Experimental report

14/03/2019

Proposal:	**7-04-157**	**Council:**	4/2017
Title:	Rotational Tunneling in CH4 II: disorder and T-state splitting		
Research area:	Physics		

This proposal is a new proposal

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Samples:	CH4 CH4 + CH2D2 mixture

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	05/06/2018	08/06/2018

Abstract:

Transitions within the tunneling multiplet of CH4 in phase II are an almost classical example of rotational tunneling. Improved high resolution neutron scattering (with larger dynamical ranges and better statistics) does provide much improved data. An experiment at the backscattering instrument BASIS of the SNS on CH2D2 thus has allowed a new way of analysis of linewidths and lineshapes. However, the T-state splitting close to the elastic line as predicted by model calculations could not be resolved on BASIS due to its energy resolution of 3ueV. We propose to use the higher energy resolution of IN16B (0.75 ueV) to measure the T-state splitting on the simpler pure CH4 and furthermore to extend the previous published data on CH2D2 from BASIS. These measurements present a critical test for the new model predictions and the simulation approach based on the pocket state formalism.

Experimental Report — Rotational Tunneling in CH4 II: disorder and T-state splitting

Proposal 7-04-157, 5-8 June 2018 on IN16B

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Experiments were performed with solid methane condensed into an Al-cell, a hollow cylinder with a wall-thickness of 0.15mm. The measurements, mostly in phase II of CH_4 (4K to 30K), were done with a resolution of 1 μeV in a range between -30 μeV and + 30 μeV.

The principal goal was the shape of the tunneling spectrum stemming from T-T transitions at the sites of orientationally ordered molecules in CH_4 II: While all 3 T-states have zero energy at a perfectly cubic site they split up in presence of a finite potential. In case of the disorder originating from the different nuclear spin species in solid CH_4 there is a distribution of these energies. The two width parameters a =2.25 μeV and b = 1.05 μeV of the distribution (describing the parts of the h-distribution with A and T-symmetry, respectively) have been found in a previous experiment [1]. Note, that these fits involved the tunnelling peaks.

Spectra of the T-T-transitions are displayed in Fig. 1(a), both for pure CH_4 (99.99% purity) and CH_4 with 7.3% CH_2D_2 admixed. In neither case the spectra display the “dip” in the spectrum at E=0, predicted by a model calculation. Obviously it is obscured by an intense (strictly) elastic peak. Preliminary model fits of the low temperature T-T data of pure methane show little sensitivity to the parameter a. For b a value of 0.74 μeV is found, smaller than the earlier result, resulting in a smaller T-T splitting. For CH_4 with 7.3% CH_2D_2 admixed we expect a slightly higher value because of the additional disorder caused by the admixture.

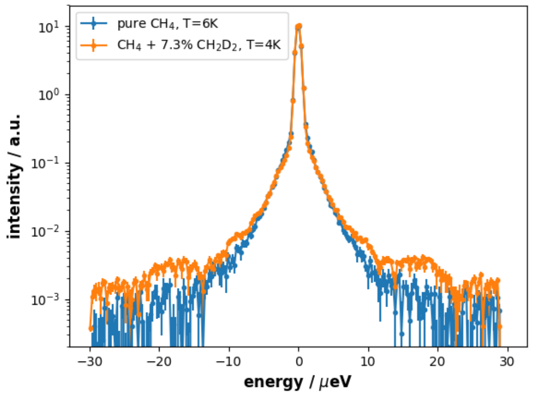

Fig. 1(a) *T-T spectrum in CH_4 II (about 8 hours, each)*

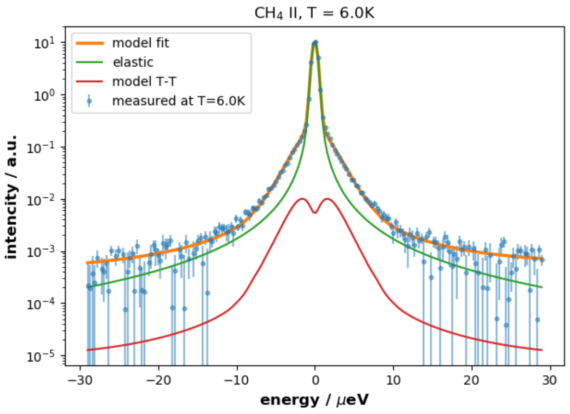

Fig. 1(b) *T-T spectrum CH_4 II, model fit; b=0.74μeV*

The analysis aims at the exact shape of the distribution of the T-states, and also at differences between the distribution with and without admixtures of CH_2D_2.

In a first experiment a moderate percentage of CH_2D_2 served to obtain tunneling spectra of CH_2D_2 in phase II (which is not accessible at low T otherwise). The above spectrum measured with much better resolution than before seems to show 3 weak peaks at energies of about 9, 18 and 27 μeV. Such a triplet with equidistant energies is typical for 2-fold symmetry (either CH_4 at a site with 2-fold symmetry or CH_2D_2 at a site with effectively tetrahedral symmetry). A preliminary assignment are T-E transitions.

The presence of a 2nd such triplet at higher energies [1] and eventual effects of orientational energies [2] remain an object of further investigation.

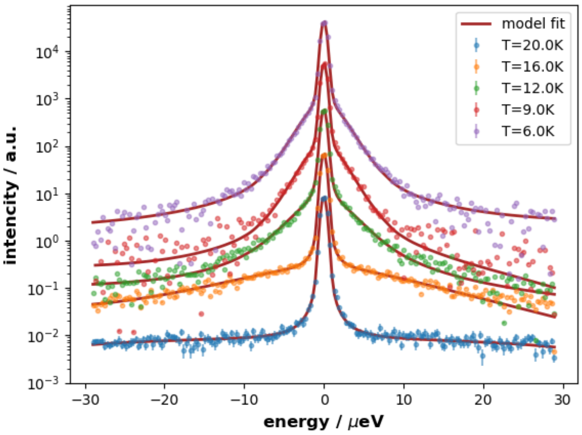

Fig. 2 *Data at selected temperatures. Note: the phase transition to the orientationally disordered phase I occurs at* T_c*=20.4 K.*

Finally the temperature dependence of the T-T transitions was measured (Fig. 2). In principle there is an almost continuous transition to rotational diffusion prevailing above the phase transition at T_c=20.4K. Fig. 2 shows the broadening of the spectrum with rising temperature which can be regarded as the effect of rotational jumps (described by Lorentzians) on an initially static distribution of transitions between T-state tunneling energies.

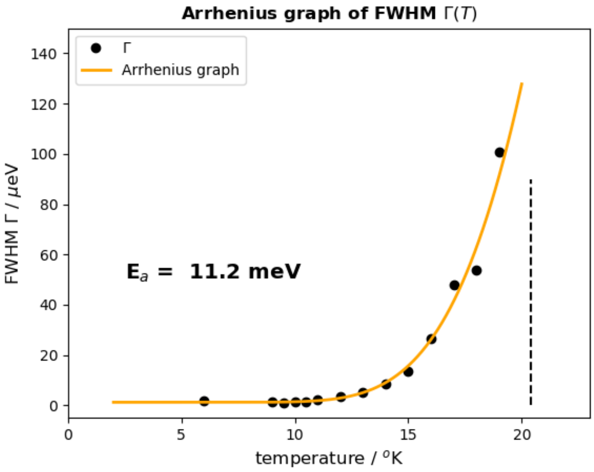

Fig.3 *Temperature dependence of the T-T peak broadening, described by Lorentzians convoluted with the model peak. The figure shows its full width at half maximum (FWHM) as function of temperature. Points are obtained from fits to the spectra; the orange line shows the log-linear fitted Arrhenius graph. The dashed line indicates the phase transition at* T_c *= 20.4 K.*

Above the phase transition temperature T_c rotational diffusion of the molecules causes quasielastic scattering with widths well above 1 meV. A measurement at T=30K has been used to determine the instrumental resolution; in this way the same sample geometry as for the lower temperature measurements is ensured. Below T_c the quasielastic scattering is much narrower. Its width increases with temperature as demonstrated by the fit results in Fig.3. The width shows a similar (almost exponential) behaviour as that obtained in a very early experiment studying the width of the (inelastic) tunneling peaks [3].

An activation energy of about 10 meV is in agreement with known librational energies. So far, effects of the decrease of the potential - when approaching the phase transition - have been ignored. A more detailed analysis is still ongoing.

References:

[1] W. Press, I. Krasnov, M. Zamponi, M. Prager, *J. Chem. Phys.* **135**, 224509 (2011)
[2] K. J. Lushington, K. Maki, J. A. Morrison, A. Heidemann, and W. Press, *J. Chem. Phys.* **75**, 4010 (1981)
[3] W. Press, A. Kollmar, *Solid State Comm.* **17**, 405 (1975)