Methyl tunnelling in trihalogeno-trimethyl-benzenes

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Results of inelastic neutron scattering (INS) from 1,3,5-trihalogeno-2,4,6-trimethyl-benzenes are reported for the chloro-, the bromo- and the iodo-case. For the whole family the spectra show numerous similarities, in the μeV as well as in the meV range. We observe three tunnelling lines of equal intensity corresponding to three crystallographically inequivalent methyl rotors. The observed librational peaks are at much lower energies than expected from a pure threefold potential. Within the halogen family a systematic reduction of the barrier height is found with larger halogen sizes. The temperature dependence of the tunnelling energies shows the most pronounced difference between TBM and TIM, where the corresponding tunnelling lines even shift in opposite directions.

1. Introduction

In this paper we want to report about the rotational excitations of the methyl groups in 1,3,5-trihalogeno-2,4,6-trimethyl-benzenes. These compounds have been chosen from the hexa-substituted benzenes for four reasons:

(1) We know from NMR measurements, that these compounds show the lowest temperature for the T_1 minimum, indicating the highest values for the tunnelling splittings.

(2) It is expected that the number of inequivalent rotors is small due to the high molecular symmetry.

(3) All the three compounds of the family show the same crystallographic structure at room temperature and there are strong arguments (NQR results, Raman spectra) that this should be true also at low temperatures.

(4) No complication of the tunnelling spectra was expected due to an orientational coupling between methyl groups (at least not within the molecules).

2. Structure

All three systems of the family, trichloro-(TCM), tribromo- (TBM), and tri-iodo-(TIM)-trimethylbenzene, crystallize in the same crystallographic P $\bar{1}$ triclinic group. There exists a center of symmetry between the two molecules present in the cell; all the molecules are stacked along the ***a*** axis, and stay parallel to each other roughly in (100) planes.

An X-ray structure determination made at 150 K for TCM, shows significantly different thermal Debye–Waller factors for the three methyl groups of one molecule correlated with slightly different environments of those methyl groups in the crystal [1]. From Raman, FIR, and NQR measurements we assume that the phase change at $T_C \sim 150$ K [2] does not cause a change of crystallographic group: so the three chlorines, as well as the three methyl groups of each independent molecule in a cell retain different environments. The transition temperatures for TBM and TIM are in the same region as for TCM.

3. μeV range of the spectrum

Experiments were performed at ILL on IN_{10} and IN_{13}, and at ISIS on IRIS. In the inelastic neutron scattering spectrum for each of the three compounds, TCM, TBM, and TIM, three tunnelling lines of equal intensity were found. We considered this as a proof of the presence of three inequivalent rotors in accordance with the crystallographic structure.

Figure 1 shows the spectra obtained on IRIS with TBM at 4 and 18 K and the fit of the spectrum assuming Lorentzian shapes. The TCM and TIM spectra show similar features.

The positions of the tunnelling lines are:

TCM:	4.3	9.2	13.1 μeV	at 1.5 K	(IN10 - ILL)
TBM:	14.1	25.1	48.8 μeV	at 4.0 K	(IRIS - RAL)
TIM:	14.4	26.7	87.4 μeV	at 1.5 K	(IRIS - RAL)

For the temperature dependent shifts of the tunnelling lines we observe:

(1) Only a weak variation for the chloro compound and for the inner lines of the other halogeno com-

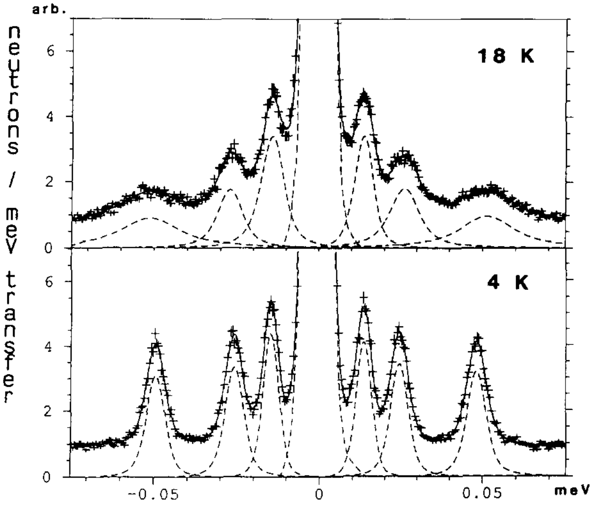

Fig. 1. Splitting of fundamental methyl rotor levels in TBM, at 4 and 18 K.

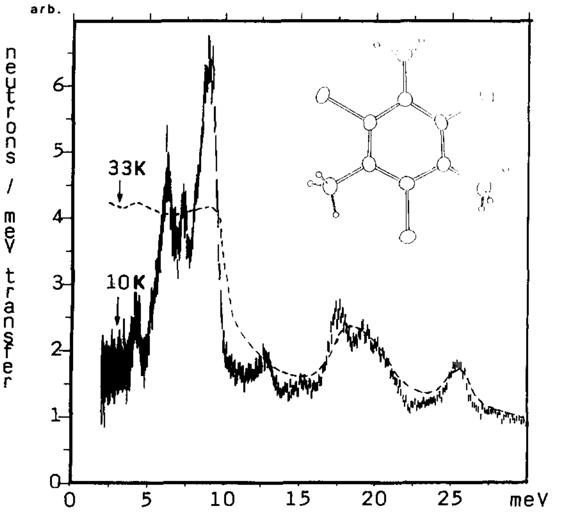

Fig. 2. First excited librational transition for methyls in TBM, at 10 and 33 K.

pounds; preliminary results for the outer line in TCM, obtained on IN10 in Grenoble, show a positive rather than a negative shifting behavior of this line versus temperature.

(2) A pronounced shifting behavior of the middle and of the outer line of the bromo and of the iodo compound.

(3) This shifting occurs even in opposite direction: the bromo compound shows a pronounced increase of the tunnelling energy at temperatures up to 20 K, whereas the iodo compound shows a pronounced decrease of the tunnelling energy at temperatures up to 17 K.

The broadening of the tunnelling line in TBM and also its shifting is well described by an Arrhenius behavior, with an activation energy of 5.4 ± 0.4 meV.

4. meV range of the spectrum

Experiments were performed at LLB on 4F1 and at ISIS on TFXA. In fig. 2 the INS spectra up to 30 meV are presented for the TBM compound at two temperatures. It shows three well resolved features between 6 and 10 meV, which are very sensitive to temperature and very likely correspond to $0 \rightarrow 1$ transitions of methyl rotors. The peak at about 8.8 meV is of somewhat higher intensity compared to the other two peaks, which can be explained by an additional mode lying in the same energy range. As well in TCM as also in TIM this type of excitation is also found, being of strong intensity and quite sensitive to temperature. In these cases it is well separated from the librational feature itself and we would attribute it to an internal mode of low frequency (in accordance with calculations using atomic pair potentials and with the fact that it is also very intensive in IR absorption). Therefore we believe that the 8.8 meV peak consists of two excitations, a methyl libration being one of them.

In TCM the librational peak is in the 9–11 meV range [3], while in TIM we found the feature in the 4–7 meV region. Both observations about the librational frequencies and about the tunnelling frequencies allow the general conclusion of a reduced barrier height when the size of the halogen is increased.

We assume that each of these three librational peaks correspond to one of the tunnelling peaks (in the opposite sequence) and attribute to each of the three rotors two potential parameters V_3 and V_6 according to the expansion of the single particle rotational potential into a threefold Fourier series $V_3 \cos \varphi + V_6 \cos 6\varphi$. Even for the choice of a stronger $|V_3|$contribution compared to the $|V_6|$ contribution (resulting also in more realistic values for the second librational energy), ratios V_6/V_3 of roughly 0.1, 0.4, 0.9 in the sequence of increasing halogen sizes have to be used to explain simultaneously the observed values for the tunnelling and librational energies. However a strong sixfold potential contribution is expected also from the symmetry of the surrounding of the methyl rotors. The values obtained for V_3 and V_6 satisfactorily allow us to interpret the features around 17–22, 16–21, and 14–20 meV, respectively, as the second librational transitions in all three cases for TCM, TBM, and TIM. This assignment also fits to the observed temperature sensitivity.

All librational features in all three halogen compounds have also been observed in FIR absorption. Not only the positions, but also the temperature dependence of the width and intensity of the absorption peaks show a very good coincidence with the properties of the librational lines in the INS spectra. To our knowledge this is the first observation of an excitation of the methyl librational transition by light absorption.

5. Conclusion

We investigated the rotational excitations of the methyl groups in the series of 1,3,5-trihalogeno-2,4,6 methyl-benzenes at low temperatures. In contrast to the expected trend considering the isolated molecule, we found a decreasing barrier height for the rotation of the methyl group with increasing size of the halogen atom. This indicates that the dominant contribution for the orientational barrier is due to the interaction with neighboring molecules, rather than due to the intramolecular interaction. Also the detected inequivalence of the three methyl groups, in accordance with the crystallographic structure, indicates the strong influence of the surrounding. In addition, this dominance of the intermolecular potential contribution can be understood within preliminary pair potential calculations (a more precise knowledge of the low temperature positions of the atoms would be desirable).

The obtained tunnelling splittings and the librational energies cannot be explained using a pure threefold barrier; a sixfold contribution at least has to be included.

The observed qualitative difference in the shifting behavior of the tunnelling line with temperature in TIM as compared to TBM may tentatively be explained by different methyl orientations in these compounds. This interpretation is in accordance with a recent Raman and TSC measurement, in which an unsystematic change in the 150 K phase transition is found for TIM as compared to the other two compounds, TBM and TCM. The observed weak positive shifting of the tunnelling line in TCM is also in accordance with this interpretation.

References

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