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Proton Motions in Methanol by Cold Neutron Scattering

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Cold neutron scattering data are reported for methyl alcohol in the liquid phase at room temperature. The quasielastic scattering was interpreted using the Larsson and Bergstedt model, that takes into account intramolecular motions and molecular diffusion. On the basis of this model, one finds for the relaxation time of the hindered rotation of the CH_3 group within the molecule a value of 2.4×10^{-12} sec. The analysis of the quasielastic scattering according to the L-B model explains in a consistent way our experimental results in a range of momentum transfers of about 0.80 – 1.55 \AA^{-1} . In the inelastic region some structure is observed at energy transfers of 22, 17, and 5 meV. The 17-meV energy transfer is associated with the $1 \rightarrow 0$ transition of the torsional oscillations of the methyl group. The activation energy for the above motion was calculated to be $E = 1.3$ kcal/mol, in good agreement with the value of the barrier height for internal rotation of the CH_3 in methanol, obtained by microwave methods.

INTRODUCTION

It is well recognized that an analysis of the scattering of cold neutrons in hydrogenous liquids gives valuable information about the dynamics of the atomic motions.¹ Through the quasielastic scattering in particular it is possible to study the nature of diffusive motions of the molecule.

In the case of liquids, several models have been worked out for the interpretation of the quasielastic scattering. The most important among these models¹ are the continuous-diffusion model, the jump-diffusion model, the spinning-globule model, and the stochastic model. However, most of these models are more realistic for the case of monatomic liquids. There is strong experimental evidence that in the case of hydrogenous liquids the motion of the protons with respect to the center of mass of the molecule contributes significantly to the quasielastic scattering. The apparent self-diffusion coefficient derived from studies of quasielastic scattering was found to be much larger than the measured macroscopic diffusion coefficient,² suggesting that a mixture of the molecular and proton motions is observed with neutrons.

Recently Larsson and Bergstedt have derived expressions for the cross section for quasielastic neutron scattering by hydrogenous liquids that include intramolecular motions.³ The motion of the proton is described as a folding of the motion of the proton with respect to the center of mass of the molecule and the motion of the center of mass itself. This model was further developed by Larsson.⁴

In this work, we study the cold neutron scattering in methanol at room temperature. Methanol is a well known H-bonded liquid that exhibits internal hindered rotation. The barrier height for this rotation, determined by microwave spectroscopy, is 1.07 kcal/mol.⁵ In the liquid phase the molecules of the methanol are associated, by strong hydrogen bonds, giving dimers and trimers.

Neutron scattering measurements on liquid methanol have previously been performed by Saunderson and Rainey⁶ and by Sampson and Carpenter.^{7,8} The quasi-

elastic scattering lines as a function of the square of the momentum transfer obtained by Saunderson and Rainey have been analyzed in terms of the continuous diffusion model.¹ The results of Sampson and Carpenter have been discussed in terms of the continuous diffusion model and of the globular diffusion model.¹ The main purpose of the present work is to analyze the quasielastic line for methanol in terms of the rotational diffusion model of Larsson and Bergstedt.^{3,4} The inelastic scattering data are also discussed.

THEORETICAL BACKGROUND

In hydrogenous compounds, the differential scattering cross section per proton, in the Van Hove formalism,⁹ neglecting the coherent contributions, can be written in the form:

$$d^2\sigma/d\Omega d\omega = (a_{\text{inc}}^2/2\pi) (\mathbf{k}/k_0) \times \int \int \exp[i(\mathbf{Q}\mathbf{r} - \omega t)] G_s(\mathbf{r}, t) d\mathbf{r} dt,$$

where a_{inc} is the bound incoherent scattering amplitude of hydrogen, and \mathbf{k}_0 and \mathbf{k} are the wave vectors of the neutron before and after scattering. $G_s(\mathbf{r}, t)$ is the space-time self-correlation function of the proton. The energy and momentum transfers in the scattering process are

$$\hbar\omega = (\hbar^2/2m) (\mathbf{k}_0^2 - \mathbf{k}^2),$$

$$\hbar\mathbf{Q} = \hbar(\mathbf{k}_0 - \mathbf{k}),$$

m being the neutron mass.

The central problem in deriving expressions for the neutron incoherent scattering cross section is to formulate the self function $G_s(\mathbf{r}, t)$. Larsson and Bergstedt (L-B) on the basis of the Van Hove formalism and by use of the method developed by Singwi and Sjölander,¹⁰ have derived an expression for the quasielastic neutron cross section for hydrogenous molecular liquids.³ It was explicitly shown that the proton motion with respect to the molecular center of mass leads to an observable and in some cases dominating broadening of the ingoing neutron line.

In this model the function $G_s(\mathbf{r}, t)$ is determined as-

suming that two types of motions occur in the liquid, namely:

(a) motions of the proton within the molecule. During the average time T_0 the protons vibrate with respect to the molecular center of gravity. At the end of this period the proton jumps a certain distance l during a short time T_1 . The origin of this jump would be hindered rotations, for instance of a CH_3 group inside a carbon chain molecule. These vibrational and jumping periods are supposed to occur repeatedly.

(b) motions of the center of gravity of the molecule. The molecule is instantaneously bound to its neighbors. After a certain time T_0' , it is assumed, the configuration around the selected molecule changes profoundly so that the molecule as a whole starts to move for a time T_1' . During T_0' the molecular center of gravity vibrates, and during T_1' it performs simple diffusion.

The proton motion will appear as a superposition of the two independent motions thus defined.

The general form for the quasielastic neutron scattering cross section is very complex. Great simplifications are, however, possible under certain assumptions regarding the relative magnitudes of the four relaxation times entering into the formulation. Only cases for which $T_0 \gg T_1$ were considered in the L-B model, which means that the rotations must be hindered, so that rotational jumps have a meaning.

Four particular cases of physical interest were considered. In all these four cases the cross section is of Lorentzian shape and the model leads to a prediction of an observable quantity, i.e., the full width ΔE of the quasielastic neutron peak as a function of the momentum transfer. They are:

Case I. $T_0' \gg T_1'$ and $T_0' \gg T_0$. This corresponds to a low temperature sample in which the molecule stays bound to its neighbors most of the time. The viscosity of the liquid must be high, of the order of 1–100 P or more, and the self-diffusion coefficient very small.

Case II. $T_0' \gg T_1'$ and $T_0 \gg T_1'$. This case is very much related to Case I, except that the internal rotations are comparatively more restricted.

Case III. $T_1' \gg T_0'$ and $T_1' \gg T_0$. This case is the extreme opposite of the first, the molecule being bound to its neighbors only a small fraction of the time. The viscosity ought to be very low, less than 1 cP, and the self-diffusion rate very high.

Case IV. $T_1' \gg T_0'$ and $T_0 \gg T_0'$. This case is quite similar to Case III, but the internal rotations are comparatively more restricted.

For methanol at room temperature, with a rather low viscosity of 5.93 mP and a relatively high diffusion coefficient of $2.35 \text{ cm}^2/\text{sec}$,¹¹ as well as a relatively free rotation of the CH_3 group,⁵ Case III is the most appropriate for interpreting the quasielastic neutron scattering.

Of particular interest in this case is the asymptotic behaviour of ΔE for large and small values of Q :

$$\Delta E = 2\hbar/6T_0(D + l^2 + \langle r_i^2 \rangle)Q^2, \quad Q \rightarrow 0,$$

$$\Delta E = 2\hbar(1/T_0 + D)Q^2, \quad Q \rightarrow \infty,$$

where D is the macroscopic self-diffusion coefficient and $\langle r_i^2 \rangle$ is the mean square radius of the thermal cloud set up by the proton.

The condition $Q \rightarrow \infty$ is already verified for $Q^2 \sim 1.5 \text{ \AA}^{-2}$, and the condition $Q \rightarrow 0$ can be used for $Q^2 = 0.1$ within an error of 10%.

The L-B model has been modified by de Graaf¹² to include cases where the condition $T_0 \gg T_1$ is not satisfied, thus allowing free molecular rotations.

The L-B model was further developed by Larsson,⁴ in order to account for results obtained with glycerol. The main difference of this modified model is to consider the molecule as a line that suffers small changes in direction in space; because of this "rotational diffusion", the position of quasiequilibrium of the proton during its vibrational period will change with time, and T_0 is then considered as a diffusive-vibrational period.

The proton jump may be understood either as a larger and sudden change of the molecular line orientation or as a partial rotation resulting in isomeric forms, as assumed in the L-B model.

The only difference for the asymptotic linewidths obtained in the above Case III would be the replacement of the macroscopic self-diffusion coefficient D by $D + \frac{2}{3}D_p$, D_p being a coefficient for rotational diffusion.

EXPERIMENTAL METHOD

The methanol experimental data reported in this paper were obtained using the cold neutron time-of-flight spectrometer at the IEA-R1 research reactor of São Paulo.¹³ This facility is similar to the ones at the Brookhaven National Laboratory¹⁴ and at the Royal Institute of Technology, Stockholm.¹⁵ A liquid nitrogen cooled Be filter transmits a cold neutron spectrum with an average energy of 3.5 meV and a full width at half-height of 2.0 meV. The neutrons scattered by the sample in study are pulsed by a curved slit slow-neutron chopper,^{16,17} operated usually at 13 000 rpm. The scattered neutrons are detected by a bank of eight ³He detectors arranged in one layer. The flight path, 3.15 m long, is evacuated in order to decrease the scattering from air. Scattering angles from 20° to 90° can be measured. The energy analysis of the scattered neutrons is performed by a multichannel time of flight analyzer.

The resolution function of the time-of-flight spectrometer was determined from the neutron spectrum elastically scattered by vanadium. A good fit to the measured elastic curve was obtained by the convolution of a sharp-edged spectrum with a Gaussian resolution with a half-width $\delta t = 54 \mu\text{sec}$, which is the expected theoretical value for our geometry.¹³

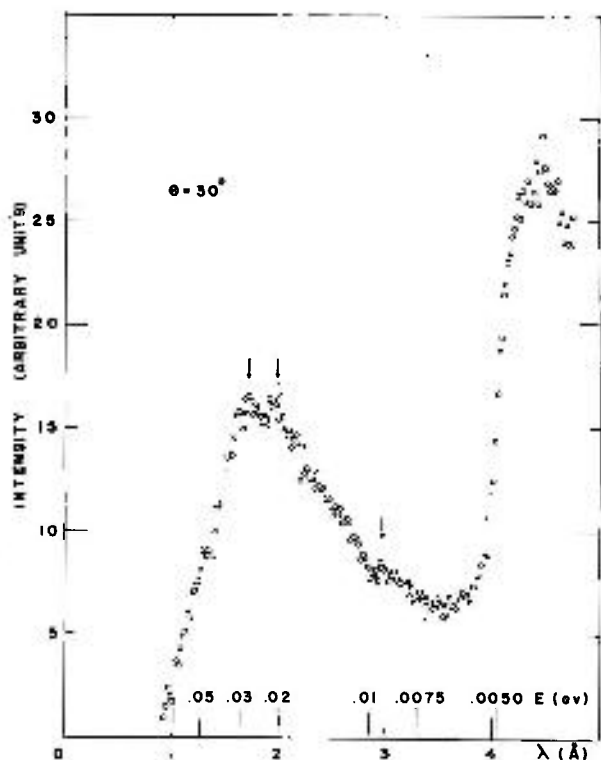


Fig. 1. Spectrum of neutrons scattered at an angle of 30° by methanol, at room temperature, as a function of neutron wavelength.

The sample of liquid methanol at room temperature (296°K) was contained in an aluminum cell. The container has the form of a cylinder with a diameter of 12 cm and a nominal thickness of 0.2 mm, presenting a transmission to 5 meV neutrons of approximately 90%.

The data are stored in punched tape form and are processed by an IBM-1620 computer which normalizes these data to monitor counts and corrects for background, detector efficiency, air scattering and chopper transmission.

RESULTS AND DISCUSSION

The measured angular and energy distributions of scattered neutrons in liquid methanol at room temperature were recorded at five scattering angles, namely 30° , 37.5° , 45° , 52.5° , and 60° . An example of raw data at the 30° scattering angle is given in Fig. 1. The corrected number of counts plotted in arbitrary units is given as a function of neutron wavelength. The observed spectrum consists of a broad inelastic region and a distinct quasielastic peak.

In order to derive the full width at half-maximum of the quasielastic peak, one must have a procedure for the separation of the inelastic part of the spectrum. In our case the inelastic spectrum is extrapolated under the quasielastic line and then subtracted.

After subtraction, the remaining peak (the quasielastic scattering) was assumed to be a result of a convolution of a Gaussian resolution function in a time-of-flight scale and a Lorentzian line broadening function in an energy scale. Previous papers^{2,8,12} show that this is an acceptable assumption.

Based on the resolution value for our spectrometer, a great number of theoretical line shapes were calculated for various Lorentzian line broadening functions, using an IBM/360 computer. The linewidth of the Lorentzian function ΔE was then obtained as a function of the full width of the observed quasielastic peak. The linewidth of the quasielastic peak determined from the observed broadening of the incident line as a function of Q^2 is given in Fig. 2. The error bars include estimates of the error introduced by the subtraction of the inelastic contribution, as well as an error in the determination of the observed broadening of the incident line. In this figure the results of Saunderson and Rainey⁶ and the ones of Sampson and Carpenter^{7,8} are also shown.

Figure 2 shows also the curves ΔE vs Q^2 for $Q \rightarrow 0$ and $Q \rightarrow \infty$ according to Case III of the Larsson and Bergstedt model.

Curve (b), corresponding to large momentum transfers, is fitted to the last three experimental points using the known macroscopic value of the diffusion coefficient for methanol. The result shows that, within the errors, the macroscopic self-diffusion coefficient alone explains the obtained linewidth, and it is not necessary to take into account the contribution of rotational diffusion for explaining our experimental results. This is understandable, since the methanol molecule is a very short carbon chain. The relaxation time for proton motions within the molecule obtained from the value of Curve

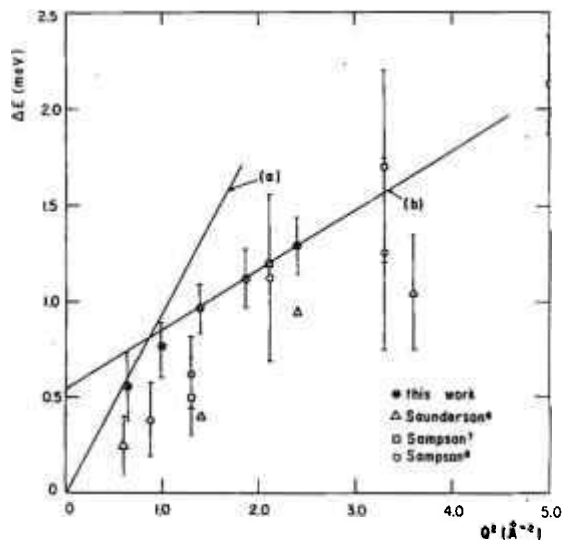


Fig. 2. Observed widths of quasielastic peak of methanol at room temperature. Curves (a) and (b) are based on the Larsson and Bergstedt model, for $Q \rightarrow 0$ and $Q \rightarrow \infty$, respectively.

(b) for $Q^2=0$ is $T_0=2.4\times 10^{-12}$ sec. This time is identified with the mean time between two successive rotational jumps of the CH_3 group.

Curve (a), corresponding to small momentum transfers, is drawn assuming¹⁸ $\langle r_i^2 \rangle = 3.6 \text{ \AA}^2$ and $l=1.8 \text{ \AA}$. The value for l is obtained from the molecular structure of methanol¹⁹ assuming the jump length as a consequence of an internal hindered rotation of the methyl group.

The slope of Curve (a) corresponds to an apparent diffusion coefficient of $7.1 \text{ cm}^2/\text{sec}$. The experimental points fall consistently below this curve.

The analysis of the broadening of the incident line on basis of the L-B model explains in a consistent way our experimental results. Therefore the quasielastic scattering observed for methanol can be interpreted satisfactorily either using the rotational-translational diffusion model as was done in this work or using the globular model with a diffusion mass of 3.5 molecules as in the work of Sampson and Carpenter.⁸

In the inelastic region the experimental spectrum obtained for methanol shows a broad and intense band in a range from about 0.05 to about 0.006 eV.

This spectrum seems to exhibit some structure at about 1.7, 2.0, and 3.0 \AA , corresponding, respectively, to energy transfers of 25, 17, and 5 meV. The origin of the peak corresponding to an energy transfer of 5 meV (40 cm^{-1}) may be attributed to a hindered translational motion of CH_3OH units in dimers and trimers.^{2,8} The peak corresponding to an energy transfer of 17 meV (137 cm^{-1}) is attributed to the $1\rightarrow 0$ transition of the torsional oscillations of the methyl group.¹⁸ The 25-meV (202 cm^{-1}) energy transfer could be due to motions associated with the hydrogen bond. Results of Raman spectroscopy in the low frequency region show a band at 190 cm^{-1} that is associated with the presence of the hydrogen bond.²⁰

The activation energy for internal rotation of the methyl group in the methanol molecule can be estimated¹² assuming that

$$1/T_0 = \omega/2\pi \exp(-E/kT),$$

where T_0 is the relaxation time for the proton vibra-

tional motion, $\omega/2\pi$ is the average frequency of torsional oscillations of the CH_3 group (that is, the number of times per second the molecular group tries to overcome the potential barrier), and E is the activation energy for internal rotation. The Boltzman factor determines the transition probability by tunneling effect. For $\omega/2\pi=4.1\times 10^{12} \text{ sec}^{-1}$, corresponding to the observed energy transfer of 17 meV, and $T_0=2.4\times 10^{-12} \text{ sec}$, determined from the quasielastic scattering analysis, one finds $E=1.3 \text{ kcal/mol}$. This value is in reasonable agreement with the value 1.07 kcal/mol derived from microwave data for the barrier hindering the internal rotation of the methyl group in methanol.⁵ This agreement gives an additional support to the interpretation of the quasielastic scattering on basis of the rotational and translational diffusion model of Larsson and Bergstedt.

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RESUMO:

Medidas do espalhamento de nêutrons frios pelo álcool metílico na fase líquida, na temperatura ambiente, são apresentadas. O espalhamento quase-elástico é interpretado de acordo com o modelo de Larsson-Bergstedt (L-B), que leva em conta movimentos intra-moleculares e difusão molecular. Resulta um valor $2,5 \times 10^{-12}$ s para o tempo de relaxação da rotação restrita do grupo CH_3 na molécula. A análise do espalhamento quase-elástico de acordo com o modelo L-B explica de uma maneira consistente os resultados experimentais no intervalo de transferência de quantidade de movimento de $0,80$ a $1,55 \text{ \AA}^{-1}$. Na região inelástica alguma estrutura é observada para transferências de energia de $22,17$ e 5 meV . A transferência de energia em 17 meV é associada com a transição $1 \rightarrow 0$ das oscilações torsionais do grupo metil. A energia de ativação para esse movimento resulta $1,3 \text{ kcal/mol}$, em bom acordo com o valor da altura da barreira para rotação interna do CH_3 no metanol, obtida por técnica de microondas.

RESUMÉE:

On présente des mesures de la diffusion de neutrons froids pour le methyl alcohol dans l'état liquide, à la temperature ambiante. La diffusion quasi-elastique est interpretée selon le modèle de Larsson-Bergstedt (L-B), qui tient compte aussi bien des mouvements intra-moleculaires comme de la diffusion moleculaire. On arrive à une valeur de $2,5 \times 10^{-12}$ s pour le temps de relaxation de la rotation restreinte du groupe CH_3 dans la molecule. L'analyse de la diffusion quasi-elastique selon le modèle de L-B explique d'une façon consistante les résultats experimentaux dans l'intervalle d'échange de quantité de mouvement de $0,80$ à $1,55 \text{ \AA}^{-1}$. Dans la region inelastique quelque structure est observée pour les transférences d'énergie de $22,17$ et 5 meV . La transférence d'énergie a 17 meV est associée avec la transistion $1 \rightarrow 0$ des oscillations torsionaux du groupe methyl. On arrive à une énergie d'activation pour ce mouvement de $1,3 \text{ kcal/mol}$, en bon accord avec la valeur de la barrière pour la rotation interne du CH_3 dans le methanol obtenue par la methode de micro-ondas.