JAERI-M
5033

Energy Distributions of Neutrons Scattered from KHF_2, $(NH_4)_2SO_4$ and Polyethylene by Neutron Energy-Loss Method

October 1972

M. SAKAMOTO, M. IIZUMI, H. MOTOHASHI

日本原子力研究所
Japan Atomic Energy Research Institute

JAERI-M 5033

Energy Distributions of Neutrons Scattered from KHF_2, $(NH_4)_2SO_4$ and Polyethylene by Neutron Energy-Loss Method

Masanobu Sakamoto, Masashi Iizumi

and

Haruhiko Motohashi

Division of Physics, Tokai, JAERI

(Received October 24, 1972)

Energy distributions of neutrons scattered from KHF_2, $(NH_4)_2SO_4$ and polyethylene at room temperature have been measured over the range of energy transfer up to about 250 mev, using two-axis crystal spectrometer with beryllium-filter-detector in JRR-3 reactor. On KHF_2, the peak at 170 mev involves the contributions from the bending and antisymmetric stretching vibrations and the peak at 32 mev corresponds to the acoustical vibration. On $(NH_4)_2SO_4$ there are two peaks at 42 mev and 29 mev, which might be due to the torsional and translational motions of ammonium ions. The spectrum on polyethylene are discussed in relation to the frequency distributions of normal modes. Based on there results some of the improvements on the experimental set up are discussed.

JAERI—M 5033

KHF_2，$(NH_4)_2SO_4$，ポリエチレンによる散乱中性子のエネルギー分布：中性子エネルギー・ロス法による

日本原子力研究所東海研究所物理部
坂本正誠，飯泉　仁，本橋治彦

（1972年10月24日受理）

KHF_2，$(NH_4)_2SO_4$，ポリエチレンにより非弾性的に散乱された中性子のエネルギー分布を，JRR－3に設置した中性子回折装置に，ベリリウム，フイルターと組合せたカウンターをつけ，高い振動数レベルによる非弾性散乱中性子を測定した。測定は室温で行いエネルギー変換量で250mev位まで測定し，それぞれの物質の格子振動，分布振動の振動スペクトルに対応する散乱スペクトルが求められた。KHF_2については170mev のピークはベンデングと非対称ストレッチイング振動であり，32mevのピークは音響波振動に対応する。$(NH_4)_2SO_4$では43mevと29mevとに2つのピークがあり，それらはアンモニウム・イオンのトージョンとトランスレーション運動によるものである。ポリエチレンのスペクトルも振動数分布との関連で論じられている。これらの結果をもとに実験装置の改良できる点を検討した。

目　次　な　し

Energy Distributions of Neutrons Scattered from KHF_2, $(NH_4)_2SO_4$ and Polyethylene by Neutron Energy-Loss Method

Masanobu Sakamoto, Masashi Iizumi

and

Haruhiko Motohashi

1. Introduction

In order to observe the high energy level transitions by the neutron spectroscopy, it is more effective to use neutron energy-loss scattering with the excitation of molecular motions than to use neutron energy-gain processes. It is because at higher energy the population of the excited levels becomes so small that the scattering cross section for the neutron energy-gain with excitation of neutrons by molecular motions approaches to zero, but the cross section for the neutron energy-loss remains finite. These behaviors of the population factors are shown in Fig. 1. Nearly ten years ago Brockhouse et al.[1] have first designed the instrument utilizing the neutron energy-loss processes, which is known as the beryllium-filter-detector method in neutron spectro-

scopy. More recent developments of such instruments and performances have been reported by Collines et al.[2)]

2. Experiments

Fig. 2 shows schematically the instrument used in this experiment, which has been designed around the existing two-axis neutron diffractometer. Monoenergetic neutrons of energy E_o are selected from the reactor spectrum by the Bragg scattering from the single crystal monochromator. The monochromatic neutron beam then passes through a soller-slit and is scattered by the sample. Before the scattered neutrons enter the counter bank, they must pass through the beryllium filter which consists of six 25mm x 50mm blocks each 100mm long. They are interleaved with cadmium foils. For the beryllium filter with 100mm in length, a transmission factor of the neutrons whose energies below the beryllium cut off of 5 mev is 5.5×10^{-1}, but it is 1.2×10^{-4} for the neutrons with energies above 5 mev, where they have large cross sections due to the Bragg scattering. Therefore practically only those neutrons with energies less than 5 mev are transmitted by this filter, and are detected by BF_3 counter.

Neutrons after passing through the filter are counted by the counter bank for a fixed time or a fixed number of counts in the monitor counter. Their mean energy E^1 is about 3 mev, and thus the mean energy transfer is given by $E = E_o - E^1 = E_o$ - 3mev. The energy scan is performed by varying the energy of the incident monoenergetic beam, E_o, by changing the Bragg angle $2\theta_M$ by a predetermined increment.

In this experiment the energy distributions of the scattered neutrons have been measured at room temperature, on the powder sample of KHF_2, $(NH_4)_2SO_4$ and polyethylene (Sholex 6050). The scattering angles at the samples were kept at 75° for the former two samples and at 60° for the other. The monochromators used in this experiment were the copper single crystal with (111) plane for the measurements on the former two samples and the beryllium single crystal with (100) plane for polyethylene. The powder samples were mounted in flat aluminium containers with a sample thickness 0.46g/cm^2 for KHF_2, 0.14g/cm^2 and 0.06g/cm^2 for $(NH_4)_2SO_4$ and 0.05g/cm^2 for polyethylene.

3. Results and Discussions

3.1 KHF_2

Fig. 3 shows the spectrum of inelastically scattered neutrons from KHF_2 which has the symmetric linear F-H-F ions with the simplest hydrogen bonding. The peak observed at 1375cm^{-1} involve the contributions from the bending and antisymmetric stretching vibrations of the linear ions. The frequencies of their vibrations have been reported as 1240cm^{-1} (155 mev) and 1470cm^{-1} (184 mev) from the infrared spectroscopy.[3] The broad and single peak observed in this experiments is probably due to the widths of these bands and the instrumental resolutions. The symmetric stretching mode with the frequency of 600cm^{-1} has been observed in Raman spectroscopy[4),5] and also appeared only weakly in neutron spectroscopy.[2),6] The absence of this mode in Fig. 3 is attributed not only to the

insufficient neutron flux in the reactor, but also to the very small cross section for this mode, because it does not involve motions of hydrogen atoms. This may constitute a type of selection rule in neutron spectroscopy. The peak at 275cm^{-1} (32 mev) should be attributed to the acoustical vibrational mode. Similar peak has been early observed by Collines et al.[2)]

3.2 $(NH_4)_2SO_4$

The result for $(NH_4)_2SO_4$ obtained at room temperature is shown in Fig. 4. This compound has an orthorhmbic structure and undergoes a ferroelectric transition at 232°K. The neutron experiments for this compound have been reported by the several authors.[7),8),9)] In Fig. 4 there are two broad peaks at 340cm^{-1} (43 mev) and 235cm^{-1} (29 mev), which might be due to the torsional and translational motion of the ammonium ions. Rush and Taylor[8)] have observed in their neutron experiments with the time-of-flight spectrometer the single and broad peak at about 300cm^{-1} (38 mev) in room temperature and the two peaks at 335cm^{-1} (42 mev) and 200cm^{-1} (25 mev) in the ferroelectric phase at 172°K. The authors have explained that a shoulder on the low-energy side of the broad peak in room temperature indicates the overlapping of separated modes. The result in this experiments clearly shows the two peaks in room temperature and gives support to the explanation of Rush and Taylor. Peak at 630cm^{-1} (79 mev) might be due to the rotational mode as assigned by Blinc and Levstek[10)] from their infrared spectroscopy.

3.3 Polyethylene

There are many observations[11)~17)] of the low frequency modes in polyethylene by neutron spectroscopy, in order to study the effects of branching, crystallinity , conformations and so on. On the other hand the only investigation of the high frequency vibrations for polyethylene by the high energy neutron technique was reported by Whittemore,[18)] who derived the frequency distribution with the broad peaks centered at about 180 mev (1440cm^{-1}) and 370 mev (2960cm^{-1}). We have measured the energy distributions of neutrons scattered from the powder sample of the crystalline linear polyethylene, Sholex 6050, over the range of energy transfer 20 mev (160cm^{-1}) to 300 mev (2400cm^{-1}).

The results for polyethylene powder obtained at room temperature is shown in Fig. 5 where the backgrounds are subtracted. The vertical lines in Fig. 5 indicate the positions of the vibrational modes for polyethylene, which are quoted from the calculations by Tasumi and Shimanouchi.[19)] The spectrum shows the broad hump in low energy region below 30 mev (240cm^{-1}), corresponding to the peaks in the frequency distribution for torsional vibrations around CC bonds (ν_9) and partly for the longitudinal vibrations along the chain axis (ν_5). These peaks have been already observed by the time of flight neutron spectrometry.[11),13)~17)] The ν_5 has the maximum energy at about 70 mev (560cm^{-1}) which is possibly corresponding to the small hump with the shoulder at about 80 mev in the spectrum. In the energy range up to 300 mev (2400cm^{-1}) from about 80 mev (640cm^{-1}) many peaks appear in

the spectrum and are attributed to some of the CH_2 rocking and twisting vibrations (ν_7 and ν_8), the CC streching mode (ν_3), the skeletal stretching mode (ν_4) and the CH_2 bending mode (ν_2). These peaks also correspond to the broad peak at 180 mev (1440 cm^{-1}), reported by Whittemore.[18] The distributions of scattered neutrons, observed between 30 mev (240 cm^{-1}) and 60 mev (480 cm^{-1}) are quite likely due to multiple phonon scatterings and to additional vibrational modes in disordered structure .

4. Final Remarks

We have shown that, even in the reactor JRR-3 with the thermal neutron flux 10^{13} n/cm^2sec, it is possible to observe the useful spectra in the energy range up to about 300 mev (2400 cm^{-1}), by means of the beryllium-filter-detector method. The resolution for this method is not as high as that for the optical method, but the relatively simple selection rule for neutron spectroscopy constitute the complementary situations to those in infrared and Raman spectroscopy.

There is another instrumental setup using the beryllium-filter-detector, in which the pulsed-white-neutron and the time-of-flight technique are used instead of the single crystal monochromator described in this report. It is interesting to compare the resolutions of the present setup with that of the pulsed-neutron setup. The energy resolutions for the former setup can be estimated by $(\Delta E/E)_c = 2\cot\theta_M\Delta\theta_M$, and for the latter it is $(\Delta E/E)_p = 2\Delta t/Lt_o$, where Δt, L and t_o are the time width of the pulsed neutron, the flight path (meter) and

the time of flight of neutrons per 1 meter. Taking $\theta_M = 9.5°$ using Be (100) plane for neutrons with energy 200 mev and $\Delta\theta_M = 0.5°$, then we have $(\Delta E/E)_c = 0.10$ for the single crystal setup. Similarly if we take L = 10 m, $t_o = 161.68$ μsec/m for neutrons of 200 mev and $\Delta t = 50$ μsec for the pulsed-neutron setup, we obtain $(\Delta E/E)_p = 0.07$. However they should be practically comparable, because there are many uncertainties in the numerical figures used in these estimations.

In order to obtain much higher intersities and better resolutions, there are some of the improvements on our setup, which are:

(1) Since the inelastic scattering cross sections are reduced at low temperature, the intensities increase by cooling the beryllium filter, effectively for low energy neutrons.

(2) It is possible to use a counter system which presents a much larger solid angle to the scattering sample.

(3) By using a crystal plane with a much smaller lattice spacing for the monochromator, for example Be (1231), (2242) or Ge (331), the resolution can be improved.

(4) Similarly the use of a better collimations for the monochromator makes the resolutions better.

With these improvements accompanied with the reduction of background noise more detailed studies of transitions with high energies would be quite feasible.

Reference

1) A.D.B. Woods, B.N. Brockhouse, M. Sakamoto and R.N. Sinclair: Inelastic Scattering of Neutrons in Solids and Liquids (IAEA, Vienna, 1961) p.487.

2) M.F. Collins, B.C. Haywood and G.C. Stirling: J. chem. Phys. 52 (1970) 1828.

3) J.A.A. Ketelaar and W. Vedder: J. chem. Phys. 19 (1951) 654.

4) L. Couture and J.P. Mathieu: Compt. Rend. 228 (1949) 555.

5) L. Couture and J.P. Mathieu: Compt. Rend. 230 (1950) 1054.

6) H. Boutine, G.J. Safford and V. Brajovic: J. chem. Phys. 39 (1963) 3135.

7) U. Dahlborg, K.E. Larsson and E. Pirkmajer: Physica 49 (1970) 1.

8) J.J. Rush and T.I. Taylor: Inelastic Scattering of Neutrons (IAEA, Vienna 1965) Vol. 2, p.333.

9) A. Bajorek, T.A. Machechina and K. Parlinski: Inelastic Scattering of Neutrons (IAEA, Vienna, 1965) Vol. 2, p.355.

10) R. Blinc and I. Levstek: J. Phys. chem. Solids 12 (1960) 295.

11) H.R. Danner, G.J. Safford, H. Boutin and M. Berger: J. chem. Phys. 40 (1964) 1417.

12) W. Myers, G.C. Summerfield and J.S. King: J. chem. Phys. 44 (1966) 184.

13) S.F. Trevino: J. chem. Phys. 45 (1966) 757.

14) W.R. Myers and P.D. Randolph: 49 (1968) 1043.

15) K. Doi, M. Sakamoto, M. Iizumi and N. Masaki: JAERI 1197 (1970) 109.

16) M. Sakamoto, K. Doi, M. Iizumi, N. Masaki, H. Motohashi, I. Kuriyama and O. Yoda: Rep. Progr. Polymer Phys. Japan 14 (1971) 167.

17) H. Berghmans, G.J. Safford and P.S. Leung: J. Polymer Sci. Part A-2. 9 (1971) 1219.

18) W.L. Whittemore: Nucl. Sci. Eng. 24 (1966) 394.

19) M. Tasumi and T. Shimanouchi: J. chem. Phys. 43 (1965) 1245.

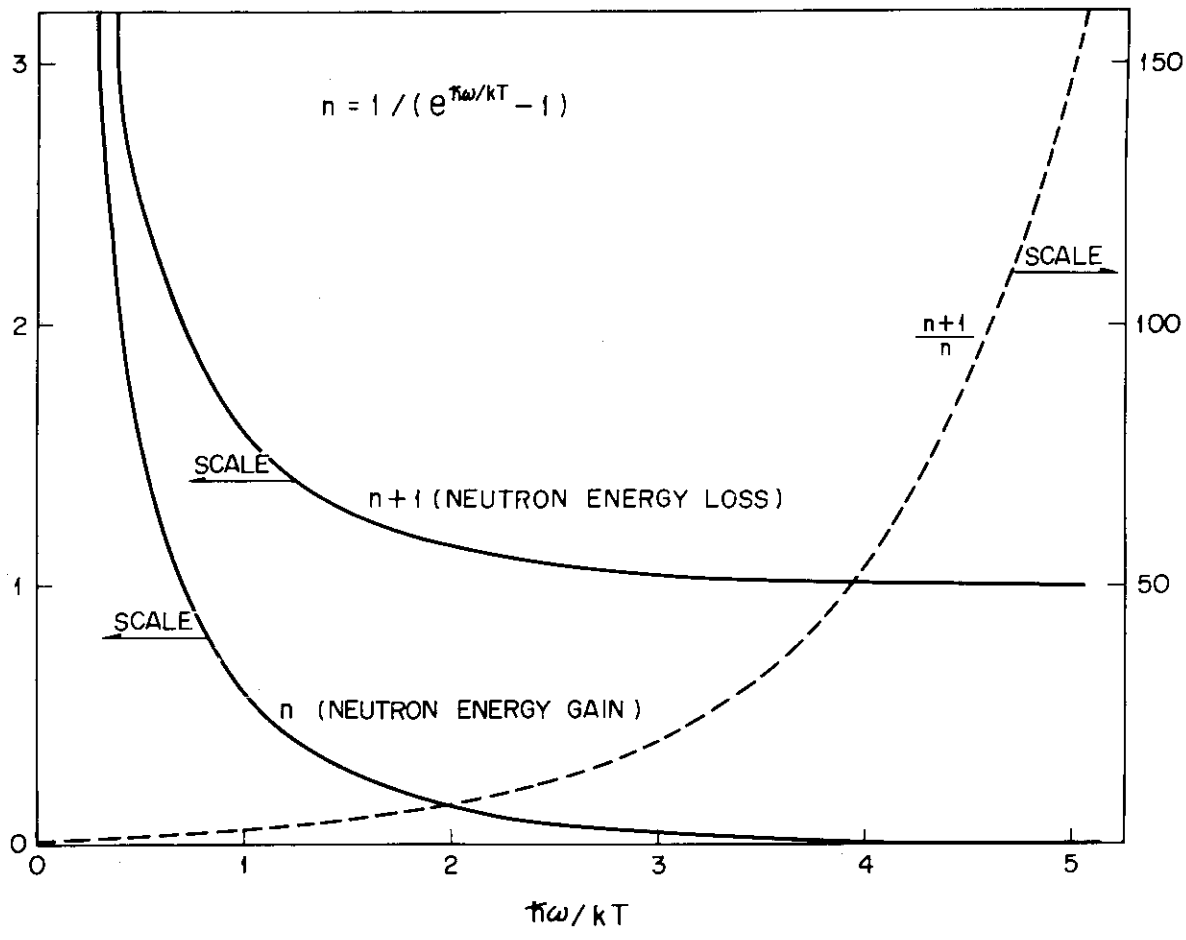

Fig. 1 The population factors as a function of hω/kT

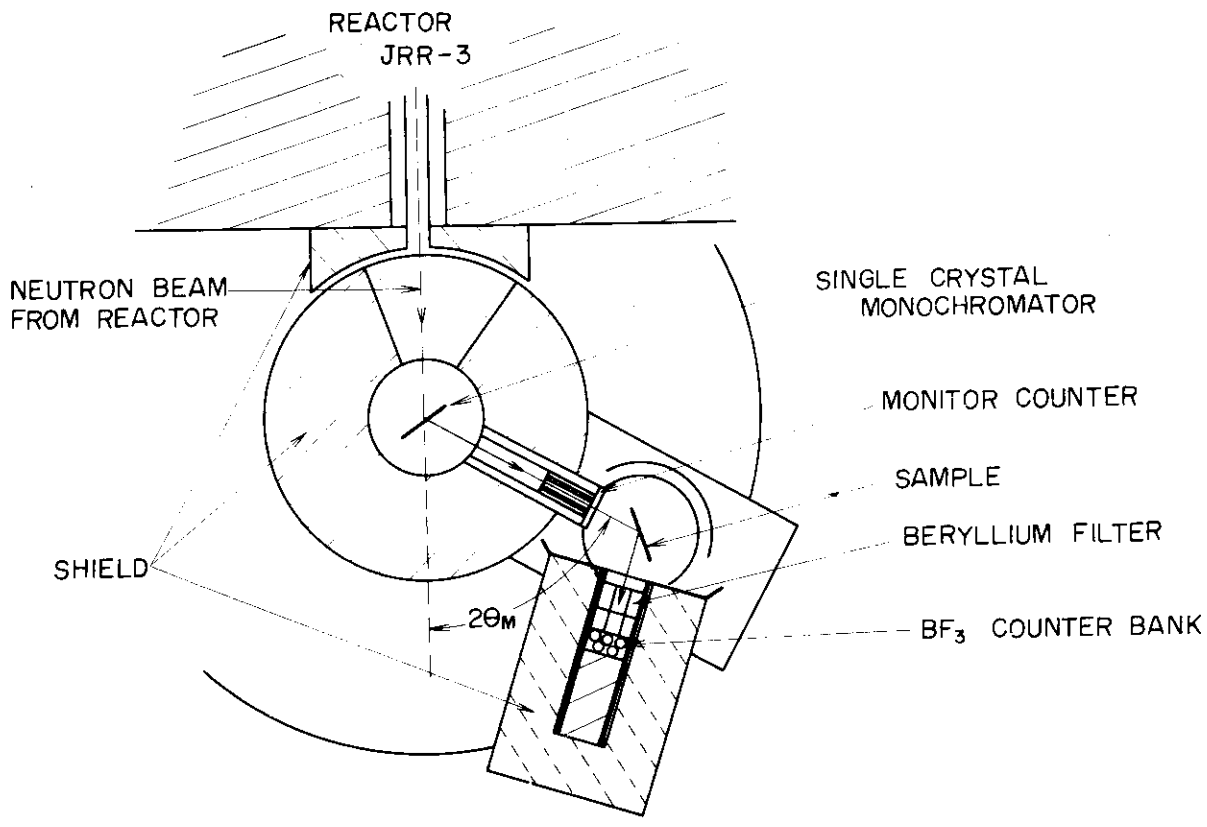

Fig. 2 The two-axis crystal spectrometer with the beryllium-filter-detector.

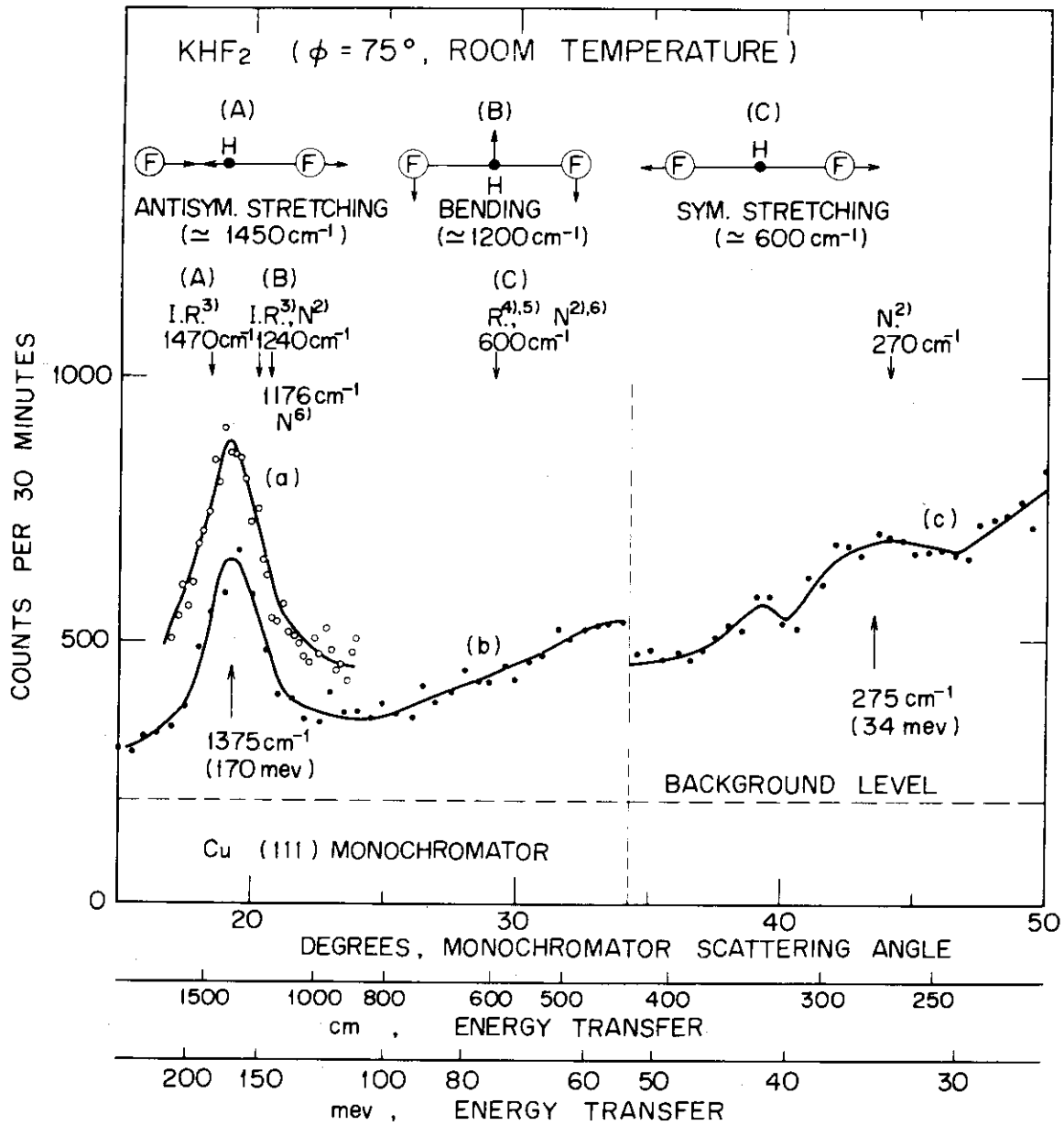

Fig. 3 Distributions of neutrons scattered by KHF_2 and a schematic representation of the motions of F-H-F ion. The three curves, (a), (b) and (c), were obtained in the slightly different conditions of the electronics for detection of neutrons.

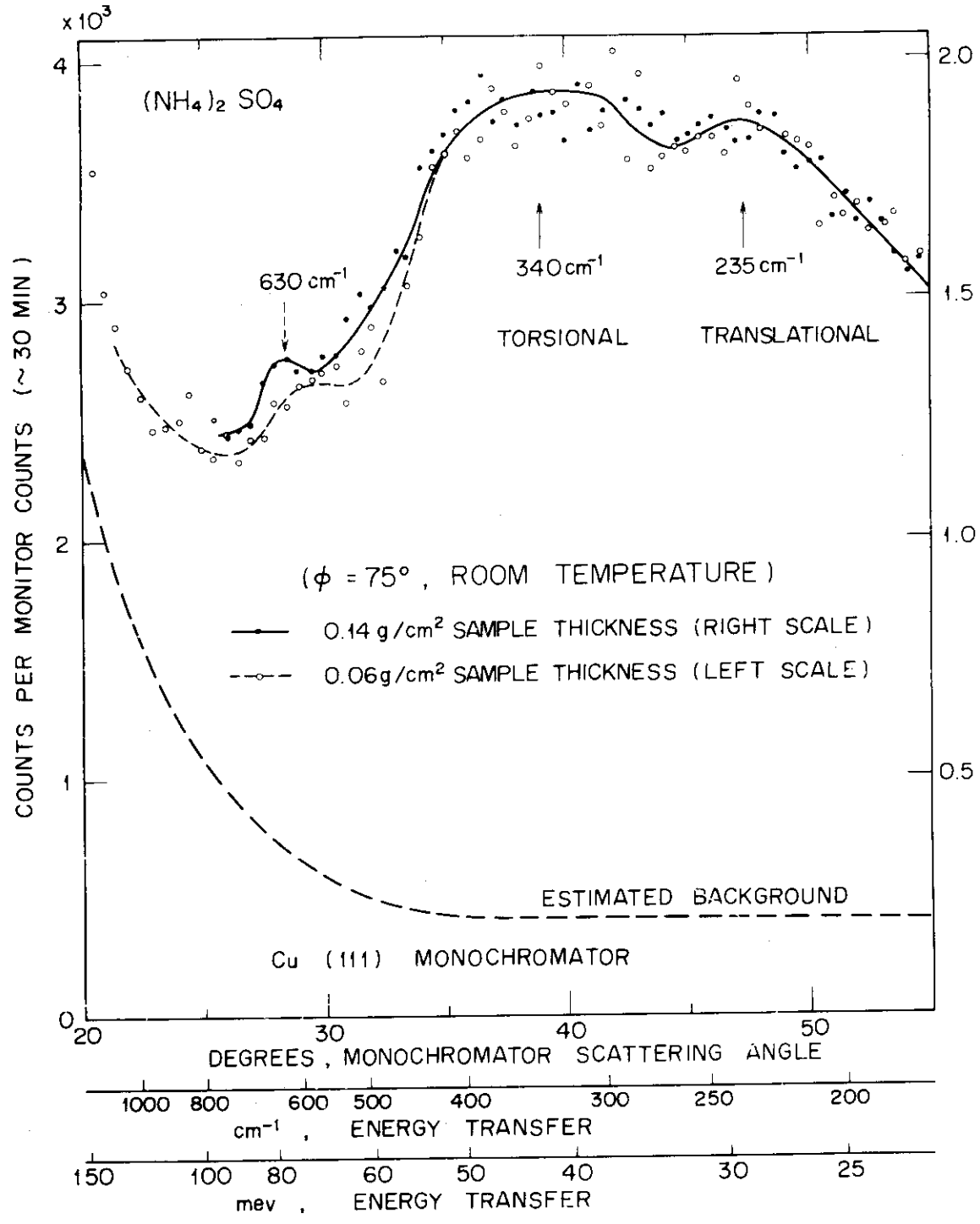

Fig. 4 Distributions of neutrons scattered by $(NH_4)_2SO_4$.

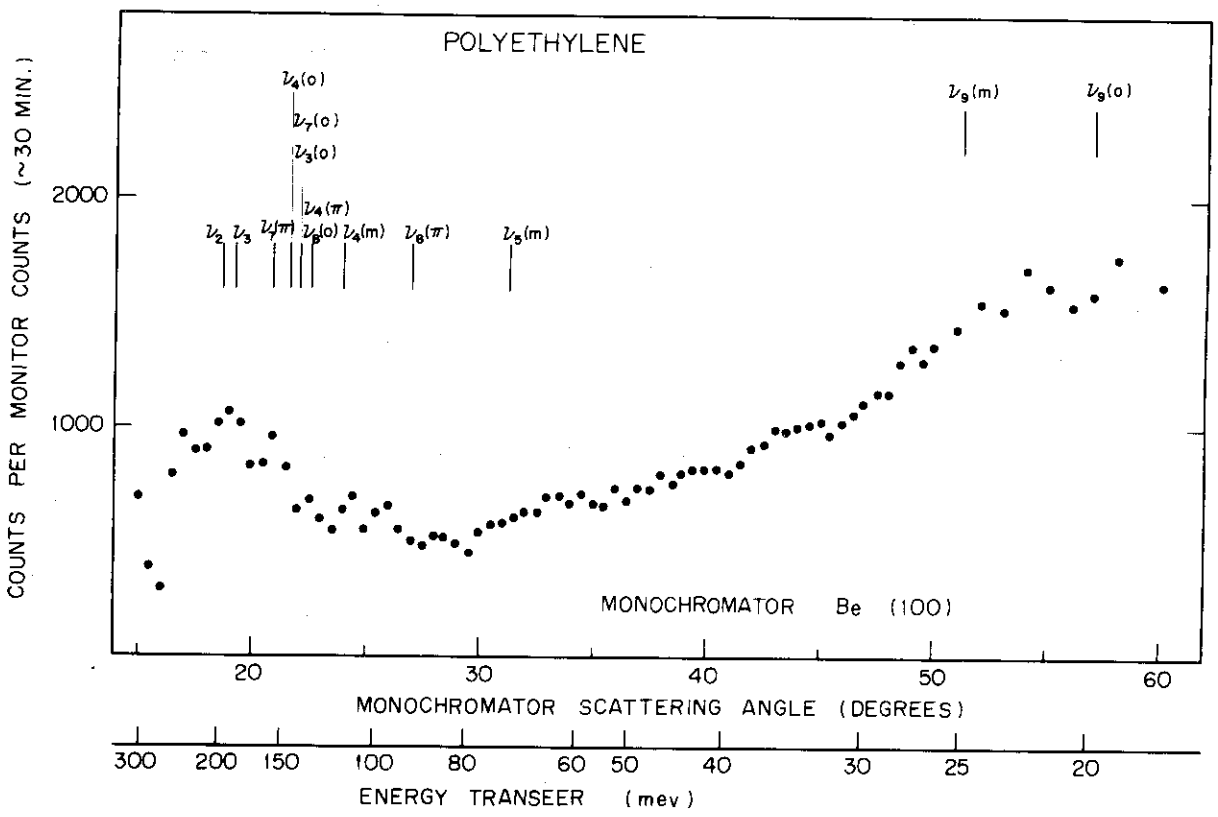

Fig. 5 Distributions of neutrons scattered by polyethylene powder.