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Rotational dynamics and coupling of methyl group rotations in methyl fluoride studied by high resolution inelastic neutron scattering

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Methyl group rotations in methyl fluoride were studied using the high flux backscattering spectrometer SPHERES at FRM-II. The asymmetry and width of the low temperature tunneling peak was used to determine if coupled rotations between neighboring methyl fluoride molecules exist. The temperature dependent broadening of the tunneling peak was used to determine the first librational transition and compared to the temperature dependent shift of the position of the tunneling peak. The results obtained by using inelastic neutron scattering confirm previous models that assume rotational coupling. This is the first neutron backscattering experiment with sub-μeV resolution at energy transfers up to 31 μeV. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Simple molecules are well suited to test different mathematical models that try to explain their complex dynamical behavior. The methyl halides belong to the most simple class of organic molecules that contain CH_3 groups. The crystal structure of methyl fluoride, chloride, bromide, and iodide is well known[1–5] and their dynamics were extensively studied by inelastic,[6,7] quasielastic neutron scattering,[8] and computational methods.[9] In general, the dynamics of rotating CH_3 groups can be described by a mean field theory, which is commonly known as the single particle model or SPM.[10] Recent quasielastic neutron scattering experiments[8] confirmed that the SPM is a suitable model to describe the dynamics and associated transitions such as tunneling and librational transitions as well as activation energies of the bromide and iodide. A thorough statistical analysis of the dynamics of the chloride and the fluoride in particular indicated that the SPM would not be the appropriate model to accurately describe the dynamics of those two molecules. Methyl fluoride—which is also of commercial interest and used in plasma etching of silicon compound films—and its crystal structure (monoclinic, space group $P2_1/n$) provides crystal lattice planes that are shared by two neighboring methyl groups. Due to fluor being the smallest of the halides it also allows two molecules to come relatively close together. Certainly, the combination of shared crystal planes and small molecules facilitates the possibility of coupled methyl group rotations. During an earlier study it was already mentioned that coupled methyl group rotations could be possible.[7] However, instrumental limitations did not allow to study the low temperature tunneling peak of methyl fluoride in detail. The third generation high resolution backscattering spectrometer SPHERES at FRM-II (Refs. 11–13) provides the possibility of using polished Si crystals for highest energy resolution, an advanced Doppler drive to access a large dynamic range and a reasonable flux at the sample making it possible to study possible coupling effects of tunneling methyl rotors.

In Secs. II and III we briefly introduce the coupling model and summarize recently published results of the mathematical model that was used to describe the dynamics of the methyl fluoride. Section IV is divided into three parts: Sec. IV A describes the instrument that was used during the experiments. Section IV B describes the sample preparation while Sec. IV C describes how the experimental data were processed. The results of the experiment are described in Sec. V and are followed by a summary in Sec. VI.

II. THEORETICAL BACKGROUND

For a methyl group the rotational reorientation usually occurs around the bond axis that links the CH_3 group to the rest of the molecule. Other atoms in the molecule and neighbors hinder the reorientational dynamics. The influence of the environment on the dynamics of the individual methyl group is usually described by a potential, which shows the symmetry of the rotating group—in case of a CH_3 group this symmetry is C_{3v}. It is usually sufficient to express the potential as the sum of the first two terms of a Fourier expansion

$$V(\varphi) = V_0 + \sum_{n=1}^{2} \frac{V_{3n}}{2}(1 - \cos(3n\varphi + \alpha_{3n})). \quad (1)$$

Excitations that are observable during a neutron scattering experiment can be calculated by solving the Schrödinger equation

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$$H|\Psi_i\rangle = E_i|\Psi_i\rangle,$$

where the Hamiltonian is given by

$$H = \left[-B\frac{d^2}{d\varphi^2} + V(\varphi) \right] \tag{2}$$

($B=0.655$ meV is the rotational constant of a methyl group) and the rotational excitations are determined by the parameters of Eq. (1). If two methyl groups are coupled to each other the Hamiltonian given in Eq. (2) needs to be modified to include at least a term that depends on two rotational angles φ_1 and φ_2 of the two interacting methyl groups.[14] Such a Hamiltonian is given by

$$H_c = H_1 + H_2 + W_{12}. \tag{3}$$

Limiting the potential given in Eq. (1) to $n=1$ simplifies the single particle terms to

$$H_i = \left[-B\frac{d^2}{d\varphi_i^2} + \frac{V_{3i}}{2}(1-\cos 3\varphi_i) \right], \quad i=1,2. \tag{4}$$

The coupling, which depends on the differences in orientation only can be expressed as

$$W_{12} = W_3 \cos(3\varphi_1 - 3\varphi_2). \tag{5}$$

For crystallographically equivalent and identical particles, the threefold potential term in Eq. (4) simplifies by applying $V_3=V_{31}=V_{32}$. The librational ground state consists of four tunneling sublevels labeled by the symmetry of the tunneling states of each of the two methyl groups and possible transitions are $AA \rightarrow AE$, $AA \rightarrow E_aE_b$, $AA \rightarrow E_aE_a$, and $E_aE_a \rightarrow E_aE_b$. Exchanged indices describe the same energy levels. From an experimental point of view coupling would show as an asymmetric peak profile and the amount of asymmetry is determined by the magnitude of the potential parameters V_3 and W_3. If the crystal structure supports coupling and a tunneling transition in the μeV range is observed the magnitude of the expected split of the tunneling sublevels is usually in the sub-μeV range and in order to be able to observe such an effect, an instrumental resolution of less than 1 μeV is required.

The energy levels are obtained by using free rotor functions $|m\rangle=\exp(im\varphi)$ and $\Psi_i=\Sigma_m\alpha_m|m\rangle$ and matrix elements H_{mn} of the Hamiltonian are obtained by standard numerical procedures provided that parameters of the rotational potentials and the coupling term are known.

The double differential cross section measured in a neutron scattering experiment is proportional to the scattering function $S(Q,\omega)$. For quantum rotational tunneling among three equivalent sites the scattering function is given by[10]

$$S(Q,\omega) = \left[\tfrac{5}{9} + \tfrac{4}{9}j_0(Qd)\right]\delta(\omega) + \tfrac{2}{9}[1-j_0(Qd)](\delta(\omega-\omega_t) + \delta(\omega+\omega_t)), \tag{6}$$

where Q is the magnitude of the momentum transfer, $j_0(Qd)=\sin(Qd)/(Qd)$ is the zeroth order spherical Bessel function, and $d=1.78$ Å is the distance between H atoms of the CH_3 group. Here, $S(Q,\omega)$ is normalized to 1, sometimes it may also be normalized to 3. For temperatures above $T=0$ K the δ-functions in Eq. (6) need to be replaced by Lorentzians with a temperature dependent full width at half maximum. The broadening of the observed tunneling transition with increasing temperature is described as an Arrhenius law,[15]

$$\Gamma(T) = \Gamma_0 \exp\left(-\frac{E_\Gamma}{k_BT}\right). \tag{7}$$

To a good approximation the line broadening is caused by the transition to the first librational level at energy E_{01} and thus $E_\Gamma \approx E_{01}$. Therefore, E_{01} can be obtained from fitting the experimentally obtained values of $\Gamma(T)$ against either T or $\ln\Gamma(T)$ versus $1/T$.

A description of the temperature dependent shift of the tunneling transition is more complicated[15] and results in a modified Arrhenius law which is given in Eq. (8),

$$\hbar\omega_t = \hbar\omega_t(T=0)\left[1 - A^{\sin}\exp\left(-\frac{E_{01}^{\sin}}{k_BT}\right)\right]. \tag{8}$$

Here a sinusoidal coupling $A^{\sin}$ is included in the Arrhenius behavior which effectively shifts the rotational potential and the corresponding tunneling transition if the temperature increases. The theory predicts $E_{01}^{\sin} \leq E_\Gamma \approx E_{01}$.

TABLE I. Calculated tunneling transitions. Values are taken from Ref. 8.

Symmetry	Transition (μeV)
$AA \rightarrow AE$	23.14
$AA \rightarrow E_aE_b$	23.00
$AA \rightarrow E_aE_a$	23.02
$E_aE_b \rightarrow E_aE_a$	0.02

III. POTENTIAL PARAMETERS OF CH_3F

Previous experiments done on methyl fluoride determined characteristic energy transitions that are summarized below:[7]

- tunneling transition $\hbar\omega_t=23.1$ μeV,
- first librational transition $E_{01}=10.0$ meV, and
- activation energy $E_A=13.9$ meV.

The analysis of those values lead to the conclusion that a coupled motion of methyl librations is the most likely model of the dynamics in CH_3F. Based on the experimental values a statistical analysis[8] determined potential parameters of $V_3=20.2$ meV and $W_3=-2.4$ meV with associated characteristic energy transitions of

- tunneling transition $\hbar\omega_t=23.14$ μeV,
- first librational transition $E_{01}=10.1$ meV, and
- activation energy $E_A=13.9$ meV.

In addition a split of the tunneling sublevels of $\delta\hbar\omega_t=0.12$ μeV was determined. The symmetry and transitions are shown in Table I.

IV. EXPERIMENT

A. Instrument

The experiment was carried out using the high resolution backscattering spectrometer SPHERES at FRM-II in Garching, Germany.[11–13] The instrument was chosen for two reasons: First, the dynamic range that extends the accessible energy transfer range to ± 31 μeV around the elastic line in the standard setup of the instrument [energy resolution of 0.65 μeV, full width half maximum (FWHM) at $\lambda = 6.27$ Å]. Second, SPHERES is the only neutron backscattering instrument worldwide which offers at such large energy transfers an energy resolution below 0.5 μeV. The improved setup with both monochromator and analyzers made of polished Si(111) crystals is under test. This particular setup would offer an energy resolution of $\delta E \sim 0.3$ μeV at the expense of losing approximately a factor of 10 of neutron intensity at the sample position compared to the standard setup of the instrument. Hence, a high initial flux was crucial for this particular experiment to allow to study an effect which is in the order of approximately 30% of the instrumental resolution. Unfortunately, we could not utilize the polished Doppler monochromator during the experiment. This had three consequences.

First, the neutron intensity at the sample position was higher than anticipated, which slightly reduced the required experimental time. This gave us the opportunity to check some results that were published earlier. Second, the resulting energy resolution of the instrument was $\delta E = 0.55$ μeV (FWHM) and slightly worse than expected and this impacted, third, on the analysis in terms of peak profile analysis as will be described later in Sec. V.

The incident neutron wavelength was $\lambda = 6.27$ Å and is determined by the Si (111) reflection and the backscattering geometry. Four spectra were taken at temperatures of 4, 24, 26, and 28 K. The different temperatures were controlled in a standard Orange cryostat. The low temperature spectrum was used to study the broadening of the tunneling peak, the remaining three temperatures were used to check characteristic transitions by determining the temperature dependent broadening and shift of the tunneling peak.

B. Sample preparation

Methyl fluoride is commercially available from Aldrich with a chemical purity of ≥99%; no further purification took place. At room temperature methyl fluoride is in a gaseous state. It has got a melting point of −142 °C and a boiling point of −78.4 °C. The sample was condensed into the sample container with dimensions $35 \times 40 \times 0.5$ mm^3. After liquefaction the sample was cooled down into the solid polycrystalline phase. The amount of sample material gave a scattering probability of about 15%. Despite the slightly higher than the usual 10% scattering probability we did not apply any further multiple scattering correction. During an inelastic scattering experiment at low temperatures the likelihood of an inelastic event is already low compared to the elastically scattered neutrons and a second inelastic scattering event therefore even less likely. The sample container was positioned under an angle of 45° to the incident beam to favor scattering at higher momentum transfers, see Eq. (6).

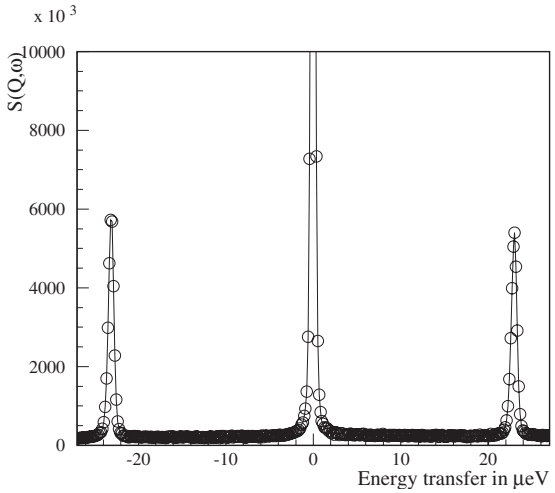

FIG. 1. Low temperature (4 K) spectrum of methyl fluoride. In order to increase the statistics, the signals of detectors which cover the angular range of 35°–134° were summed up.

C. Data processing

By using standard programs[16] the experimental data were transformed into $S_{\mathrm{expt}}(Q,\omega)$ from which the relevant experimental observables were determined. The manipulation of the data sets involved the following four steps:

- background determination,
- determination of the resolution function,
- convolution of the theoretical spectrum with the resolution function, and
- fit of the convoluted spectrum to $S_{\mathrm{expt}}(Q,\omega)$ in order to obtain linewidths and positions.

V. RESULTS

The low temperature spectrum of methyl fluoride is shown in Fig. 1. In order to increase the statistics and benefit from the Q dependence of Eq. (6) signals from detectors 6 to 15 were summed up. This corresponds to an average scattering angle of 84°. Besides the elastic line two distinct peaks at 23.1 μeV are visible on the neutron energy loss and neutron energy gain side. Figure 2 shows the tunneling peak on the neutron energy gain side. Although the energy resolution was not as good as we would have wished for the tunneling peak is in fact broader that the instrumental resolution. It is clear that this could not be detected in earlier experiments due to limitations in the resolution at large energy transfers of the instrument which was used.[7]

Since the instrumental resolution of SPHERES is constant over the whole dynamic range this feature of the peak—being significantly broader than the resolution function—would imply that the broadening is indeed of physical nature. In addition, a slight asymmetry of the peak can be seen although this certainly less pronounced as in a

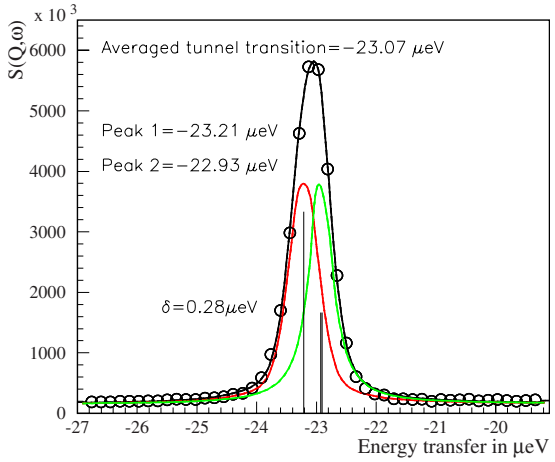

FIG. 2. (Color online) Low temperature tunneling peak. Two Lorentzians with relative intensities of 1:1 were used to describe the experimental peak.

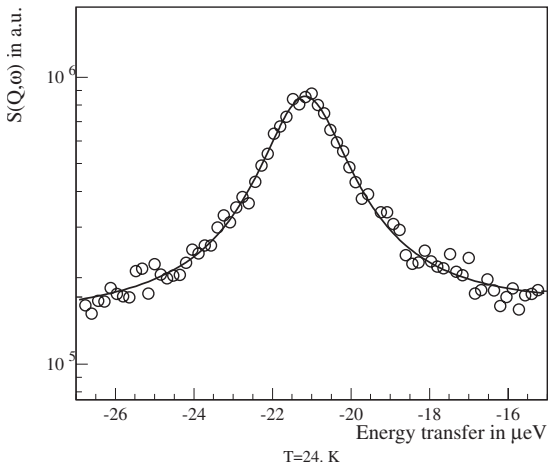

FIG. 3. Temperature dependent line broadening of the tunneling peak at 24 K.

previous study of *m*-xylene.[17] In order to obtain a value of the split of the tunneling sublevels three Lorentzians, representing the $AA \rightarrow AE$, $AA \rightarrow E_aE_b$, and $AA \rightarrow E_aE_a$ transitions with relative intensities 2:1:1 should be used. Due to the slightly worse than expected instrumental resolution (see above) in combination with the expected small difference of only 0.02 μeV between the $AA \rightarrow E_aE_b$ and $AA \rightarrow E_aE_a$ transitions we were not able to describe both transitions separately. Hence, we decided to fit the tunneling peak with two Lorentzians only. During the fit we required the integrated relative intensities to be 1:1. The result of the fit is also shown in Fig. 2. From the fit we obtained a mean tunneling transition of $\hbar\omega_t = 23.07$ μeV and tunneling transitions of $\hbar\omega_t = -23.21$ μeV and $\hbar\omega_t = -22.93$ μeV, which represent the $AA \rightarrow AE$ and the combined $AA \rightarrow E_aE_b$ and $AA \rightarrow E_aE_a$ transitions, respectively. The experimentally determined split of the tunneling sublevels is $\delta = 0.28$ μeV. This is roughly a factor of 2 higher than the recently reported value of $\delta = 0.12$ μeV and certainly worked in our favor considering an experimental resolution of $\delta E = 0.55$ μeV. However, taking into account that the abovementioned coupling model considered only threefold and no further higher order contributions to the rotational potential or other than next-neighbor interactions, we conclude that there is a good agreement between the experimental findings and previous calculations.

We also determined temperature dependent parameters of the tunneling transition—the linewidths as well as the positions. We are aware that doing this based on three experimental points only is just a check of earlier results; however we would like to show the data for completion. Fitting an Arrhenius law as shown in Eq. (7) to the temperature dependent broadening of the tunneling peak yields $E_\Gamma = 9.1$ meV, which we associated with the librational transition E_{01}. An example of the fit is shown in Fig. 3 for a temperature of 24 K. A fit of Eq. (8) to the temperature dependent position of the tunneling peaks yields $\hbar\omega_t(0) = 23.1$ μeV and $E_{01}^{\sin} = 9.0$ meV, Fig. 4. The obtained values agree with theoretical predictions and the experiment overall confirms and improves previously published results.

From the parameters that were obtained during the fit of the low temperature tunneling peak, see Fig. 2, we can derive an estimate of the threefold part of the rotational potential V_3 and the coupling term W_3 that are shown in Eq. (3). For a combination of $(V_3, W_3) = (19.28, -3.10$ meV) we obtain the following transitions:

- $AA \rightarrow AE$: $\hbar\omega_t = 23.10$ μeV,
- $AA \rightarrow E_aE_b$: $\hbar\omega_t = 22.90$ μeV,
- $AA \rightarrow E_aE_a$: $\hbar\omega_t = 22.93$ μeV,
- $\delta\hbar\omega_t = 0.2$ μeV,
- $E_{01} = 10.1$ meV,
- $E_A = 14.3$ meV.

The relative strength of the coupling is in the order of

$$\epsilon = \frac{V_3}{V_3 + |W_3|} = \frac{19.28}{19.28 + 3.10} = 0.86.$$

Overall, this agrees quite well with a value of $\epsilon = 0.89$ that can be obtained from the values given in Ref. 8. If we combine the calculated $AA \rightarrow E_aE_b$ and $AA \rightarrow E_aE_a$ transitions we get a averaged transition of $\hbar\omega_t = 22.92$ μeV which agrees with the position of the Lorentzian used to model those two transitions, see Fig. 2. The transition to the first librational

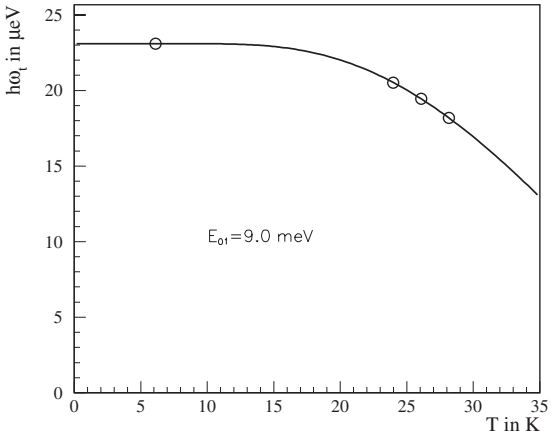

FIG. 4. Temperature dependent and positions of the tunneling peak. The data were collected between in a temperature range of 24 K $\leq T \leq$ 28 K.

level, assuming the coupling model and the derived potential parameters, agrees with previous experiments.[7] Only the activation energy is higher than the recently reported experimental value of 13.9 meV but still within the reported experimental error of ± 0.7 meV.[8] In addition, methyl fluoride shows the most complex density of states of all of the halides. In particular librations around the CH_3F bond axis show lower amplitudes than those perpendicular to it, and this constant variation of distance between two molecules could alter the potential parameters and thus potentially explain the difference between the calculated and observed split of the tunneling sublevels.

In summary, there is a good agreement between the experimental findings and previous calculations and the dynamics can well be described by a model that assumes coupling between librational motions of methyl groups.

VI. SUMMARY

High resolution inelastic experiments were carried out to obtain information about the broadening and asymmetry of the low temperature rotational tunneling transition in methyl fluoride. At low temperatures the width and the slight asymmetry of the tunneling peak can be described by two Lorentzians, convoluted with the instrumental resolution function representing the $AA \rightarrow AE$ and the combined $AA \rightarrow E_a E_b$ and $AA \rightarrow E_a E_a$ transitions, respectively. The experimental results confirm and endorse the recently published suggestion that coupling exists between those methyl groups in CH_3F that share a common crystallographic plane. Due to instrumental limitations in terms of resolution at large tunneling transitions this coupling could not be observed during earlier experiments. For the first time a "highest" resolution experiment, well below the typical 1 μeV resolution of backscattering spectrometers, in combination with a large dynamic range was done utilizing the polished Si(111) analyzer segments available at SPHERES, FRM-II.

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