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Inelastic-neutron-scattering study of the sine-Gordon breather interactions in isotopic mixtures of 4-methyl-pyridine

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The inelastic-neutron-scattering spectrum of totally hydrogenated 4-methyl-pyridine (4MP-h_7) at 0.5 K reveals three bands whose widths are limited to the resolution function of the spectrometer: 9 μeV. Within the quantum sine-Gordon theory, these bands are assigned to in-phase (537 μeV) and out-of-phase (470 μeV) tunneling transitions and to the traveling transition of the breather mode (516 μeV). The spectra of isotopic mixtures with the totally deuterated analogue (4MP-d_7), containing 85%, 65%, and 50% of 4MP-h_7, respectively, were obtained at 1.8 K with the same resolution. The frequency of the breather traveling state is progressively shifted downwards to 506 μeV. The frequency shift is represented with the breather mode in clusters of hydrogenated molecules. Simultaneously, an additional band is observed between 490 and 497 μeV whose intensity is proportional to the amount of deuterated molecules. This band is attributed to the breather-mode interaction with isolated deuterated molecules. The breather wave form and the effective potential for the impurity are calculated. For the sample containing 50% of each isotopomer, new bands at 478 and 464 μeV are attributed to the breather mode in rather small hydrogenated clusters with deuterated clusters as reflective boundaries. [S0163-1829(98)09441-7]

I. INTRODUCTION

The rotational dynamics of methyl-groups in the 4-methyl-pyridine crystal (4MP or γ-picoline, C_7H_7N) are nearly free.[1] Inelastic-neutron-scattering (INS) experiments revealed a band at 515 μeV and partially resolved weaker bands at 468 and 535 μeV tentatively attributed to coupled pairs of methyl-groups.[2] However, further studies on isotopic mixtures of the fully-hydrogenated (4MP-h_7) and fully-deuterated (4MP-d_7) molecules have shown dramatic frequency shifts depending on concentration and temperature.[3] Within the sine-Gordon theory, the main band at 515 μeV was interpreted as the transition to the first-excited traveling-state of the massive quantum-pseudoparticle referred to as the sine-Gordon breather. The weaker sidebands correspond to collective tunneling transitions for the chain, either in phase (535 μeV) or out of phase (468 μeV).[3]

We present INS spectra of isotopic mixtures at higher resolution (~9 μeV) than in previous experiments. For rather modest concentrations of deuterated molecules, the breather mode interacting with single deuterated molecules in large domains of hydrogenated analogues is observed. A theoretical model is presented.

II. EXPERIMENT

The deuterated compound (C_7D_7N) was prepared according to Ref. 3. Liquid mixtures of 4MP-h_7 and 4MP-d_7 at room temperature were introduced into a cylindrical aluminum can of 20 mm diameter. An internal coaxial cylinder of 18 mm diameter defined a sample thickness of 1 mm. Cans were loaded into a liquid-helium cryostat. The temperature was controlled at 1.8 ± 0.2 K. One run with a flat sample of pure 4MP-h_7 was carried out at 0.5 ± 0.05 K using a liquid ^{3}He dilution insert in the liquid ^{4}He cryostat. The neutron-scattering experiments were carried out on the IN5 time-of-flight spectrometer at the Institut Laue-Langevin (Grenoble, France). The elastic resolution was selected to be 9 μeV.

III. INS SPECTRA

The INS spectrum of the isotopically pure 4MP-h_7 at 0.5 K (Fig. 1) shows three bands at 470, 516, and 537 μeV which were tentatively decomposed into Gaussian profiles (see Fig. 1 and Table I). The estimated full widths at half-maximum correspond to the spectrometer resolution. There is no evidence for the fourth band around 500 μeV suggested by earlier experiments.[2]

In the isotopic mixtures the weak bands at 470 and 537 μeV disappear rapidly with increasing concentrations in deuterated molecules. A band appears at 497 μeV, which could not be resolved in previous experiments[3] (see 85% of 4MP-h_7 in Fig. 1 and Table I). The frequency shifts smoothly down to 490 μeV. Simultaneously, the band at 516 μeV (100% 4MP-h_7) shifts downwards to 506 μeV (50% 4MP-h_7) and its width also increases slightly (see Table I). The frequency shift is best fitted with a parabola (see Fig. 2). The intensity ratio for the two bands at ~510 and 490 μeV

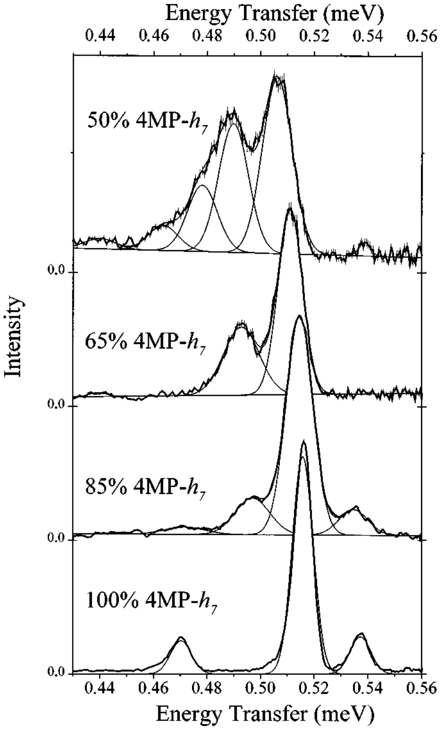

FIG. 1. Inelastic-neutron-scattering spectra of isotopic mixtures of the totally hydrogenated 4-methyl-pyridine molecule (4MP-h_7) and perdeuterated analogue (4MP-d_7). The temperature was 0.5 K for the isotopically pure sample (100% 4MP-h_7) and 1.8 K for the mixtures.

follows closely the concentration ratio for the samples containing 85% and 65% of 4MP-h_7 (see Table I). Finally, the spectrum of the sample containing 50% of 4MP-h_7 was tentatively decomposed into five components (Fig. 1 and Table I).

The quantum sine-Gordon model for infinite chains of coupled rotors is the only one to provide a comprehensive view of the methyl-group dynamics in 4MP (see Table II) and isotopic mixtures.[3] In the strong-coupling regime, kinks, phonons (rotons), and breathers are the elementary excitations. However, the kink density vanishes at low temperature and rotons are beyond the energy transfer range under investigation. Only the breather mode contributes to the spectra.

For energy transfer below the dissociation threshold corresponding to the creation of a kink-antikink pair, the kinetic energy spectrum of the breather is ${}^qE_{Bn} = \sqrt{{}^qE_{B0}^2 + n^2\hbar^2\omega_c^2}$. The band at 516 μeV in pure 4MP-h_7 (Fig. 1) corresponds to the $0\rightarrow 1$ transition. The bands at 537 and 470 μeV are attributed to the in-phase and out-of-phase collective tunneling of the chain. The numerical values given in Table II confirm that the observations are amenable to the theory with reasonable accuracy. This is remarkable since the sine-Gordon equation is an approximation of the Hamiltonian for the chain that is already an approximation of the real system under consideration.

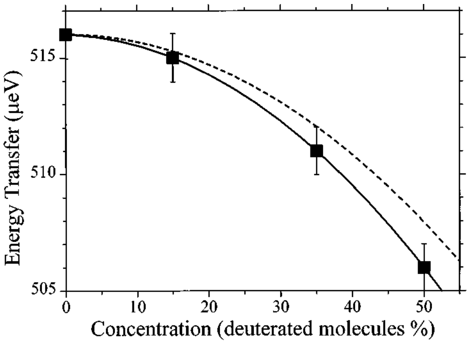

FIG. 2. Variation of the main band frequency with the concentration of deuterated molecules. Data points (■); best fit (solid line $\nu = 516(1-0.074c_d^2)$; theory according to Eq. (2) (dashed).

In isotopic mixtures, the hydrogenated and deuterated molecules are totally miscible and the crystal structures for the two isotopomers are identical.[4] Molecules are statistically distributed among clusters of various sizes (s_h and s_d, respectively). The translational invariance is broken and bound states are observed. The frequency shifts previously observed could be explained assuming that cluster boundaries are reflective walls that contain the breather.[3] The kinetic energy spectrum is then

$$\nu_{sn} = \sqrt{{}^qE_{B0}^2 + n^2\hbar^2\omega_c^2} - \sqrt{{}^qE_{B0}^2 + \hbar^2\,\frac{\omega_c^2}{s_h^2}},$$

$$\text{with } n = \pm 1, \pm 2, \ldots;\ s_h = 1, 2, \ldots . \quad (1)$$

In the present work, Eq. (1) accounts for the frequency shift of the main breather band from 516 to 506 μeV (Fig. 2). For a low concentration, the deuterated molecules are largely isolated. For a single chain the mean size of hydrogenated clusters is proportional to the inverse of the concentration of deuterated molecules: $\overline{s_h} \sim 1/c_d$. However, each pair of molecules along the c crystal axis[4] is twofold degenerate. Moreover, each chain is also twofold degenerate (chains parallel to a or b are equivalent). Consequently, the mean cluster size for a chain is $\overline{s_h} \sim 4/c_d$. Expansion of Eq. (1) gives

$$\overline{\nu_{01}} \cong \frac{\hbar^2\omega_c^2}{2\,{}^qE_{B0}^2}\left(1-\frac{c_d^2}{16}\right), \quad c_d \ll 1. \quad (2)$$

This equation is rather close to the observation (see Fig. 2). The observed frequency shift is essentially due to the collective nature of the dynamics and the potential terms are vir-

TABLE I. Band decomposition into Gaussian components of the inelastic-neutron-scattering spectra of isotopic mixtures of fully hydrogenated (4MP-h_7) and fully deuterated (4MP-d_7) 4-methyl-pyridine.

	100% 4MP-h_7			85% 4MP-h_7			65% 4MP-h_7		50% 4MP-h_7				
Frequency (μeV)	537	516	470	535	515	497	511	492	506	490	478	464	440
FWHM (μeV)	9	9	9	13	12	15	11	16	13	13	13	13	13
Area (%)	13	75.5	11.5	9	71	15	64	34	43	31	16	6	2

TABLE II. The soliton and breather mode in the sine-Gordon potential: $V(\theta_j)=(3.66/2)(1-\cos 3\theta_j)+(5.46/2)\{1-\cos 3(\theta_{j+1}-\theta_j)\}$. V and θ are in meV and radian units, respectively. L is the lattice parameter.

4MP-h_7	4MP-d_7	
0.695	0.347	Rotational constant $F=h^2/8\pi^2 I_r$
3.38	2.33	$\hbar\omega_0$
4.13	2.85	$\hbar\omega_c$
17.64(16.25)		${}^{q}E_{B0}$: calculated (observed) energy at rest of the renormalized semiclassical breather
2.17	1.49	$\hbar\omega_B$: internal frequency of the semiclassical breather
0.537(0.537)	0.141(0.100[a])	Calculated (observed) in-phase tunneling frequencies.
0.470(0.470)	0.074(0.100[a])	Calculated (observed) out-of-phase tunneling frequencies.
0.516(0.516)	0.250(~0.223[a])	Calculated (observed) frequencies for the 01 transition of the breather mode traveling in an infinite chain.

[a] After Ref. 3.

tually independent of the concentration in deuterated molecules. The chain dynamics are essentially one dimensional (1D) in nature, with no significant contribution of the methyl-methyl interaction within the close-contact pairs along the c axis. These conclusions are in marked contrast to the strong correlation of adjacent methyl-groups supposed by Ohms and co-workers.[4]

The band at ~490 μeV in isotopic mixtures (see Fig. 1) cannot be rationalized in the same way. The frequency corresponds roughly to clusters with $s_h=4$ or 5. However, the width is comparable to the resolution function of the spectrometer and the intensity is virtually proportional to the amount of deuterated molecules. In contrast to these observations, the amount of small clusters should be negligible for low concentrations of deuterated molecules, the intensity of the related bands should be proportional to the square of the concentration and the bands should be broadened by the distribution of cluster sizes. Therefore, this band is better attributed to the breather interacting with isolated deuterated molecules.

The Hamiltonian representing an infinite chain of hydrogenated molecules containing a single deuterated molecule at site $j=0$ can be written as

$$H=\sum_j -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2}+\frac{V_0}{2}(1-\cos 3\theta_j)+\frac{V_c}{2}[1-\cos 3(\theta_{j+1}-\theta_j)]+\frac{\hbar^2}{4I_r}\frac{\partial^2}{\partial\theta_0^2}. \quad (3)$$

The impurity is equivalent to a driving force at frequency ω_B (the internal frequency of the breather), below the lowest roton frequency at ω_0. A solution of the approximate Hamiltonian linearized with respect to the potential minimum is the standing plasma wave (see Fig. 3).[5] The wave form of a breather centered at x_B interacting with the impurity is

$$\Theta(x,t)=\Phi_B(x-x_B,t)-\Phi_B(-x_B,t)\times\frac{\exp(-\sqrt{1-\omega_B^2/\omega_0^2}|x|)}{2\sqrt{1-\omega_B^2/\omega_0^2}}. \quad (4)$$

The breather is attracted by the heavy impurity and the effective potential averaged over the fast internal oscillation is[5]

$$U_{\mathrm{eff}}(x)=-4F\cos\mu\cosh(x\sin\mu)\times[1+\cot^2\mu\cosh^2(x\sin\mu)]^{-3/2} \quad (5)$$

with

$$\mu=\frac{(3i)^2}{16[1-(3i)^2/8\pi]}. \quad (6)$$

The shape of the effective potential (see Fig. 4) resembles the form of the breather wave. The width at half-minimum (ΔU_{eff}~4–5 lattice sites) gives the amplitude of the breather center-of-mass oscillations around the impurity. Thus, the traveling transition is anticipated between 485 and 500 μeV

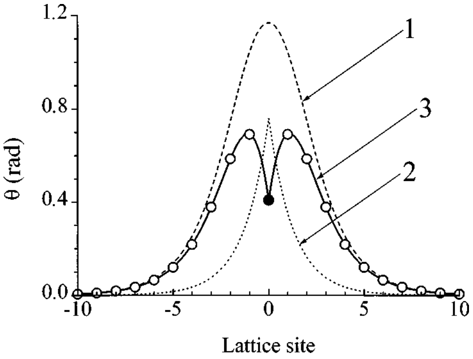

FIG. 3. Wave form of the breather (1, dash), of the plasma wave (2, short dash) and of the breather (3, solid line) interacting with a single deuterated impurity (●) surrounded by hydrogenated molecules (○).

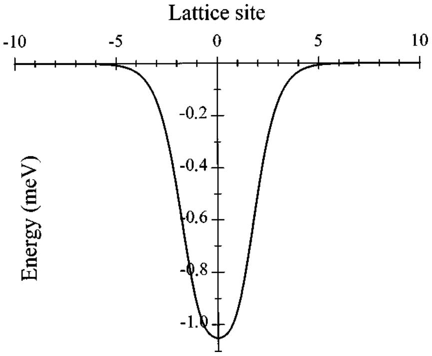

FIG. 4. Effective potential averaged over the internal oscillation for the breather interacting with an isolated deuterated molecule surrounded by hydrogenated molecules.

in accord with the observed frequencies. Impurities separated by more than ~5 lattice sites are virtually isolated. The energy at half-minimum of the effective potential is ~0.5 meV/6 K. This interaction can be observed only at a low temperature. The frequency of the perturbed traveling state should increase with temperature, up to the frequency of the unperturbed breather.[3]

Owing to the fourfold degeneracy of the molecular sites, the amount of nearby impurities is only ~1% for the mixture containing 65% of 4MP-h_7. The spectra of the mixtures containing 85% and 65% of 4MP-h_7 do not reveal any change, apart from intensities. There is only a rather small frequency shift of ~5 μeV. The effective potential created by isolated impurities is largely concentration independent.

In the spectrum of the mixture containing 50% of 4MP-h_7 two bands at 478 and 464 μeV may correspond to breathers in clusters containing four and three lattice sites, respectively. The relative intensity of the band at 490 μeV, compared to that at 506 μeV, is slightly different from the 1:1 ratio. The oversimplified statistics used above is no longer relevant. Clusters of deuterated molecules should be also considered.[3]

IV. CONCLUSION

The INS spectra at high resolution of isotopic mixtures of 4MP-h_7 and 4MP-d_7 molecules reveal aspects of the methyl-group dynamics amenable to the quantum sine-Gordon theory. First, the band frequencies observed in pure 4MP-h_7 are well represented. Second, the frequency shift of the breather traveling state is represented with clusters of hydrogenated molecules with reflective boundaries formed by isolated deuterated analogues. Each molecular site is fourfold degenerate and the dynamics are essentially 1D in nature. Third, the breather interaction with isolated deuterated molecules is well characterized. Fourth, at higher concentration (50% of deuterated molecules), additional bands are attributed to breathers in clusters containing three or four hydrogenated molecules.

The collective nature of the methyl group dynamics in 4MP is thus demonstrated by a very large number of experimental data. The effective potential is largely independent of the amount of deuterated species in the crystal.

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