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ЛАБОРАТОРИЯ НЕЙТРОННОЙ ФИЗИКИ

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## II. METHYL IODIDE

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## 1. Introduction

The molecular dynamics of crystalline and liquid methyl iodide have been studied up to now by spectroscopical methods. Mador and Quinn [1], Dows [2] and Lafferty and Robinson [3] applied for this study the infra-red absorption, and Mitsuo Ito [4] used the Raman spectroscopy. Mador and Quinn performed measurements in the wave number region 800 $cm^{-1}$ - 4500 $cm^{-1}$. Dows in the region 500 $cm^{-1}$ - 3000 $cm^{-1}$, Lafferty and Robinson in the region 30 $cm^{-1}$ - 130 $cm^{-1}$, and Mitsuo Ito in the region from very low frequencies to about 3000$cm^{-1}$.

The results obtained led to evidence of there being two separate parts in the spectrum of crystalline methyl iodide, the lattice vibration region (low frequencies, below ca. 120 $cm^{-1}$) and the intramolecular vibration region (frequencies ca. 500$cm^{-1}$).

In the lattice vibration region Mitsuo Ito obtained at - 190°C bands at 47, 58, and 84$cm^{-1}$, which were interpreted by him as being caused by translational vibrations, and bands at 94 $cm^{-1}$, 104 $cm^{-1}$, and 112 $cm^{-1}$, which he interpreted as being caused by torsional vibrations. In the same region Lafferty and Robinson obtained the frequencies 35.8 $cm^{-1}$, 55 $cm^{-1}$ and 118 $cm^{-1}$. Dows obtained the frequency 105 $cm^{-1}$. It should be pointed out here that Dows's value 105 $cm^{-1}$ was obtained not directly but from an analysis of the combination bands. The interpretation of the bands given by Mitsuo Ito based on the fact that, as a rule, translational bands (T) occur at lower frequencies than librational ones (R) and that they all show a temperature dependence. Lafferty and Robinson gave a similar interpretation on the basis of a comparison of spectra of a normal and deuterized substance.

It should be mentioned here that the crystal structure of methyl iodide has not yet been determined. Burbank /5/ determined only the structure of methyl chloride at - 120°C and showed that it has the $C_{2v}$ symmetry. According to the opinion expressed in papers /2/, /3/, /4/ the symmetry of the methyl iodide crystal is certainly lower, i.e. its structure is more complicated, than that of $CH_3Cl$. In view of this fact, a lack of selection rules and the appearance of all six bands in the lattice vibration spectrum of the crystalline $CH_3Cl$ may be expected.

In the intramolecular vibration region there is a good agreement between the data of Dows and Mitsuo Ito. Both authors observe a band at ca. 520 $cm^{-1}$, which is interpreted as the mode $\nu_3$ of the $CH_3I$ - molecule, at ca. 890 $cm^{-1}$ ( $\nu_6$ of $CH_3I$ ), at ca.1240 $cm^{-1}$ ( $\nu_2$ of $CH_3I$), at ca. 1400 $cm^{-1}$ ( $\nu_5$ of $CH_3I$), at ca. 2930 $cm^{-1}$ ( $\nu_1$ of $CH_3I$), and at ca. 3030 $cm^{-1}$ ( $\nu_4$ of $CH_3I$).

It seemed interesting to carry out an investigation of the dynamics of methyl iodide in a wide temperature region by the inelastic neutron scattering method in order to obtain information complementary to that given by spectroscopy methods.

## 2. Experimental results

Experimental technique and results representations is the same as describe in part I /6/. Figs. 1 and 2 present the results obtained for methyl iodide at temperatures: -160°C, -120°C, -75°C, and -20°C (melting point: -64°C).

For crystalline $CH_3I$ there are bands at 117 $cm^{-1}$, 202 $cm^{-1}$, ca. 320 $cm^{-1}$, ca. 500 $cm^{-1}$, and ca. 1200 $cm^{-1}$.

For liquid $CH_3I$ one obtains a continious spectrum on which, at higher frequencies, the same bands as those for solid substance are visible.

For crystalline methyl iodide the beryllium cut-off, which gives the intensity of quasielastically scattered neutrons, is steep but is of a relatively low intensity. For the liquid substance this cut-off practically vanishes.



Fig. 3 presents the intensity distribution of scattered neutrons obtained for solid $CH_3I$ at - 160°C by applying the Zn-monocrystal situated behind the Be-filter. For comparison, the result from Fig. 1 for -160°C (corresponding to the ordinary Be-filter method) is also presented in Fig. 3. Owing to a better resolution, one may now see four bands in the lattice vibration region. Also at higher frequencies the peaks are much better resolved than in the ordinary Be-filter method.

## 3. Discussion

Our results are in general agreement with those obtained by spectroscopical methods /2/, /3/, /4/. This concerns the lattice vibration region as well as the intramolecular vibration region.

The bands, which had not been observed until now, are those at ca. 320 $cm^{-1}$ and at 202 $cm^{-1}$. They may probably be interpreted as being higher harmonics of torsional bands (R).

All results obtained by spectroscopy (IR and Raman) as well as our INS results are assembled in Table I. In the last column of this Table there is a proposed interpretation, essentially the same as that previously given in papers /2/, /3/, /4/.

It should by pointed out that our measurements at the lowest frequencies, performed with the Zn-monocrystal, though not sufficiently accurate to give information concerning frequency values, gave evidence of four in region where Mitsuo Ito observed lattice vibration peaks.

It should also be stressed that the failure to appear in our spectra of the band at ca. 890 $cm^{-1}$ ( $\nu_6$ of $CH_3I$) is unexplained.

A practically continuons neutron spectrum for liquid methyl iodide may be treated as a proof of freedom of translations and rotations of $CH_3I$-molecules in the liquid. This is in agreement with results obtained previously /7/, /8/ with neutrons for liquid $CH_3I$ at room temperature.

The small intensity of the quasielastic part of the spectrum for crystalline $CH_3I$ is justified in view of the small frequency values of lattice vibrations which cause a small temperature value.

Table 1

Vibration frequencies ($cm^{-1}$) observed in crystalline $CH_3I$

| Dows [2] -190°C | Lafferty Robinson [3] -190°C | Mitsuo Ito [4] -190°C | This work -160°C | Interpretation |
|---|---|---|---|---|
| | 35.8 | 47 | Four bands are visible in INS when higher resolution is appl. | $T_x$, $T_y$ |
| | 55.0 | 58 | | |
| | | 84 | | $T_z$ |
| | | 94 | | $R_z$ |
| 105 | | 104 | | |
| | 118.0 | 112 | 117 | $R_x$, $R_y$ |
| | | | 202 | 2R |
| | | | ca 320 | 3R |
| 519 | | 508 | | |
| 523 | | 525 | ca 500 | $\nu_3$ of $CH_3I$ |
| 888 | | 888 | -? | $\nu_6$ of $CH_3I$ |
| 1236 | | 1232 | ca 1200 | $\nu_2$ of $CH_3I$ |
| 1240 | | | | |

The entire disappearance of the quasielastic part for the liquid may again be considered as a proof of almost complete freedom of translational and rotational motions.

We are planning to repeat in the future the INS measurements with the Zn-monocrystal, but with better statistics in order to improve the accuracy of frequency determination, especially in the lattice vibration region.

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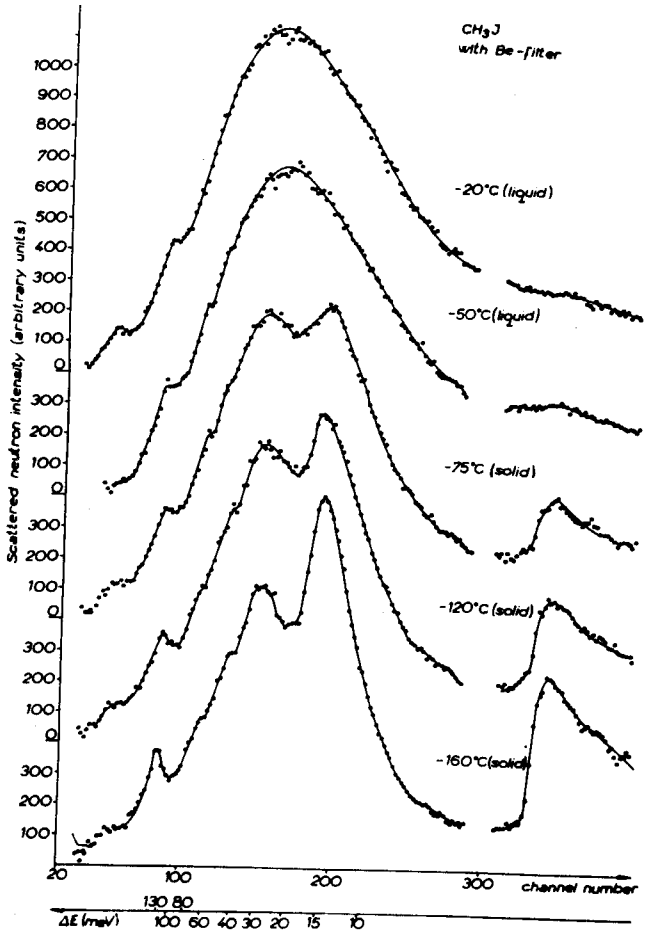


Fig. 1. The intensity of neutrons scattered from methyl iodide, at various temperatures, as a function of the analyser channel number. Channel width 64 $\mu$ sec. The lower scale gives the energy transfer for inelastically scattered neutrons. Be-filter technique.



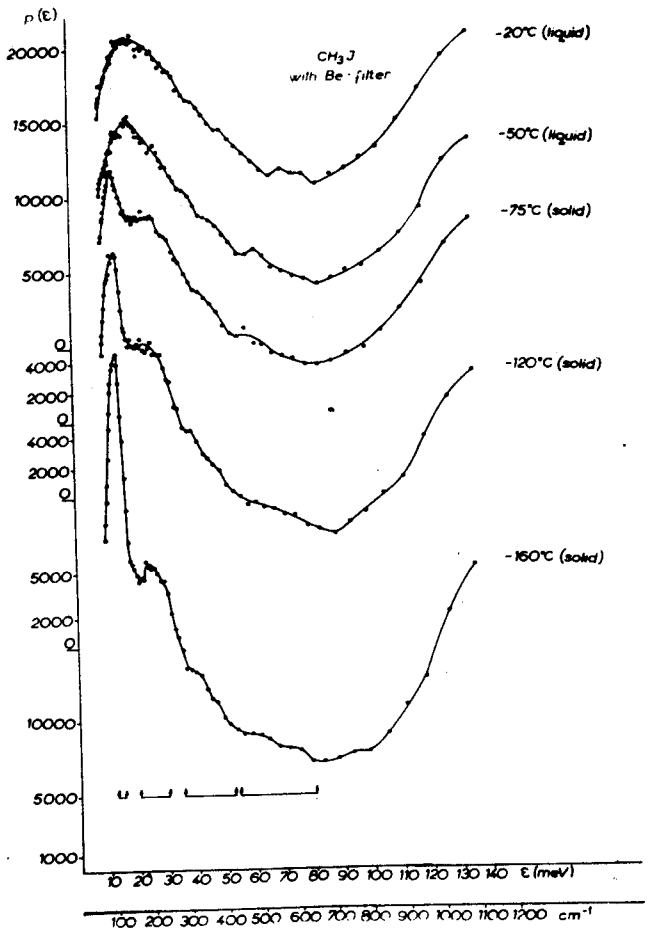


Fig. 2. The $p(\epsilon)$ function for methyl iodide at various temperatures, obtained on the basis of data of Fig. 1. Sectors with arrows indicate the bands discussed in the text.

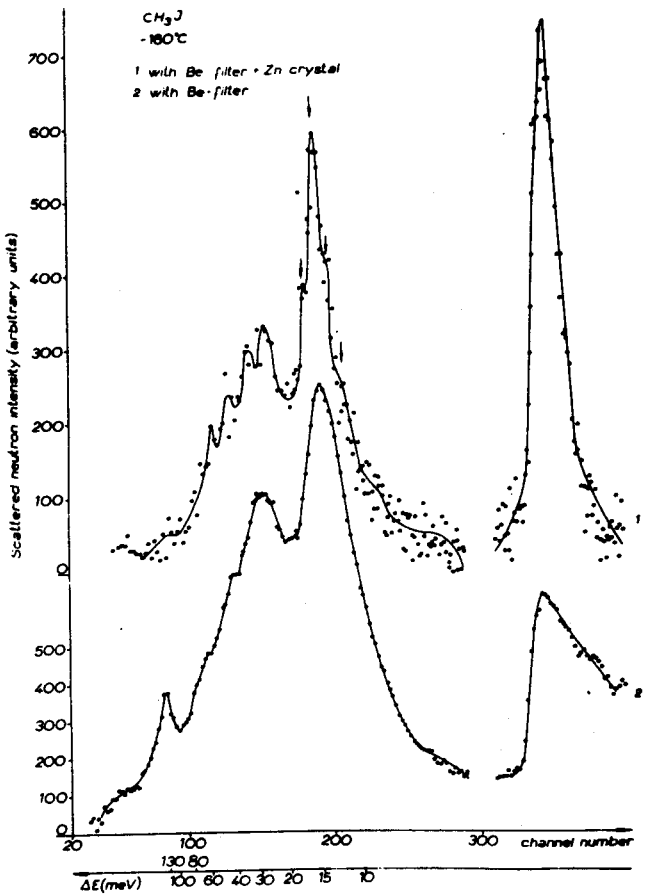


Fig. 3. The intensity of neutrons scattered from methyl iodide at $-160^{\circ}C$ as a function of the channel number. A comparison between the Be-filter technique and the Be-filter + Zn-monocrystal technique. Arrows indicate approximate positions of lattice vibration bands. Other explanations as in Fig. 1.