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Angaben zur Veröffentlichung / Publication details:

Heidemann, A., J. Eckert, L. Passell, and Wolfgang Häusler. 1987. "Pressure dependence of tunneling and librational modes of coupled methyl groups in lithium acetate." *Zeitschrift für Physik B Condensed Matter* 66 (1): 75–81. https://doi.org/10.1007/bf01312764.

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Pressure Dependence of Tunneling and Librational Modes of Coupled Methyl Groups in Lithium Acetate

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The pressure dependence of the tunneling and librational modes of the coupled methyl groups in lithium acetate dihydrate was studied by inelastic neutron scattering at liquid helium temperatures and the results compared with detailed model calculations. An increase of both the single particle and coupling potential parameters with increasing pressure was observed.

I. Introduction

Coupling effects in rotational tunneling of CH_3 groups and CH_4 molecules have recently been observed in three different compounds: lithium acetate (LIAC) [1], manganese acetate (MNAC) [2] and solid methane CH_4 in phase II [3]. In LIAC and MNAC, the results were explained by a "two-coupled-methyl-groups" model. This model has been explored in more detail recently by Häusler and Hüller [4]. Both the tunneling and librational modes were calculated for various combinations of the single particle and coupling potential parameters V_3 and W_3 which occur in the Hamiltonian $\mathscr{H}$ describing a pair of coupled CH_3 groups tunneling around a common axis:

$$\mathscr{H} = -\frac{\hbar^2}{2I}\left\{\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2}{\partial\theta^2}\right\}+V(\phi,\theta) \tag{1}$$

where $V(\phi,\theta) = -V_3(\cos 3\phi - \cos 3\theta) - W_3 \cos 3(\phi - \theta)$, ϕ and θ are the rotational coordinates of the two methyl groups and I is the moment of inertia of a single CH_3 group.

The idea behind the present investigation was to compare the results of these calculations with experiments where the potential parameters V_3 and W_3 were gradually changed by applying an external pressure to the sample. The system LIAC was chosen because it can be considered as *the* best experimentally accessible system containing a pair of coupled methyl groups [1]. Both the tunneling and librational spectra were measured by inelastic neutron scattering (INS) as a function of external hydrostatic pressure up to 5.5 kbar. In Sect. II we present the experimental details and results; an analysis in terms of the model Hamiltonian is given in Sect. III.

II. Experiments and Results

The neutron scattering experiments were carried out at the Brookhaven high flux reactor. All tunneling

mode studies were made on the $H9$ triple-axis cold neutron spectrometer. Energy scans were performed with a fixed final energy of 3 meV and at a fixed momentum transfer Q of 1.8 $Å^{-1}$. Using collimations of $60'-20'-60'-40'-40'$, an energy resolution of 58 μeV (FWHM) was achieved. Higher order contamination of the beam was eliminated with a liquid-nitrogen-cooled beryllium filter in front of the monochromator. Librational motions were measured on the $H7$ triple-axis thermal neutron spectrometer. These scans were performed in the neutron energy loss mode with a fixed final energy of 14.77 meV and at a fixed Q-value of 2.0 $Å^{-1}$. Higher order beam contamination was removed with a graphite filter behind the analyzer. With collimations of $40'-40'-40'-40'$, an energy resolution of 0.88 meV (FWHM) was obtained. The sample, 0.22 g of polycrystalline lithium acetate ($LiCH_3COO.2D_2O$), was sealed in an aluminium container (sample size $21\times7\times1$ mm^3) sitting in a pressure cell which was, in turn, mounted in a variable temperature liquid helium cryostat. The pressure transferring medium was liquid helium. Up to 6kbar of pressure could be applied. Most of the measurements were carried out at 4.5 K. Temperature stability was typically ±0.1 K.

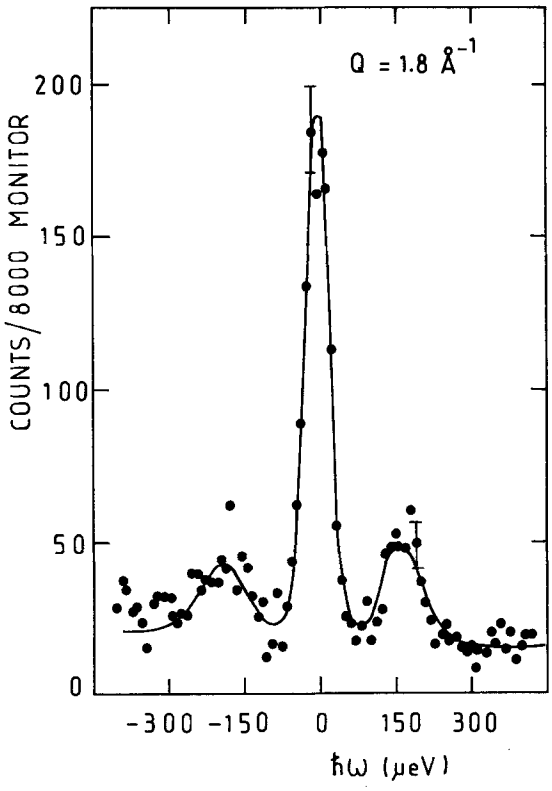

Fig. 1. INS spectrum of LIAC at 4.5 K and 4.2 kbar obtained using the H-9 triple-axis spectrometer. The continuous line is a guide to the eye

1. *H9 Results*

Figure 1 shows an INS spectrum obtained with LIAC at 4.5 K and 4.2 kbar. Apart from a strong elastic peak, two well-defined inelastic peaks are observed from neutrons scattering inelastically by tunneling methyl groups. Taking advantage of the fact that the background conditions were more favorable on the neutron energy loss side, most of the data were taken there. Energy loss peaks measured at four representative pressures are plotted in Fig. 2. Increasing pressure clearly decreases both the frequency and line width of the excitations.

Compared to the results of [1] (which were obtained at zero pressure), good agreement is found although the energy resolution of 58 μeV was not sufficient to resolve the fine structure of the inelastic peaks. According to [1] and [4], three lines occur with an intensity ratio of 1:1:2, the strong line having the highest frequency. We therefore fitted the inelastic peak with a scattering law $S(\omega)$ consisting of a sum of three Gaussians $G(\omega)$ convoluted with the resolution function:

$$S(\omega)=S_0[2G(\omega-\omega_0)+G(\omega-\omega_1)+G(\omega-\omega_2)]+BG \qquad (3)$$

with

$$G(\omega)=e^{-\frac{\omega^2}{\delta^2}\cdot 4\ln 2}, \quad \omega_0-\omega_1=\Delta\omega_1,\ \omega_1-\omega_2=\Delta\omega_2,$$

and BG being an energy-transfer-independent background. The quality of the data was not sufficient to determine $\Delta\omega_1$ and $\Delta\omega_2$ separately. Therefore we used the approximation $\Delta\omega_1=\Delta\omega_2=\Delta\omega$, which is approximately valid at zero pressure. The resulting fit parameters ω_0 and $\Delta\omega$ are plotted as a function of pressure in Fig. 3. Both decrease approximately linearly with increasing pressure. The intrinsic line width δ turned out to be rather small: values between 20 ± 10 and 10 ± 5 μeV were obtained at low and high pressure respectively.

2. *H7 Results*

Figure 4 shows two INS spectra measured with LIAC at atmospheric pressure and at 4.2 and 77 K respectively. The inelastic structure observed at low temperature in the energy range between 1 and 10 meV is smeared out and becomes a quasi-elastic spectrum

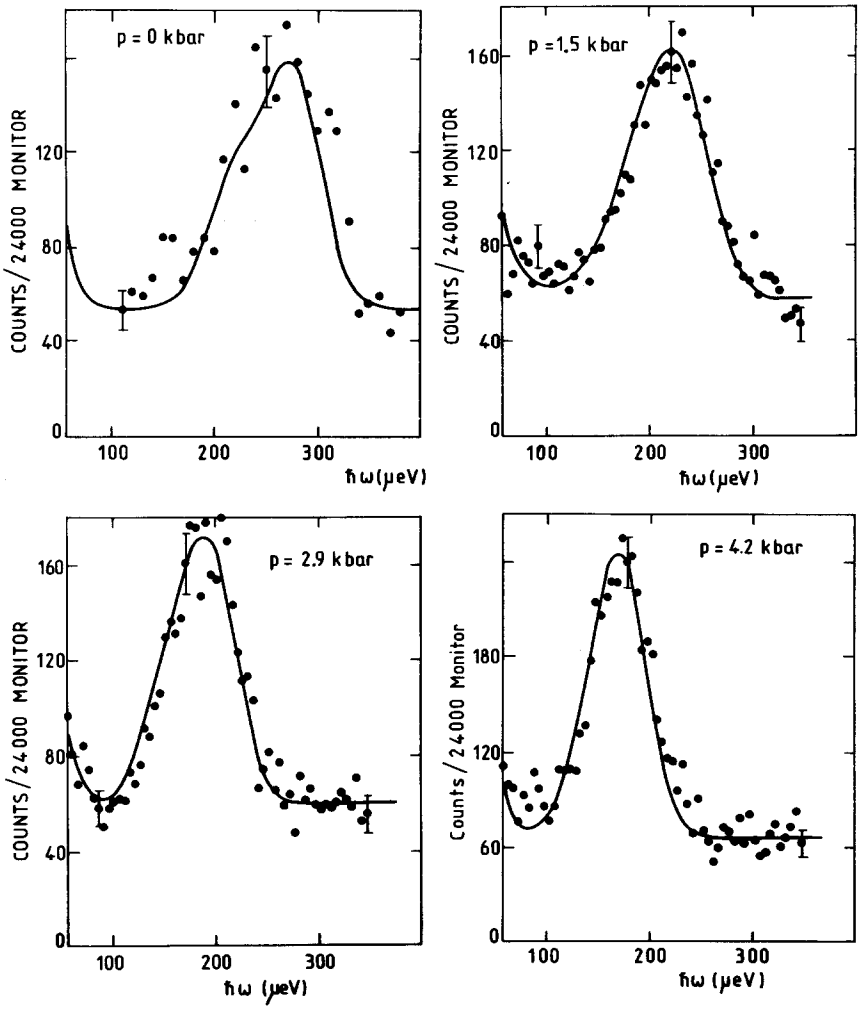

Fig. 2. INS spectra of LIAC at 4.5 K and four different pressures. Spectrometer *H*9. The continuous lines are the result of a fit as described in the text

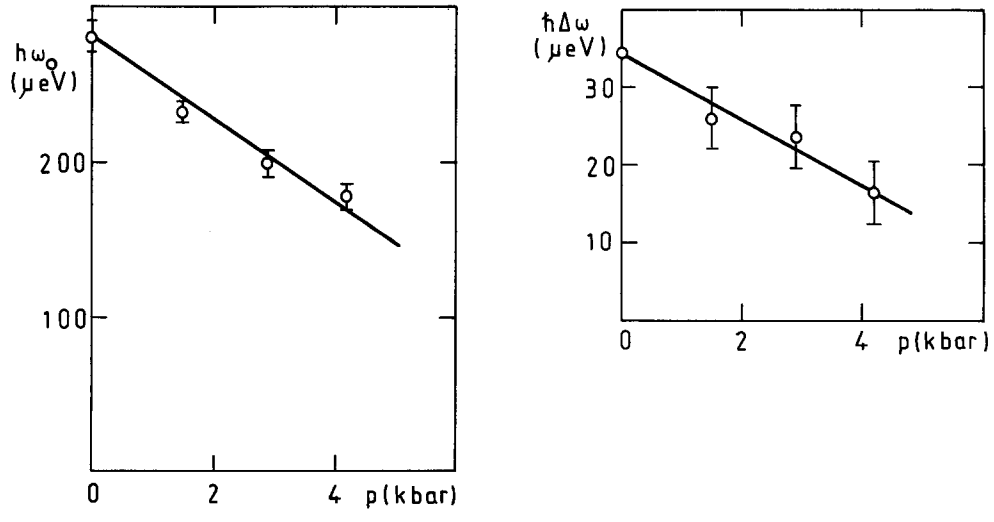

Fig. 3. Tunneling frequency ω_0 and the splitting $\Delta\omega$ as a function of pressure

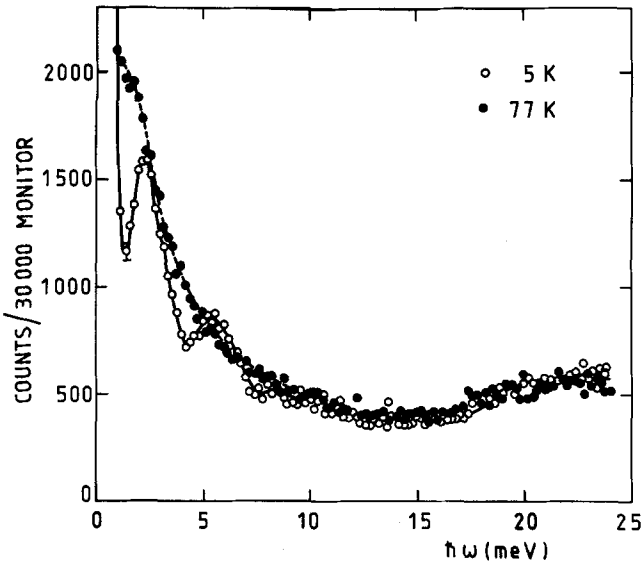

Fig. 4. INS spectra of LIAC at atmospheric pressure and two different temperatures. Spectrometer *H*7. The continuous and dashed lines are guides to the eye

at the higher temperature but the inelastic features occuring between about 10 and 25 meV are nearly temperature independent. They are therefore assumed to be vibrational modes. The excitations in the range from 1 to 10 meV, however, are pressumed to arise from the librational motions of the CH_3 groups.

Figure 5 shows the pressure dependence of the INS spectra of LIAC at 4.5 K. The most prominent feature is a peak at 2.2 meV at atmospheric pressure which shifts to 3.15 meV at 5.5 kbar. Its pressure dependence is plotted in Fig. 6. A more or less linear increase of frequency with pressure is found.

The peak at about 5.5 meV seems to be relatively pressure independent. There are also two weak and partly resolved peaks in the range from 7 to 13 meV. Statistical limitations made it difficult to extract information about their pressure dependence.

The data obtained at atmospheric pressure are in good agreement with those of [1]. The latter experiment was, however, performed with more than twice

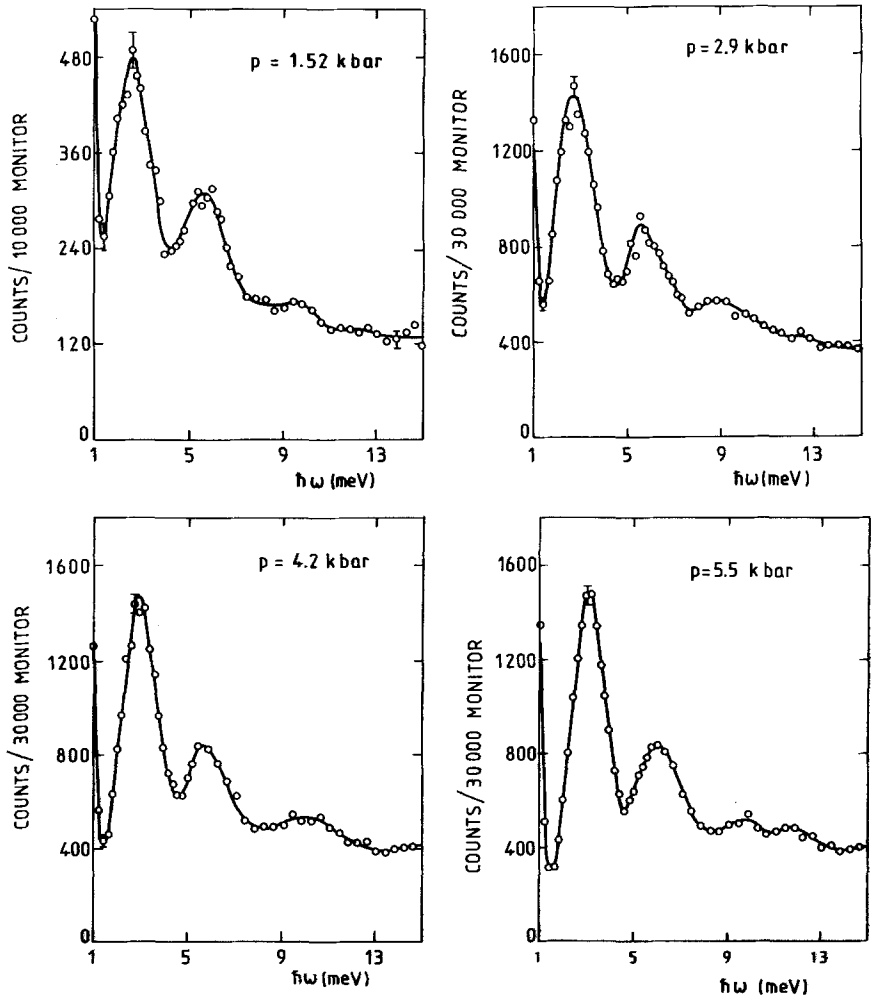

Fig. 5. INS spectra of LIAC at 4.5 K and four different pressures. Spectrometer *H*7. The continuous lines are guides to the eye

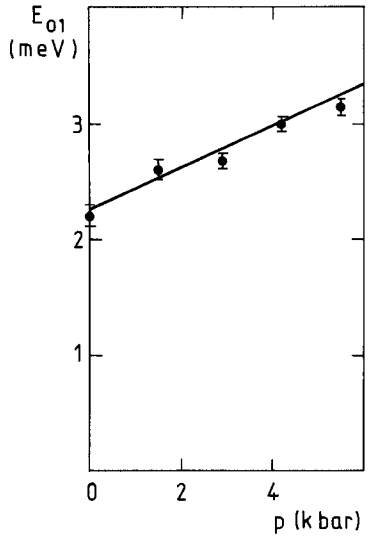

Fig. 6. Pressure dependence of the frequency of the lowest lying librational transition

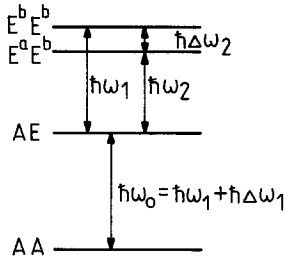

Fig. 7. Energy level scheme of coupled CH_3 groups in LIAC

Table 1.

p (kbar)	0	2	4
V_3/B	2.96	3.56 ± 0.12	4.3 ± 0.2
W_3/B	−6.58	$-6.6\ \pm0.6$	-7.1 ± 1.8

Table 2.

p (kbar)	0	2	4
$\Delta\omega_1$ (μeV)	37.0	23.3	14.3
$\Delta\omega_2$ (μeV)	36.3	28.4	20.1
$\Delta\omega$ (μeV)	36.7	25.9	17.2

as good resolution and therefore revealed more fine structure. (The sample size was about ten times that of this experiment!).

III. Discussion

1. *Tunneling Spectrum*

The tunneling frequency ω_0 fixes a curve in the parameter space of V_3 and W_3 via Eq. (1). Two additional curves in the V_3-W_3 parameter space are determined by $\Delta\omega_1$ and $\Delta\omega_2$ (see Fig. 7 for notation). If, for a given pressure p, the experimental values of ω_0, $\Delta\omega_1$ and $\Delta\omega_2$ are such that the three curves intersect (or come close to intersecting) at one point, then the model Hamiltonian presumably gives a good description of the system. The quality of our data did not allow a separate determination of $\Delta\omega_1$ and $\Delta\omega_2$. Therefore the best we could do was to determine a second curve from the average $\Delta\omega=\frac{1}{2}(\Delta\omega_1+\Delta\omega_2)$. From the intersection of the two curves we than obtained parameters V_3 and W_3 listed in Table 1. The error bars correspond to the uncertainty of the fitted values for ω_0 and $\Delta\omega$.

With these parameters we then recalculated the values for $\Delta\omega_1$ and $\Delta\omega_2$ given in Table 2. Apparently the assumption $\Delta\omega_1=\Delta\omega_2$ is not a good one for LIAC under elevated pressure. However, both $\Delta\omega_1$ and $\Delta\omega_2$ decrease with increasing pressure.

Looking at Table 1 we see that V_3 increases more rapidly with pressure than the absolute value of W_3. If we assume equal and linear scaling of all atom distances as a function of pressure (assumption A) and if we further assume

i. an octopole-octopole interaction between the two paired CH_3 groups and

ii. an octopole-monopole interaction between one CH_3 group and the neighbouring lattice atoms,

then we expect (for not too high pressure) a linear dependence between the pressure change δp and the changes δV_3 and δW_3 of the parameters V_3 and W_3 [5] yielding:

$$\frac{\delta W_3/W_3}{\delta V_3/V_3}=\frac{7}{4}.$$

Such a relatively strong increase of the coupling potential would produce a line broadening of the tunneling peak with increasing pressure. We observe, however, the opposite: the peak becomes narrower at elevated pressure! Our experiment therefore shows that assumption A is not valid. We plan to determine the pressure dependence of the crystal structure of LIAC by neutron diffraction to clarify this point.

2. *Librational Spectrum*

Table 3 shows a comparison of the measured and calculated energies E_1 of the lowest-lying librational

Table 3.

p (kbar)	0	2	4
$E_1^{meas.}$ (meV)	2.2	2.53	2.9
E_1^{cal} (meV)	3.05	3.55	4.0
$*E_1^{cal}$ (meV)	4.2	4.7	5.3

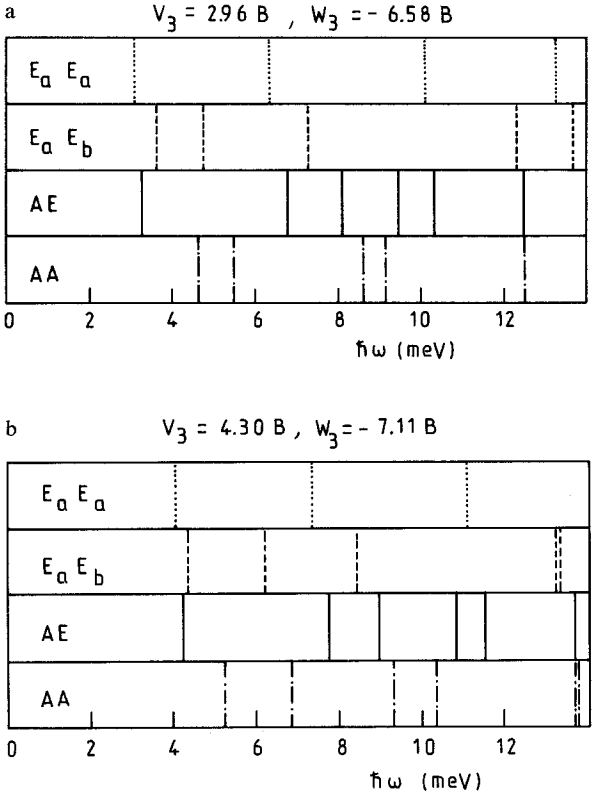

Fig. 8. Librational spectra according to model (1) with parameters V_3, W_3 of Table 1 refering to the transitions from the averaged tunneling multiplet

peaks. The measured values were taken from the straight line in Fig. 6. The calculated values E_1^{cal} refer to the transition from the average tunneling multiplet:

$$\bar{E}^0 = \tfrac{1}{8}(2E^0_{AA} + 4E^0_{AE} + E^0_{E_aE_b} + E^0_{E_aE_a})$$

to the first excited AE-symmetric state, which might be of dominant intensity because of the high multiplicities of AE-symmetric states. Figure 8 shows the librational spectra of model Hamiltonian (1) for transitions from $\bar{E}^0$ corresponding to parameter values (V_3, W_3) from Table 1. These spectra are obtained by diagonalisation of the Hamilton matrix. Figure 8a shows additional eigenvalues compared with Fig. 7a from [4]. In the mean time it turned out that the sparse matrix method might overlook a few of the *excited* eigenvalues of a given Hamiltonian although it is more accurate than diagonalisation. So the authors of [4] would like to emphasize that diagonalisation and sparse matrix method should complement one another and Fig. 7a from [4] has to be replaced by Fig. 8a from this paper. We note in passing that part of the discrepancy between the values of E_1 calculated by Clough et al. [1] and by Häusler et al. [4] is also due to an error in the computer-program used in [1]. From Table 3 we find a ratio E_1^{cal}/E_1^{meas} of about 1.5 which indicates that (1) is not a very good model Hamiltonian for LIAC.

If we assume no interaction between CH_3 groups and use a threefold cosine single particle potential, then we obtain the values E_1^{cal} which appear in the third row of Table 3 signifying the transition from the averaged tunneling multiplet to the E-symmetric level of the first librational state. Clearly the introduction of an interaction between CH_3 groups brings the theoretical values closer to the experimental ones. Qualitatively at least, the coupling model gives a good description of the pressure dependence of the lowest lying librational transition.

IV. Conclusions

From the analysis of the pressure dependence of the tunneling and librational spectrum of LIAC we can draw the following conclusions:

1. The model of pairs of coupled CH_3 groups in LIAC is confirmed.

2. The single particle potential increases more strongly with increasing pressure than the absolute value of the interaction potential. This clearly indicates that the crystal structure of LIAC cannot be described by assuming equal and linear scaling of all atom distances as a function of pressure. A crystal structure determination of LIAC under pressure is needed to confirm this result.

3. An improvement of model (1) is needed to give more quantitative agreement between measured and calculated tunneling and librational energies.

An investigation of the isotope effect on the tunneling of coupled methyl groups in LIAC is currently under way.

We would like to thank S. Clough, A. Hüller and W. Press for many stimulating discussions.

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