous limit, when variations of θ from site to site are small, this Hamiltonian is integrable and all excitations are well-known.^{7,8,9,10,11,12,13,14,15,16,17,18,19} Kinks, antikinks and breathers are elementary excitations. Rotons (phonons) are beyond the tunnelling frequency range. At a low temperature, the kink density vanishes at thermal equilibrium. Only breathers may survive. In the quantum regime there is only one mass state, owing to the threefold symmetry of methyl groups. The breather wave behaves as a dimensionless pseudo particle. It can travel freely along the chain if the associated de Broglie wavelength is an integer fraction of the lattice parameter. The kinetic energy spectrum is

$${}^q E_{B,l,n} = \sqrt{{}^q E_{B,l,0}^2 + n^2 \hbar^2 \omega_c^2}; \quad n = 0, \pm 1, \pm 2 \dots \tag{6}$$

The INS band observed at 517 μeV was thus assigned to the $|0\rangle \rightarrow |1\rangle$ transition, in rather good agreement with the values for V_0 and V_c estimated independently from the tunnelling transitions. However, the theoretical framework is not totally satisfactory as Eqs (1) and (5) do not apply to the same dynamical regime. The tunnelling energy band is not included in

the strong coupling limit that does not account for the periodicity of the coupling potential. In the next section we report experimental data that discard the energy band scheme.

3. SPECTRA

The first measurements ever reported of the tunnelling transition in 4-methylpyridine showed a single band at $\approx 520 \mu\text{eV}$, with a limited resolution of $\approx 200 \mu\text{eV}$.²⁰ With a better resolution of $\approx 15 \mu\text{eV}$, this band was found to be split into several components.²¹ As well as the main band at $510 \mu\text{eV}$, weaker bands at 468 and $535 \mu\text{eV}$ were partially resolved. Further analysis of the main band at $510 \mu\text{eV}$ revealed that it could be decomposed into unresolved components at ≈ 515 and $500 \mu\text{eV}$. However, with a better resolution of $\approx 9 \mu\text{eV}$ and a sample at the very low temperature of 0.5 K , the fourth component was not confirmed.⁵ Finally, the spectra with the best resolution ever obtained of $\approx 1 \mu\text{eV}$, shown in Figure 1, have revealed new features.⁴

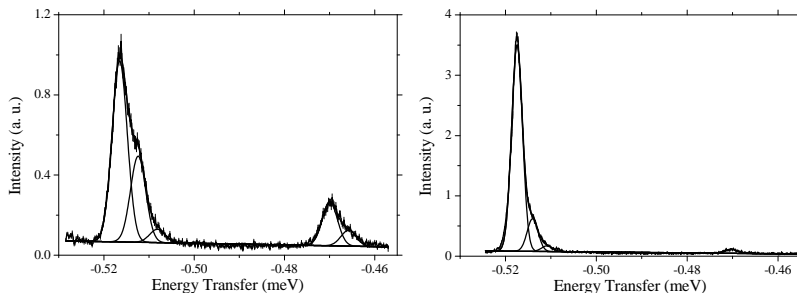


Figure 1. Inelastic neutron scattering spectra of 4-methylpyridine at 1.6 K , after ref. 4. Left: after $\approx 5 \text{ h}$. Right: after $\approx 70 \text{ h}$.

First, the main band previously assigned to the breather mode can be actually decomposed into 3 Gaussian profiles centered at 517.5 , 513.8 and $510.6 \mu\text{eV}$. The weaker band tentatively assigned to anti-phase tunnelling can be decomposed into two components at 470.5 and $467.4 \mu\text{eV}$. Second, the weaker components of the breather mode at 513.8 and $510.6 \mu\text{eV}$ and the tunnelling bands disappear progressively with time, whilst the band intensity at $517.5 \mu\text{eV}$ increases. All observations confirm the assignment of the transition at $517.5 \mu\text{eV}$ to the $|0\rangle \rightarrow |1\rangle$ transition of the breather travelling mode. The intensity decay suggests that other transitions arise from unstable species or states.

4. Multi-Kinks

Within the sine-Gordon theory, a kink or an antikink travelling along the chain can rotate the methyl groups by $\pm 2\pi/3$. This is analogous to a classical jump over the potential barrier. In contrast to the breather mode, these excitations are not parts of the ground state and must be created (for example thermally). The renormalized energy at rest of a kink is ${}^q E_{K0} \approx 11.5$ meV,² and the energy required for the creation of a pair comprising a kink and an antikink from a breather is ≈ 5.32 meV. Transitions in the 0.5 meV are not appropriate for the creation of pairs.

In the quantum regime kinks and antikinks can be regarded as dimensionless particles and diffraction by the discrete lattice gives a quantization rule analogous to that for the breather travelling mode:

$$E_K(n) = \sqrt{{}^q E_{K0}^2 + n^2 \hbar^2 \omega_c^2}; \quad n = 0, \pm 1, \pm 2 \dots \quad (7)$$

With this equation, the $|0\rangle \rightarrow |1\rangle$ transition is calculated at ≈ 720 μeV , quite far from the observed frequency. The $|0\rangle \rightarrow |2\rangle$ transition is at ≈ 2.7 meV, *etc.* Therefore, Eq. (7) is not appropriate for the transitions observed at 470 and 535 μeV .

In order to get rid of the translational quantization we consider spatially extended pseudo particles composed of several kinks or antikinks, which are solutions of the sine-Gordon equation.^{23,24,25} We can thus build pseudo particles with well defined kinetic momentum values composed of any number of elementary excitations with the same velocity. It has been conjectured that kink positions should obey the Fermi statistics.⁷ Consequently, the planar waves associated to the translation of each kink or antikink should have different spatial phases, presumably distributed at random. The amplitude of the planar wave associated to the composed particles should diminish as the number of kinks or antikinks increases and the quantization rule holding for dimensionless particles should be progressively relaxed. Then, free translation may occur at any energy and the discrete nature of the chain can be ignored.

The probability of creation, from the ground state, of pseudo particles composed of a large number of kinks or antikinks, all with the same velocity, is infinitely small at a low temperature. However, infrared and Raman spectra of 4-methylpyridine have shown that the sine-Gordon dynamics appears only below ≈ 100 K.²² Above this temperature methyl groups are disordered and a large number of pseudo particles can be created as the sample is cooled down. In the classical sine-Gordon equation the number of kinks is strictly equal to the number of antikinks. This is no longer true for a disordered chain at high temperature and we speculate that after

annihilation of all existing pairs, *via* collisions, the remaining unpaired kinks or antikinks can exchange kinetic momentum and thus give rise to non dispersive pseudo particles. In the sine-Gordon equation, there is no channel available for these excitation to decay. We suppose that in a real crystal, such excitations can have long enough life times to be observed.

If we ignore interactions between kinks or antikinks, the energy at rest of a N -soliton, made of N elementary excitations, is $N^q E_{K0}$. The propagation of such pseudo particles along the chain represents collective rotation of the methyl groups and the energy at rest is the activation energy for semiclassical jumping over the potential barrier.

In order to account for tunnelling it is necessary to reconsider the fully periodical Hamiltonian and we suppose that the sine-Gordon excitations are also solutions of Eq. (1), at least to a level of accuracy compatible with the observed life times. Then, the rotational periodicity of the wave functions in Eq. (3) imposes quantization of the kinetic momentum according to Eq. (4)

$$p = t\hbar/r ; \quad t = 0, \pm 1, \pm 2, \dots \quad (8)$$

Furthermore, free translation along the chain takes place only if the kinetic energy is within the tunnelling energy band. The spectrum is then

$$E_{op} \leq E(N, n) = \sqrt{N^{2q} E_{K0}^2 + t^2 \hbar^2 \omega_c^2 L^2 / r^2} \leq E_{ip}. \quad (9)$$

Table 1. Comparison of the calculated transitions for the travelling frequencies of N -solitons with observed frequencies

N	$N^q E_{K0}(\text{meV})$	$\nu_{0 \rightarrow 1} (\mu\text{eV})$	
		Calc.	Obs.
22	253.0	540	539 ⁵
23	264.5	517	514 ⁴
24	276.0	495	≈ 500 ²¹
25	287.5	475	472 ⁵

Numerical values obtained with $L \approx 4r$, according to the crystal structure,²⁶ are compared to the observed frequencies in Table 1. The bands at 539 and 472 μeV correspond to $N = 22$ and 25, respectively. The frequency calculated for $N = 24$ is close to those reported previously for transient bands. The transient bands at $\approx 514 \mu\text{eV}$ in the spectra presented in Figure 1 are close to the frequency calculated for $N = 23$. These bands are very close in energy to the breather travelling transition. However, there is no interaction between these dynamics because they correspond to quite different values of the momentum transfer (1 \AA^{-1} and 1.5 \AA^{-1} ,

respectively). The overall agreement with observations is encouraging and can be certainly improved as E_{ip} and E_{op} do not correspond any longer to observed transitions. This gives more flexibility to the determination of V_0 and V_c .

However, this model does not account for the “hyperfine” structure of the bands at 513.8–510.6 and 470.5–467.4 μeV . Furthermore, whilst the bands at ≈ 472 and 514 μeV decay at about the same rates, the band at ≈ 500 μeV seems to disappear more rapidly. In Figure 1 it has already vanished after ≈ 5 h. These pending problems deserve further investigations.

5. Concluding remarks

Collective rotational dynamics can be represented with pseudo particles that are solutions of the sine-Gordon equation in the continuous limit.

The breather mode represents localized oscillations of the methyl groups with respect to their equilibrium positions. The localized wave form can travel along the chain without dispersion. It can be regarded as a dimensionless pseudo particle. Diffraction by the chain lattice gives rise to quantization of the kinetic momentum.

Tunnelling is a nontrivial problem for infinite chains of coupled methyl groups. Extended states with an energy band structure are in conflict with experiments and transient species must be considered. We suppose that pseudo particles composed of large numbers of kinks or antikinks travelling at the same velocity appear spontaneously as the sample is cooled down. Because of the exclusion principle for fermions, these pseudo particles have spatial extension and are no longer sensitive to the discreteness of the chain lattice. We further suppose that these pseudo particles are also hosted by the fully periodical Hamiltonian. Then, quantization of the kinetic momentum arises from the rotational periodicity of the tunnelling states and free translational occurs for kinetic energy values within the tunnelling energy band. The calculated spectrum fits the observed transitions, but does not account for further splitting of the bands. These pseudo particles disappear naturally at a low temperature, at thermal equilibrium.

We finally conclude that analytical solutions of the sine-Gordon equation are sufficiently close to solutions of the exact Hamiltonian for an isolated infinite chain of coupled methyl groups to account for the spectra.

In the introduction of this talk we referred to nonlinear dynamics giving rise to spatially localized non-dissipative waves in an extended lattice. We suspect that this may be true only in the classical regime. In the quantum regime, non-dispersive excitations behave as dimensionless pseudo particles

and localization occurs in momentum space rather than in direct space.

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