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Dynamics of Liquid CH_4 from Cold-Neutron Scattering

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The scattering of 4.1 Å neutrons by liquid CH_4 at 98°K has been studied at several angles using a rotating-crystal spectrometer. The spectra at all angles show a broad inelastic hump associated primarily with the rotational motions and a quasi-elastic peak which is related to the translational motions. The width of the quasi-elastic peak follows the simple diffusion behavior over almost the entire range of present experiments, and leads to a value of 2.2×10^{-5} cm^2/sec for the diffusion coefficient. A more detailed analysis suggests that the delay time in the onset of simple diffusion behavior is similar to that in argon. The data clearly show that if the translations are viewed in terms of the Langevin model, then it is not necessary to consider a wavelength-dependent damping factor such as has been recently proposed by Griffing. High-resolution data taken at 15° scattering angle do not reveal any sharp inelastic peaks, which should be present if the rotations are free. From this it is concluded that the rotations are hindered in the liquid state, in accord with earlier spectroscopic work, but in disagreement with the neutron work of Hautecler and Stiller. Calculations based on a model in which the rotations are free and the translations follow the simple diffusion model show poor agreement with experiments. Consideration of a more realistic model for the translations, based on the results of the computer experiments of Nijboer and Rahman for argon, yields only a slight improvement. It is suggested that a proper treatment of the hindered rotations is necessary to obtain agreement with experiment.

I. INTRODUCTION

THE scattering of slow neutrons by liquid methane has been the subject of several investigations both from experimental[1–6] and theoretical[4,7] points of view. It is well known that methane is a spherical-top molecule and that the intermolecular forces are relatively weak. These properties suggest (i) that molecular rotation might be free in the liquid state as it is in the gaseous state, and (ii) that the translational motions may be similar to those in liquids like argon. With a proper choice of incident-neutron energy, it is possible to use the neutron-scattering technique to study both rotational and translational motions.

The rotational motions in liquid methane have been investigated earlier by Raman scattering[8] and infrared absorption[9] experiments. These measurements do not show any evidence of discrete rotational levels and it was concluded that while the higher rotational levels are essentially free, the lower ones may be hindered. A number of neutron-scattering investigations of the rotational motions have also been reported. The first measurements were those of Hautecler and Stiller[1] who used a beryllium detector spectrometer and concluded that they could actually observe transitions between rotational levels as steps in the scattered-neutron spectrum. Later measurements of Harker and Brugger,[2] and Whittemore[3] were performed with poorer resolution and were not designed to look for the existence of discrete rotational levels. Harker and Brugger's general conclusion, however, was that the rotational motions are rather similar to those in the gaseous state when examined under conditions of *large momentum transfer.* More recently, Janik *et al.*,[5] and Otnes[6] have studied cold-neutron scattering from liquid methane, but in view of the fact that the entire beryllium-filtered spectrum was used as the incident beam, these measurements are not sufficiently informative as to the possible existence of discrete rotational levels in the liquid state. Thus the situation regarding the state of rotational motion in liquid methane does not seem quite clear.

In order to clarify the situation with regard to the rotations and also in order to obtain information about translational motions, some measurements were performed in this laboratory using cold neutrons and a line input spectrum.[4] These measurements have now been repeated with greater statistical accuracy and further extended to several other scattering angles, especially in the forward direction, where data have been obtained with high resolution. This paper describes the results of these investigations. The following section gives a brief account of the general theoretical considerations involved in the scattering of neutrons by liquid methane and also discusses a specific model in which the rotations of the molecule are regarded as *completely free*, and the translations are assumed to be describable by simple diffusion. Section III contains a description of the apparatus and experimental observations. A discussion of the latter in relation to the model described in Sec. II and other models is presented in Sec. IV following which, finally, there is a summary.

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[1] S. Hautecler and H. Stiller, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 423.

[2] Y. D. Harker and R. M. Brugger, J. Chem. Phys. **42**, 275 (1965).

[3] W. L. Whittemore, Nucl. Sci. Eng. **18**, 182 (1964).

[4] B. A. Dasannacharya, G. Venkataraman, and K. Usha Deniz, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1965), Vol. 2, p. 157.

[5] J. A. Janik, J. M. Janik, J. Mellor, and H. Palevsky, J. Phys. Chem. Solids **25**, 1091 (1964).

[6] K. Otnes (private communication).

[7] G. W. Griffing, J. Chem. Phys. **43**, 3328 (1965).

[8] M. F. Crawford, H. L. Welsh, and J. H. Harold, Can. J. Phys. **30**, 81 (1952).

[9] G. E. Ewing, J. Chem. Phys. **40**, 179 (1964).

II. THEORETICAL CONSIDERATIONS

The scattering of neutrons by methane consists predominantly of incoherent scattering from the protons. Interference effects within a molecule as well as effects connected with the correlated motion of different molecules will, therefore, be neglected in the following treatment.

When slow neutrons are scattered by a molecular system they exchange energy with the vibrational, rotational, and translational modes of the system. Assuming that vibrations, rotations, and translations do not interact with each other, the partial differential cross section per proton for incoherent scattering can be written as[10–12]

$$\frac{d^2\sigma_{\rm inc}}{d\Omega dE}=\frac{a_p^2}{2\pi\hbar}\frac{k}{k_0}\int e^{-i\omega t}I_V(Q,t)I_R(Q,t)I_T(Q,t)dt\,, \qquad (1)$$

where a_p is the bound incoherent-scattering amplitude for the proton, $\mathbf{k}_0$ and $\mathbf{k}$ denote the incident- and scattered-neutron wave vectors, $\mathbf{Q}=\mathbf{k}-\mathbf{k}_0$ is the wave-vector transfer, and $\hbar\omega=(\hbar^2/2m)(k^2-k_0^2)$ is the energy transfer. The quantities I_V, I_R, and I_T represent the intermediate scattering functions for the vibrational, rotational, and translational modes of motion, respectively. Following the customary practice, we shall assume that the internal vibrations of the CH$_4$ molecule are not excited either thermally or by the neutron. We then have[12,13]

$$I_V(Q,t)\approx\exp(-Q^2\gamma)\,, \qquad (2)$$

the quantity on the right-hand side being the Debye-Waller factor associated with the zero-point vibrations of the proton. Let us denote by $S_R(Q,\omega)$ and $S_T(Q,\omega)$ the Fourier transforms over time of $I_R(Q,t)$ and $I_T(Q,t)$:

$$S_R(Q,\omega)=\frac{1}{2\pi}\int e^{-i\omega t}I_R(Q,t)dt\,, \qquad (3a)$$

$$S_T(Q,\omega)=\frac{1}{2\pi}\int e^{-i\omega t}I_T(Q,t)dt\,. \qquad (3b)$$

We then obtain for the differential cross section the result

$$\frac{d^2\sigma_{\rm inc}}{d\Omega dE}=\frac{a_p^2}{\hbar}\frac{k}{k_0}e^{-Q^2\gamma}\int d\omega' S_R(Q,\,\omega-\omega')S_T(Q,\omega')\,. \qquad (4)$$

The rotational part of the inelastic scattering will thus be modified by the translations, and the extent of the modifications is important in determining the ultimate shape of the spectrum. For example, one can show using the appropriate expressions for I_R and I_T that the rotational peaks in the energy distribution of neutrons scattered by gaseous methane at room temperature are so much broadened because of translation that they cannot be seen separately even with ideal resolution, if the usually available neutron wavelengths and scattering angles are used.[12,14] To see whether it will be possible to observe the discrete rotational levels in the liquid state, if they exist, we consider a model in which the rotations are *completely free*, and the translations are described by a simple diffusion model. The latter is a fairly reasonable assumption for our present purposes especially when one remembers that the forces in methane are weak van der Waal-type forces between spherical-top molecules. Using $I_R(Q,t)$ and $I_T(Q,t)$ appropriate to these assumptions and ignoring any possible nuclear-spin correlations,[15] the partial differential cross section can be shown to be given by (for details see Ref. 4)

$$\frac{d^2\sigma_{\rm inc}}{d\Omega dE}=\frac{a_p^2}{2\pi\hbar}\frac{k}{k_0}e^{-Q^2\gamma}\sum_{jJ}\left[\frac{2DQ^2}{(DQ^2)^2+[(\epsilon-\beta)/\hbar]^2}\right.$$
$$\left.\times\exp\left(-\frac{\epsilon-\beta}{2k_BT}\right)\right]\frac{2J+1}{2j+1}B_j(T)\sum_{n=|j-J|}^{j+J}j_n^2(Qb_p)\,. \qquad (5)$$

Here D is the diffusion coefficient, and j, J are the initial and final rotational quantum numbers, respectively; j_n is the spherical Bessel function of order n and b_p is the C-H bond length. Further,

$$\beta=(\hbar^2/2I)[j(j+1)-J(J+1)]\,, \qquad (6)$$

with I the moment of inertia of the molecule. The quantity $B_j(T)$ is the population factor and is given by

$$B_j(T)=\frac{(2j+1)^2\exp[-\hbar^2j(j+1)/2Ik_BT]}{\sum_j(2j+1)^2\exp[-\hbar^2j(j+1)/2Ik_BT]}\,. \qquad (7)$$

From Eqs. (5) and (6) we see that the scattered spectrum consists of a series of Lorentzians, one located at the incident energy and others at energies corresponding to the various rotational transitions. All peaks are diffusion broadened and the width $2\hbar DQ^2$ is governed by the momentum transfer involved. Clearly, therefore, the rotational structure, if any, is best examined under conditions of small momentum transfer. This is, in fact, quite general and independent of the type of model assumed for the translational motions.

It may also be pointed out here that if the rotations

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[10] A. C. Zemach and R. J. Glauber, Phys. Rev. **106**, 290 (1957).

[11] A. Rahman, J. Nucl. Energy **A13**, 128 (1961).

[12] G. W. Griffing, Phys. Rev. **124**, 1489 (1961).

[13] T. J. Kreiger and M. J. Nelkin, Phys. Rev. **106**, 290 (1957).

[14] G. Venkataraman, K. R. Rao, B. A. Dasannacharya, and P. K. Dayanidhi, Proc. Phys. Soc. (London) **89**, 379 (1966).

[15] The effect of nuclear spin correlations has been discussed in detail by S. K. Sinha and G. Venkataraman [Phys. Rev. **149**, 1 (1966)]. They show that the effect is important only in situations where the rotational peaks can be clearly resolved. The formulas for the scattering in such cases are very complicated. The effects of spin correlations may, however, be taken into account qualitatively by considering the appropriate weights for the rotation levels.

are *hindered,* the effect will be to broaden out the rotational peaks. Since in any case they are smeared out at large Q, one can as a first approximation use $I_R(Q,t)$ of the free rotator in place of that for the hindered rotator for describing the scattered-neutron spectra at large momentum transfers.

III. APPARATUS AND EXPERIMENTAL DETAILS

All the measurements were carried out using the rotating crystal spectrometer at the CIRUS, Trombay. This spectrometer gives bursts of neutrons of wavelength 4.1 Å (4.87 MeV) at the rate of 16 000 bursts per minute. The monochromatic bursts are produced by Bragg-reflecting beryllium filtered neutrons off the (111) planes of an aluminium single crystal spinning at 8000 rpm. The sample is placed at a distance of ~65 cm from the center of the rotating crystal. The neutrons after scattering are detected in a set of six BF_3 counters at the end of a 3-m flight path. The counters are filled at a pressure of 60 cm of mercury with BF_3 gas enriched to 90% in B^{10}. The counters are 5 cm in diameter and 45 cm long and cover a total horizontal span of ~6.5°. The detector bank together with its shielding is mounted on a trolley on rails and the scattering angle can be varied continuously over the range 0–100°. The spectra are recorded in a 100-channel time analyzer, usually with 32-μsec channel width, which can be changed to 8 or 16 μsec when required. The resolution (full width at half-maximum at incident energy) of the spectrometer is roughly 0.4 MeV, but depends on the angle of scattering and the shape of the sample. (This is discussed in detail later.) The resolution can be improved by about a factor of 2 by introducing a Soller collimator between the rotating crystal and the sample.

The measurements were performed with a 1-mm-thick sample at 98°K in transmission geometry. The sample[16] was contained in an aluminum container with 0.75-mm wall thickness. The time-of-flight distributions were taken at 12 angles of scattering between 15° and 90°, the low-angle (15° and $22\frac{1}{2}$°) measurements being performed with higher resolution. Some typical distributions are shown in Fig. 1 after corrections for the container contribution (which was very small), air scattering, and variation of detector efficiency with energy. The distributions shown are on an arbitrary scale and are not normalized to each other in any way. A normal feature of all the distributions is a broad inelastic spectrum with an overriding quasi-elastic spectrum. In the following section, we shall give a discussion of these two regions of the spectra separately.

In order to get reliable values for the widths of the quasi-elastic peaks, it is important to know the resolution of the spectrometer accurately at each of the scattering angles. This was measured by wrapping the empty sample holder with a thin sheet of polythene and observing the distribution of elastically scattered neutrons. Fig. 2 shows the observed full width at

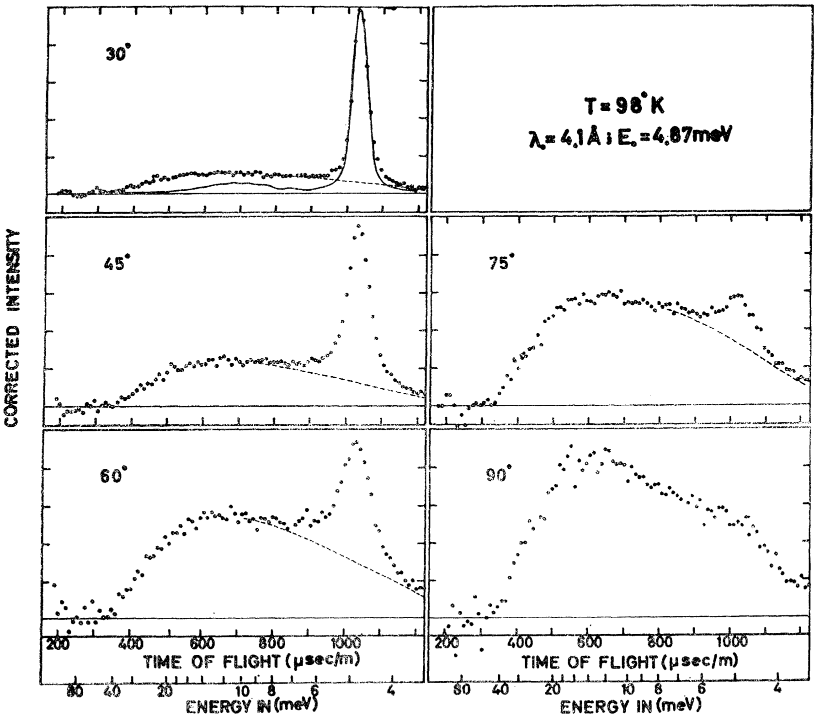

FIG. 1. Time-of-flight spectra obtained on scattering 4.1 Å neutrons by liquid methane at 98°K. The solid curve shown along with the 30° pattern is calculated according to Eq. (5) with $D=2.2\times10^{-5}$ cm²/sec, and broadened with experimentally measured resolution. The theoretical and the observed distributions have been normalized at the quasi-elastic peak. The dashed lines denote the inelastic background subtracted in order to isolate the quasi-elastic scattering.

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[16] C. P. grade methane gas supplied by Matheson Gas Company was used in the experiments.

half-maximum (FWHM) of these distributions as a function of scattering angle. It can be seen that the time-of-flight resolution varies from ~35 μsec/m (~3.5×10^{-4} eV) to ~55 μsec/m (~5×10^{-4} eV) as the scattering angle varies from 30° to 90°. The measurements at 15° and $22\frac{1}{2}$° were performed with a higher resolution of 2×10^{-4} eV.

IV. DISCUSSION

As already remarked, almost all the observed spectra show a distinct quasi-elastic peak and a broad inelastic hump. The quasi-elastic peak essentially gives information about the long-time translational behavior, while the inelastic part gives information about the rotations and also the short-time translational motions. In a proper discussion of the observed results, one must treat both regions together. It is, however, often convenient to consider them separately, and accordingly we shall first discuss the results for quasi-elastic scattering.

A. Quasi-Elastic Scattering

The quantity of interest here is the full width at half-maximum of the quasi-elastic peak and its variation with Q_0 [$=4\pi\sin(\frac{1}{2}\phi)/\lambda_0$, where ϕ is the scattering angle and λ_0 the incident wavelength]. In order to derive the width, one must first have some procedure for subtracting the inelastic background under the quasi-elastic peaks. This, in fact, proves to be one of the major difficulties in evaluating the widths. There is no rigorous method and approximate procedures must be employed. Larsson and Dahlborg[17] discuss this in detail for a filter-chopper setup. In our case perhaps the situation is somewhat simpler in view of the symmetrical nature of the ingoing spectrum. We have interpolated the inelastic background under the quasi-elastic peak by drawing a smooth curve (shown as dashed lines in Fig. 1) between the two wings. The lines are, of course, somewhat arbitrary. The quasi-elastic peaks derived after subtracting the inelastic contribution found in the above manner are assumed to be the result of a convolution of a Lorentzian distribution with a Gaussian resolution function The true widths are extracted using this assumption and the measured resolution widths. The widths obtained in this manner are plotted against Q_0^2 in Fig. 3. The error bars are based on counting statistics alone. In the simple diffusion model, the width should increase linearly with Q_0^2 with a slope of $2\hbar D$.[18] Our data in fact show such a behavior (with the possible exception of the last point which, however, is subject to large errors) and this in some measure lends support to our assumption of the simple diffusion model for I_T in Sec. II. The value of D derived by fitting a straight line [curve (b) of Fig. 3] to the first seven points is 2.2×10^{-5} cm²/sec. This is to be compared with the value of 2.7×10^{-5} cm²/sec obtained from macroscopic measurements.[19]

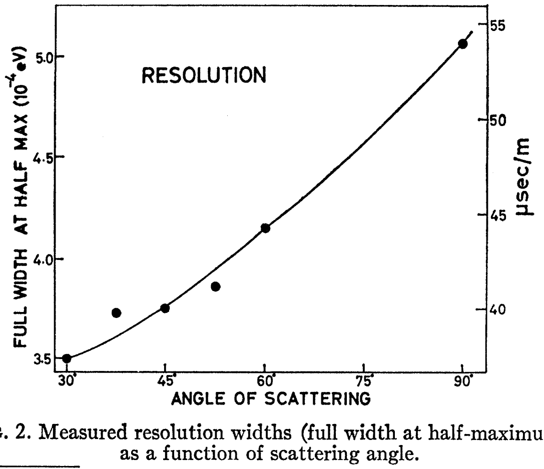

FIG. 2. Measured resolution widths (full width at half-maximum) as a function of scattering angle.

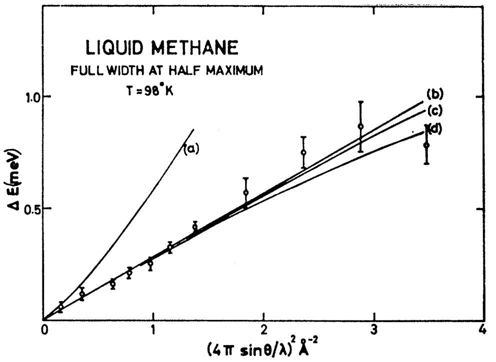

FIG. 3. Width of the quasi-elastic peak (after correcting for instrumental resolution) as a function of $Q_0=4\pi(\sin\frac{1}{2}\phi)/\lambda_0$. The solid curves are theoretical curves based on various models discussed in the text. (a) Griffing's model with Q-dependent damping constant; (b) simple diffusion model with $D=2.2\times10^{-5}$ cm²/sec; (c) and (d) Egelstaff's model with $c=0.5\times10^{-12}$ and 1×10^{-12} sec, respectively.

Although the simple diffusion model is able to explain our quasi-elastic data fairly well, we know that the model cannot completely describe any physical system especially for short times.[18] It is, therefore, useful to examine whether our data can be understood in terms of more detailed models. For this purpose we first consider a model due to Egelstaff[20] in which $I_T(Q,t)$ has the form

$$I_T(Q,t)=\exp\{-Q^2D[(y^2+c^2)^{1/2}-c]\}, \tag{8}$$

where y is a complex time which in the classical approximation becomes equal to real time t and c is a "characteristic time" of the liquid related to the delay in the onset of the simple diffusion behavior. Analysis of the

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[17] K. E. Larsson and U. Dahlborg, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 318.

[18] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

[19] J. Naghizadeh and S. A. Rice, J. Chem. Phys. **36**, 2710 (1962).

[20] P. A. Egelstaff, Advan. Phys. **11**, 203 (1962).

results for water and a few other liquids suggests that "delay time" is between 2–5 times larger than c. The curves (c) and (d) in Fig. 3 show the behavior of the quasi-elastic width for $c=0.5\times10^{-12}$ and 1×10^{-12} sec, respectively. Comparison with experiment suggests that c should be less than 0.5×10^{-12} sec. This is of the same order of magnitude as the value one would obtain for liquid argon using the delay time of 1×10^{-12} sec quoted by Dasannacharya and Rao.[21]

We next consider a model proposed recently by Griffing[7] in order to explain the results of Harker and Brugger[2] and some of our preliminary results.[4] Griffing assumes that the diffusion process in liquid methane can be described by Langevin's equation and, following Vineyard,[18] writes $I_T(Q,t)$ as

$$I_T(Q,t)=\exp\left[-\frac{i\hbar Q^2}{2M\eta}\phi(\eta t)-\frac{Q^2k_BT}{2M\eta^2}\phi^2(\eta t)-\frac{Q^2}{2}X(t)\right], \quad (9)$$

where

$$\phi(x)=(1-e^{-x})$$

and

$$X(t)=\frac{2k_BT}{M\eta}\left[t-\frac{2}{\eta}\phi(\eta t)+\frac{\phi(2\eta t)}{2\eta}\right].$$

The quantity η is the damping constant which occurs in the Langevin equation and is related to D by the expression

$$\eta=k_BT/MD \quad (10)$$

with M the mass of the molecule. Using this model for the translational motions, Griffing tried to fit our earlier data[4] for 30° scattering angle and the data of Harker and Brugger obtained at three different angles using incident neutrons of energy ~25 MeV and higher. Since the use of η given by Eq. (10) did not give proper fits, Griffing considered a Q-dependent η in Eq. (9), the dependence being given by

$$\eta(Q)=\eta(0)\exp(-\lambda Q), \quad (11)$$

where $\eta(0)$ is defined by Eq. (10). Using Eq. (11) and a value of 0.657 Å for λ, Griffing was able to obtain agreement with experiment. We believe that it is not necessary to consider a Q-dependent η for methane if one takes proper account of resolution effects which are extremely important in the region of the quasi-elastic peak. For example, let us consider the first point in Fig. 6 of Griffing's paper in which $\eta(Q)$ is plotted against Q. This point, derived by fitting to our earlier results at the 30° scattering angle, corresponds to a wave-vector transfer of 0.8 $Å^{-1}$. The actual quasi-elastic width here is ~0.18 MeV as compared to a resolution width of 0.35 MeV (see our Figs. 2 and 3). Similarly for the third point (in Griffing's figure) at $Q=1.56$ $Å^{-1}$ derived from Harker and Brugger's measurements, the true width is ~0.75 MeV (see our Fig. 2), compared to the resolution of ~2 MeV employed by Harker and Brugger. With such large resolution widths involved, the necessity of taking proper account of them while fitting the data is clear. This is further confirmed by actually computing the quasi-elastic widths using Eqs. (9) and (11). If we use Griffing's value for λ, and the value of 2.3×10^{13} sec^{-1} for η as derived from $D=2.2\times10^{-5}$ cm^2/sec, we find the quasi-elastic width to be given by the curve (a) in Fig. 3 which evidently yields values much in excess of those obtained experimentally. On the other hand, if we use a constant value of $\eta=2.3\times10^{13}$ sec^{-1}, the calculations give good agreement[22] For the sake of completeness we might mention that the widths obtained by considering only the energy-loss side of the data without any corrections for inelastic scattering[4] yield values which are not more than 20% above those quoted in Fig. 3. Even these, which are the upper limits to the quasi-elastic widths, are much lower than those predicted by Griffing's model. Clearly therefore, the Q dependence of η, if any, should be rather weak.

It is noteworthy that our results for the quasi-elastic widths can be understood on the basis of three different models, all of which seem reasonable. This serves to emphasize the difficulty in distinguishing between the validity of the different models on the basis of quasi-elastic data alone, unless the data are of very high accuracy. It is, in fact, necessary to consider the shape of the over-all spectrum as we shall see later.

B. Inelastic Scattering

As indicated earlier, the primary interest in the inelastic spectrum is to find whether discrete rotational levels exist in liquid methane in the same sense as they do in the gas. From our preliminary measurements,[4] we had concluded that they do not. This conclusion was based on a comparison of the observed spectrum at 30° with that computed according to the model described in Sec. II. The computed spectrum was not folded with instrumental resolution function; but, from qualitative considerations about resolution broadening, it was felt that it should be possible to see at least some transitions between lower levels. Since then, calculations have been made taking proper account of resolution effects, and the results for 30° are shown by the full line in Fig. 1. It is seen that with our resolution at 30°, it is not possible to answer categorically the question regarding the existance of discrete peaks in the scattered spectrum. Calculations were then made for a scattering angle of 15° and corresponding to an improved resolution (FWHM=0.2 MeV). The result is shown as an inset in Fig. 4 and it is clear that peaks, if

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[21] B. A. Dasannacharya and K. R. Rao, Phys. Rev. **137**, A417 (1965).

[22] In passing it may be noted that these objections are not applicable to the fits made by Griffing to half-width curves of other substances using $D(Q)=D(0)e^{-\lambda Q}$, since those fits were done on the corrected widths.

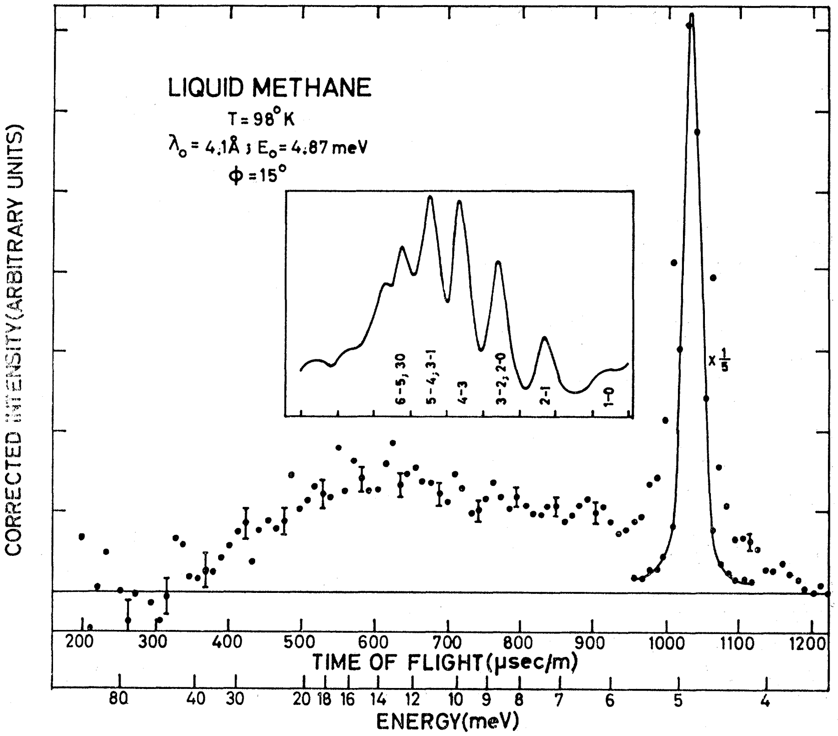

FIG. 4. Spectrum observed at 15° scattering angle with high resolution. The inset shows the spectrum expected if the rotations are free. The theoretical spectrum has been resolution broadened.

they exist, should be seen in this situation.[23] Consideration of a more detailed model for the translations will lead to the same conclusion, since at small Q the simple diffusion behavior is dominant. The experimental results obtained corresponding to the conditions of the calculation are also shown in the same figure. No discrete peaks are seen within the accuracy of the experiment. This has to be contrasted with the measurements of Hautecler and Stiller,[1] who using a 1-mm-thick sample similar to ours and working at a much larger scattering angle (70°) reported evidence for discrete rotational peaks. Our results, however, are consistent with infrared[9] and Raman[8] spectroscopic measurements made with high resolution, and suggest that the rotations are hindered in the liquid state.

Crawford *et al.*[8] suggest that the absence of rotational peaks is due to the splitting of the rotational levels by intermolecular interactions. In a liquid the interactions fluctuate and this results in a smearing of the levels. The center of gravity of the level, however, is assumed not to change because the interactions are weak. Calculations made by us along these lines indicate that this will not give the required agreement.

It is interesting to look at the general shape of the inelastic spectrum predicted by our model (of Sec. II) for different angles of scattering, especially in relation to the experimentally observed spectrum. These are plotted in Fig. 5 for scattering angles 30°, 45°, 60°, and 90° after applying appropriate resolution corrections. One notices that the maximum of the inelastic part is at the same time of flight (∼690 μsec/m = 2.72 Å) at all angles but there are significant differences in the shapes of the curves especially at smaller times of flight. Experimentally, on the other hand, one finds that the inelastic distributions are quite similar at all angles[24] and the peak of the distributions is nearer to 630 μsec/m (∼2.5 Å). The differences may be due to multiple scattering.

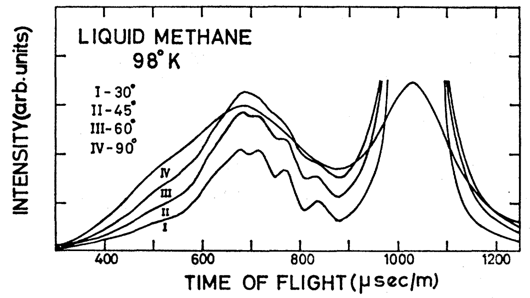

FIG. 5. Spectra calculated using Eq. (5) with $D = 2.2 \times 10^{-5}$ cm^2/sec after appropriate resolution broadening.

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[23] In the theoretical curve shown in Fig. 4, the effects of spin correlations have not been taken into account. Qualitatively their effect (see Ref. 15) will be to decrease slightly the peak heights of the $(1 \rightarrow 0)$, $(2 \rightarrow 1)$, and $(3 \rightarrow 2,\ 2 \rightarrow 0)$ transitions (by ∼25%, 25%, and 7%, respectively); the $(4 \rightarrow 3)$ transition will be enhanced (by ∼7%) etc. The rotational peaks will still be resolved clearly.

[24] This has also been noticed by J. A. Janik, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. 2, p. 243.

C. Over-All Spectrum

Finally it seems worthwhile to give some consideration to the shape of the total spectrum and examine to what extent our model is in agreement with our observations. If the quasi-elastic peak at any angle is normalized to the theory, then the maximum height of the theoretical inelastic spectrum is roughly 60% of the experimental maximum. In other words the theoretical quasi-elastic peak is more prominent than is observed experimentally. It is possible that one of the causes for this discrepancy is multiple scattering. Another reason could be that our model is inadequate. The discrepancy observed is probably due to both causes.

We shall now examine how the shape of the theoretical spectrum would be modified by the second cause, namely, considering a more realistic model. There are two respects in which our present model could be improved. One is to consider a more realistic model for the translations than the simple diffusion model. Secondly, the $I_R(Q,t)$ must be characteristic of a hindered rotator rather than of a free rotator. The general nature of the function for polyatomic molecules is at present not known. We expect, however, the function to have a "free-rotator" behavior at small times and to have the characteristics of rotational diffusion at long times.[25] Although the directions in which the improvements are to be effected are clear, the manner in which they are to be made is not, since little is known in detail about both translations and rotations in liquids. We have, however, tried a few simple extensions of our model in which the simple diffusion behavior was replaced by more a sophisticated description of the translations. The rotations were assumed to be free as before. The object was to see whether this leads to at least a partial improvement in the agreement between theory and experiment. In the first model of this type we considered, the translations were assumed to follow the Egelstaff model[19] [see Eq. (8)]. This did not result in an improvement. The use of the Langevin model for the translations with a fixed η also did not improve the agreement. We finally considered a model in which the translations were derived by the principle of corresponding states[26,27] from the mean-square displacement for argon obtained recently by Nijboer and Rahman[28] from computer experiments. Now it is known that argon and methane do not obey the corresponding-states principle exactly.[19] Qualitatively, however, there is a great deal of similarity between the two liquids and this must be true of atomic motions also.

The calculations using the corresponding states approach were carried out as follows. We first start with the curve of the mean square displacement $\langle r^2\rangle_a$ versus time of the argon atom obtained by Nijboer and Rahman (see their Fig. 1) for argon at 85.5°K, and from this derive the behavior of $\langle r^2\rangle_m$ as a function of time for methane using the prescriptions

$$\langle r^2\rangle_m=(\sigma_m/\sigma_a)^2\langle r^2\rangle_a\,,$$

$$t_m=\left(\frac{\sigma_m}{\sigma_a}\right)\left(\frac{M_m}{M_a}\frac{\epsilon_a}{\epsilon_m}\right)^{1/2}t_a\,. \qquad (12)$$

σ and ϵ are the usual parameters of the Lennard-Jones potential, and M is the mass of the molecule. The values for σ and ϵ used by us were taken from the work of Hirschfelder *et al.*[29] The mean-square displacements thus derived are appropriate to a temperature of 94.5°K and lead to a diffusion coefficient of 3.54×10^{-5} cm²/sec. To derive $S_T(Q,\omega)$ from the values of $\langle r^2\rangle_m$, we make the well-known Gaussian approximation[18] whence

$$S_T(Q,\omega)=\frac{1}{\pi}\int_0^\infty \cos\omega t\,\exp\{-Q^2\langle r^2\rangle_m/6\}dt\,. \qquad (13)$$

The required cross section is then given by

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega dE}=\frac{a_p{}^2}{\hbar}\frac{k}{k_0}e^{-Q^2\gamma}\sum_{jJ}\left\{S_T\left(Q,\frac{\epsilon-\beta}{\hbar}\right)\exp\left(-\frac{\epsilon-\beta}{2k_BT}\right)\right\}$$
$$\times\frac{2J+1}{2j+1}B_j(T)\sum_{n=|j-J|}^{j+J}j_n{}^2(Qb_p)\,. \qquad (14)$$

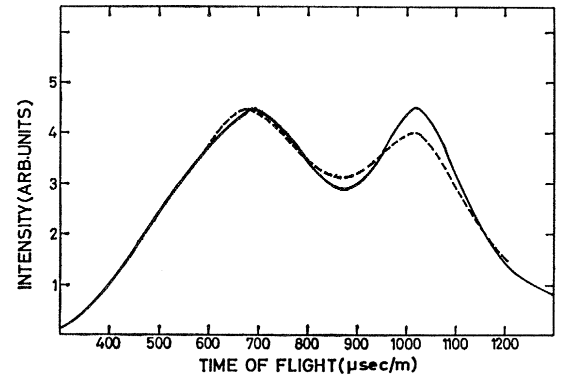

FIG. 6. Computed spectra at 90° scattering angle according to two different models. The solid curve is based on Eq. (5) with $D=3.54\times10^{-5}$ cm²/sec (i.e., rotations free and translations according to the simple diffusion model). The dashed curve is the spectrum for a model in which the rotations are free and the translations are derived from the computer experiments of Nijboer and Rahaman for argon, by the application of the corresponding-states principle. The Gaussian approximation has been used in calculating the latter spectrum.

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[25] Functions of this type for diatomic rotators have recently been considered by V. F. Sears [Can. J. Phys. 44, 1299 (1966)]; see also the work of R. Gordon [J. Chem. Phys. 42, 3658 (1965)] and H. Shimizu [*ibid.* 43, 2453 (1965)], who discuss similar relaxation functions which feature infrared absorption and Raman scattering.

[26] G. H. Vineyard, Phys. Rev. **119**, 1150 (1960).

[27] V. F. Sears, Can. J. Phys. 44, 867 (1966).

[28] B. R. A. Nijboer and A. Rahman, Physica **32**, 415 (1966).

[29] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1111.

The spectrum evaluated using Eq. (14) for a scattering angle of 90° is shown as a dashed line in Fig. 6. The solid line in the figure shows the spectrum based on Eq. (5) with a value of 3.54×10^{-5} cm^2/sec for D. It is seen from the figure that the use of corresponding states leads to a slight improvement to the extent that the quasi-elastic peak comes down and the valley gets filled. The effect on the whole, however, is small and it seems that hindering of rotations rather than translations is responsible for the reduced quasi-elastic scattering (apart, of course, from multiple-scattering effects which are difficult to estimate).

In this connection it will not be out of place to point out that even in gaseious methane, where multiple scattering is quite small, theory[6,14] predicts in the region of low Q, smaller inelastic scattering relative to the quasi-elastic than is observed experimentally.[6,30] It is likely that the discrepancy here is also due to hindering of rotations.[31] In the case of gas the hindering will be rather small and confined to large times i.e., $I_R(Q,t)$ will be different from the free-rotator value only at large times. This will show up as a discrepancy in the small-Q data. In the case of the liquid where the hindering effects start earlier, the discrepancy will be apparent at intermediate Q values. Only at small times may one expect free-rotator behavior and this is precisely what Harker and Brugger observe in their large-Q data.

V. SUMMARY AND CONCLUSIONS

Scattering of cold neutrons by liquid methane has been measured at 12 angles of scattering between 15° and 90°. The width of the quasi-elastic peak follows the simple diffusion behavior at least up to $Q_0=1.75$ Å^{-1} and gives a value of 2.2×10^{-5} cm^2/sec for the diffusion coefficient. It is remarked in this connection that the interaction time for liquid methane in a model suggested by Egelstaff should be less than 0.5×10^{-12} sec just as in the case of liquid argon. It is also noted that if one uses the Langevin model to describe the quasi-elastic scattering, it is not necessary to use a Q dependent damping parameter as suggested by Griffing.

The inelastic scattering pattern taken at small angle of scattering should show discrete peaks in the inelastic part of the spectrum if the rotations are completely free. No such peaks were observed even in the smallest momentum transfer experiment. From this we conclude that the motions are actually hindered to a small extent. These observations, though in contradiction to the earlier neutron results of Hautecler and Stiller, are in agreement with the infrared-absorption and Raman-scattering experiments.

A theoretical model, assuming a simple diffusion mechanism of translation and a quantum-mechanical treatment of free rotations used to calculate the scattered spectrum, is unable to explain the details of the observed spectrum. An improved version of this model, using a more realistic description of the translations derived by the principle of corresponding states from the results of the computer experiments on argon by Nijboer and Rahman, shows improvement but does not seem quantitatively adequate. It is conjectured that this disagreement, and the disagreement one gets at small Q between theory and experiment in the case of gaseous methane, are due to the same cause, i.e., hindering of the rotations, though the effect is much larger in the case of the liquid. The discrepancy could be reduced by considering a proper treatment of the rotations.

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[30] F. J. Webb, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. 1, p. 457.

[31] Since this manuscript was submitted for publication, we have received from Dr. V. F. Sears a report prior to publication in which it is shown that the ratio of quasi-elastic to inelastic scattering is indeed reduced when hindering effects are considered. We wish to thank Dr. Sears for sending us his results prior to publication.