Quasielastic Scattering of Thermal Neutrons by CH₃OH and CH₃SH*

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We report measurements of the line broadening of thermal neutrons quasielastically scattered from room temperature methyl alcohol and methyl mercaptan in the liquid phase. The linewidths for CH₃SH are found to be approximately twice those of CH₃OH. This is interpreted to be additional evidence of the relative freedom of molecular motions and lack of hydrogen bonding in CH₃SH. The linewidth data are discussed in terms of the simple diffusion model, and for methanol, in terms of a globular diffusion model. For methanol a diffusion constant of 3.25×10^{-5} cm² sec⁻¹ and a diffusing globule mass of ~3.5 molecules are in agreement with the data. An upper limit of $D = 6.5 \times 10^{-5}$ cm² sec⁻¹ is found for the diffusion constant of CH₃SH.

INTRODUCTION

The molecular dynamics of hydrogenous liquids has been one of the areas investigated by the technique of slow neutron scattering.[1] This paper reports measurements of the line broadening of thermal neutrons quasielastically scattered by liquid methyl alcohol CH₃OH and liquid methyl mercaptan CH₃SH at room temperature.

These two structurally similar molecules form an interesting pair for comparative study because of their different hydrogen-bonding properties. Association by hydrogen bonding is known to be predominant in methanol, while very little association is believed to occur in methyl mercaptan.[2] Additional information on the role that association plays in influencing the molecular dynamics of these molecules can be obtained from inelastic neutron scattering measurements.

Neutron inelastic scattering studies of methanol have been reported by Saunderson and Rainey,[3] Aldren, Eden, and White (CH₃OD and CD₃OH),[4] and Sampson and Carpenter.[5] These are the first reported measurements on methyl mercaptan (preliminary data having been presented in Ref. 5).

The above mentioned studies have reported both inelastic and quasielastic scattering data. This paper will discuss only the quasielastic scattering from these molecules. The results of companion inelastic scattering measurements have been presented elsewhere.[5,6]

Previous quasielastic data[3,4] have been analyzed in terms of the simple diffusion model.[7] While the agreement with this model has been quite good, it is, nevertheless, not satisfying from a physical viewpoint. Because of the strongly associated nature of liquid methanol, one would expect that single-particle center-of-mass diffusion would be unlikely.

The present results for methanol and methyl mercaptan are discussed in terms of the simple diffusion model and a globular diffusion model. We also comment on the influence of rotational-diffusion contributions to the line broadening.

EXPERIMENT

The measurements were performed on the phased chopper time-of-flight (TOF) spectrometer at the University of Michigan's 2 MW Ford nuclear reactor. This spectrometer is similar to the former Chalk River scattering law spectrometer developed by Egelstaff and co-workers at Chalk River and Harwell.[8,9] Details of the routine operation of the University of Michigan spectrometer have been described elsewhere.[5,10—12]

The samples and sample holders have been previously described.[6,13] Sample transmissions varied from 0.77–0.92 with the normal of the planar targets at a 45° angle to the incident beam.

The quasielastic linewidth data were accumulated by cycling a sample and an empty target into the beam on an 8-min counting cycle. The signal from the sample was counted for 6 min while background from the empty dummy target was counted for 2 min. The signal

[1] K. E. Larsson, *Thermal Neutron Scattering*, P. A. Egelstaff, Ed. (Academic Press Inc., New York, 1965), pp. 347–413.

[2] K. Krynicki and J. G. Powles, Proc. Phys. Soc. (London) **83**, 983 (1964).

[3] D. H. Saunderson and V. S. Rainey, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 413.

[4] B. K. Aldren, R. C. Eden, and J. W. White, Discussions Faraday Soc. **43**, 169 (1967).

[5] T. E. Sampson and J. M. Carpenter, *Neutron Inelastic Scattering* (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 491.

[6] Thomas E. Sampson, Ph.D. thesis, University of Michigan, 1969 (unpublished).

[7] George H. Vineyard, Phys. Rev. **110**, 999 (1958).

[8] P. A. Egelstaff, S. J. Cocking, and T. K. Alexander, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 165.

[9] R. M. Brugger, *Thermal Neutron Scattering*, P. A. Egelstaff, Ed. (Academic Press Inc., New York, 1965), pp. 76–80.

[10] P. F. Zweifel, "Neutron Cross Sections and Spectra Studies," University of Michigan, Rept. 03712-5-P, 1964.

[11] E. A. Straker, J. Chem. Phys. **43**, 4134 (1965).

[12] E. A. Straker, Ph.D. thesis, University of Michigan, 1965 (unpublished).

[13] T. E. Sampson and J. M. Carpenter, Nucl. Instr. Methods **50**, 179 (1967).

and background were stored in separate portions of the memory of a TMC 1024 channel TOF analyzer. Typical runs lasted from two to five days. Before or after each run the spectrometer resolution was measured by cycling a 4 in.×2.5 in.×0.125 in. thick room-temperature vanadium target with an open beam. The orientation and position of the vanadium target were the same as that of the liquid samples. Several resolution runs were repeated and the FWHM of the elastic peak of the different runs agreed, usually to better than 5%.

Data were accumulated at scattering angles of 22.1°, 31.2°, and 47.5° using incident neutron energies from 13–46 meV. Energy resolution was about 8% of E_0.

DATA ANALYSIS

The modest spectrometer resolution made isolation of the quasielastic peak and subsequent analysis difficult.

The analysis proceeded on the assumption that the observed spectrum could be interpreted as a resolution-boradened Lorentzian function of the energy transfer. The Lorentzian linewidth was obtained as follows:

The spectrometer resolution was represented analytically by fitting a function of form

$$\exp\left(-\sum_{n=0}^{4} a_n t^n\right)$$

to the vanadium TOF resolution data. The quasielastic peak was then isolated by estimating and subtracting the inelastic background from the liquid data. A Debye–Waller factor (DWF) was included in the assumed Lorentzian symmetrized scattering law. This cross section expression, with the linewidth as a parameter, was convoluted numerically on a TOF scale with the fitted resolution function and compared with the isolated quasielastic peak. If no value of the linewidth parameter gave a reasonable fit, the inelastic background subtraction was modified and the procedure repeated. This procedure forces the isolated quasielastic peak to have a Lorentzian form. The resolution of these measurements is not good enough to draw any conclusions regarding the true line shape if it is not Lorentzian. However, previous measurements on many other liquids show that this is a workable assumption, and theoretical models[7,14,15] also support this choice. Indeed, it is only with resolution of the order of 0.1 meV, a factor of 10–30 better than these measurements, that one might comment with any certainty on the true form of the line shape.[16]

DWF's measured for CH$_3$OD and CD$_3$OH[4] were assumed to represent separate DWF's for the methyl and hydroxy protons, respectively. The weighted sum of these factors was used in the convolution calculation.

Although this technique has been used previously,[17] this treatment is inconsistent since the fact that the DWF's are different for the two types of protons indicates that the low-frequency portions of the scattering law are also different. Thus, although a weighted sum is not correct, it was found that the magnitude of the DWF had negligible effect on the linewidth determined by the convolution fitting procedure. This was determined by comparing the best fit values of the linewidth using different values of the DWF.

For CH$_3$SH a DWF of $\exp(-0.6Q^2)$, where Q is the momentum transfer in Å^{-1}, was assumed. While this is a strongly varying DWF, it is the same as that measured for CH$_3$OD,[4] and is reasonable from all the evidence supporting the idea that molecular motions in CH$_3$SH are much less restricted than those in CH$_3$OH.

A fit of the line shape, obtained as described above, to typical TOF data is shown in Fig. 1. The inelastic background subtraction was modified once from the original estimate to obtain this fit. The procedure of modifying the inelastic background subtraction to force the isolated quasielastic peak to be Lorentzian resulted, in most cases, in a somewhat unphysical appearing background subtraction. This was manifested in the appearance of a bump in the background subtracted on the neutron energy gain side of the quasielastic peak. This bump could arise from having neglected multiple scattering or from using an incorrect DWF. Also, the true line shape may not be Lorentzian. However, the differences in the Lorentzian linewidths derived from different background subtractions were only typically 0.1 meV in a total width of several meV. Thus the procedure of forcing the isolated quasielastic peak to be Lorentzian is not thought to seriously affect the linewidths derived from these measurements.

Multiple scattering has been neglected in these measurements. This is justified on the basis of the results
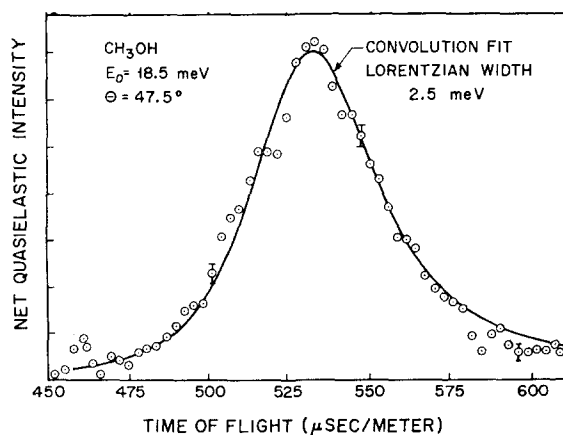

FIG. 1. Typical convolution fit to isolated quasielastic peak.

14 K. S. Singwi and A. Sjölander, Phys. Rev. 119, 863 (1960).
15 K.-E. Larsson and L. Bergstedt, Phys. Rev. 151, 117 (1966).
16 U. Dahlborg, B. Friberg, K. E. Larsson, and E. Pirkmajer, *Neutron Inelastic Scattering* (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 581.

17 K. E. Larsson and U. Dahlborg, Physica 30, 156 (1964).

of Slaggie[18,19] and Brugger.[20] It is noted in Slaggie's calculations and Brugger's experimental correction for water, that the multiple scattering correction factor is very nearly constant for small energy transfers under conditions approximating those of the linewidth measurements presented here. The larger corrections come at energy transfers larger than those used in fitting the quasielastic peak linewidth data. This leads one to the conclusion that multiple scattering does not alter the shape of the quasielastic peak appreciably. Similar conclusions using the same argument have been reached by DeGraaf.[21]

The uncertainty in the quasielastic linewidths (Figs. 2 and 3) is assumed to arise from independent uncertainties in the resolution measurement and the observed isolated quasielastic peak. The resolution width uncertainty was estimated by the reproducibility of repeated resolution measurements. The uncertainty in the isolated quasielastic peak width was estimated from the differences in this width obtained by different inelastic background subtraction. These uncertainties were combined by assuming that the observed quasielastic linewidth was represented by the convolution of a Gaussian resolution function with a Lorentzian linewidth.[6] While this assumption may not be adequate for the extraction of the Lorentzian width from the observed data, it is sufficient for the estimation of the Lorentzian width uncertainties.

RESULTS

The quasielastic linewidths measured in these experiments are presented in Fig. 2. The straight lines are least-squares fits to the data, and the diffusion constants
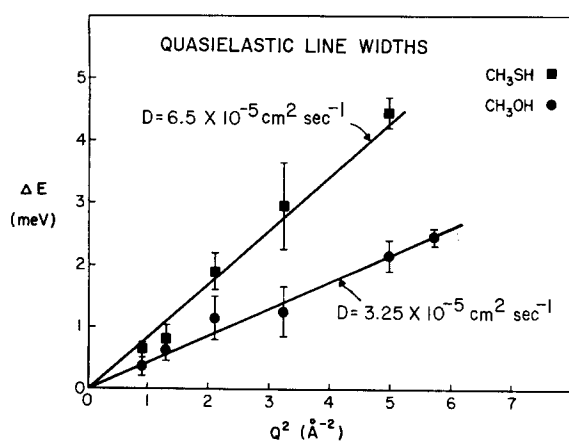

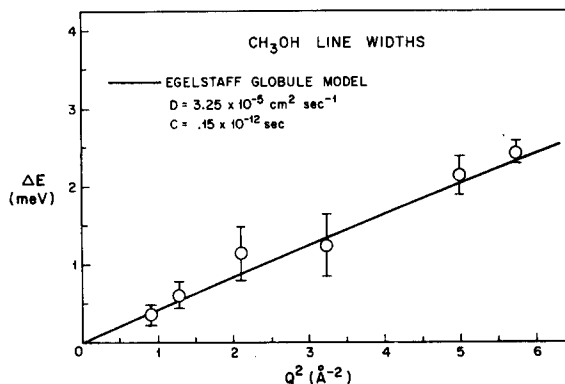FIG. 2. Quasielastic linewidths for CH_3SH and CH_3OH.

FIG. 3. CH_3OH linewidths and globule model comparison.

D are derived from these fits in the simple diffusion approximation.[7]

Macroscopic measurements of D for methanol[22] yield a diffusion constant of 2.1×10^{-5} cm² sec⁻¹ at 20°C. The cold neutron scattering results of Saunderson and Rainey[3] and Aldren, Eden, and White[4] are in good agreement with this macroscopic measurement.

The diffusion constant for CH_3OH derived from these measurements, $D = 3.25 \times 10^{-5}$ cm² sec⁻¹, is somewhat larger than the cold neutron results and the macroscopic measurement. However, the differences are probably not significant in view of the relatively poor resolution of the present measurements.

In the above discussion the interpretation of the neutron measurements in terms of a macroscopic diffusion coefficient has more or less been implied. It is well known that a neutron quasielastic scattering experiment measures mainly proton motions on a time scale of the order of 10^{-12} sec. In addition to proton motion caused by center-of-mass diffusion, the neutron also "sees" proton jumping motions due to molecular reorientation, rotation, or jumps in a hydrogen bond, and the relaxation of proton and center-of-mass vibrational motion. Neutron experiments indicate that molecular diffusion is a combination of translational, rotational, and vibrational displacements. When an apparent diffusion constant is derived from neutron data on the basis of the simple diffusion model, as above, it may not, and often will not be the same as that determined by a macroscopic measurement. Thus, one should exercise care in comparing neutron measured diffusion constants with macroscopic measurements.

Because of the strong hydrogen bonding occurring in methanol, single-particle center-of-mass diffusion is an unlikely process. The globular diffusion model of Egelstaff[23,24] is a physically more reasonable model for associated methanol. In this model self-diffusion is

[18] E. L. Slaggie, *Neutron Thermalization and Reactor Spectra* (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 311.
[19] E. L. Slaggie, Nucl. Sci. Eng. **30**, 199 (1967).
[20] R. M. Brugger, Nucl. Sci. Eng. **33**, 187 (1968).
[21] L. A. DeGraaf, thesis, Technische Hogeschool, Delft, The Netherlands, 1967 (unpublished).

[22] R. E. Rathbun and A. L. Babb, J. Phys. Chem. **65**, 1072 (1961).
[23] P. A. Egelstaff, Advan. Phys. **11**, 203 (1962).
[24] P. A. Egelstaff, *An Introduction to the Liquid State* (Academic Press Inc., New York, 1967), p. 127.

pictured as a cooperative phenomenon in which neighboring molecules move together collectively in Brownian motion. This model also reasonably represents the methanol linewidths using a diffusion constant D of 3.25×10^{-5} cm^2 sec^{-1} and a delay time parameter[23,24] $c = 0.15 \times 10^{-12}$ sec as shown in Fig. 3. The parameter c can be taken to be the delay time before the onset of diffusive motion and/or it can also be related to the diffusing globule mass. The above value of c yields a globule mass of ~ 3.5 molecules, a number in good agreement with association numbers determined by other methods.[25-27] Such good agreement is probably fortuitous because a range of globule masses on the order of one to five molecules could equally well represent the data. In view of the rather crude model, though, even order-of-magnitude agreement is comforting.

These results say, then, that simple diffusion of an aggregate of three or four molecules, with a delay time before the onset of diffusion on the order of 10^{-13} sec is in agreement with these data on methanol.

The results for CH$_3$SH, Fig. 2, can be represented by the simple diffusion model with a self-diffusion constant of 6.5×10^{-5} cm^2 sec^{-1}. Macroscopic viscosity and/or diffusion constant data to compare with these results have not been reported.

The fact that the linewidths for CH$_3$SH are approximately twice those of CH$_3$OH is additional evidence of the relative freedom of molecular motions in CH$_3$SH. Since the measurements for CH$_3$SH were performed at room temperature, above its atmospheric pressure boiling point of 5.96°C, it is expected that the viscosity is low and the self-diffusion rate high for methyl mercaptan under these conditions.

The work of Larsson and co-workers[15,17,28,29] has demonstrated that the contributions to quasielastic linewidths arising from proton motion with respect to the molecular center of mass can be very significant. The Larsson–Bergstedt model[15] takes these so-called rotational contributions into account and has been used successfully to fit linewidth data at several temperatures for n-propyl alcohol and pentane. However, in addition to the relaxation times for the vibratory and diffusive motions for both the proton and the molecular center of mass, the model also contains several other parameters. It could be argued that any data might be fit using all these parameters. Although several can be

determined separately from the neutron scattering data, data at several temperatures are still needed before the fits are meaningful.

In the Larsson–Bergstedt model (Cases III and IV) which are expected to hold for low viscosity, non-associated liquids, rotational diffusion does contribute to the quasielastic linewidth. The slope of a linewidth vs Q^2 plot (as Figs. 2 and 3) as $Q^2 \rightarrow 0$ contains contributions from the proton jump length, center-of-mass self-diffusion constant, and radius of the thermal cloud of the proton.

It would be desirable to analyze the CH$_3$SH data in terms of this model. However, there is not sufficient data available to meaningfully extract the various contributions to the CH$_3$SH linewidths from the Larsson-Bergstedt model. Thus, $D = 6.5 \times 10^{-5}$ cm^2 sec^{-1}, derived from these measurements, should be taken as an upper limit for the self-diffusion constant of liquid methyl mercaptan at room temperature. This is because of the neglect of possible rotational diffusion contributions to the measured linewidths.

The results for CH$_3$OH could also be discussed in terms of a rotational diffusion contribution. This is less likely in the case of methanol, because cold neutron measurements are in good agreement with the simple diffusion model. The low viscosity of methanol coupled with hydrogen bonding makes it seem likely that translational diffusion dominates. The results of the present measurements, although not in exact agreement with the macroscopic diffusion constant, are in agreement with a globular diffusion model which does not include rotational contributions.

CONCLUSIONS

Quasielastic linewidth measurements on CH$_3$OH and CH$_3$SH have been compared and show additional evidence of the lack of hydrogen bonding in CH$_3$SH.

The data for methanol yield a self-diffusion constant of 3.25×10^{-5} cm^2 sec^{-1} on the basis of a simple diffusion model. This is somewhat larger than previous neutron and macroscopic results, but the difference is not believed to be significant in view of the relatively large uncertainty in the present measurements. Using a globular diffusion model for methanol, the data yield a diffusing globule mass of ~ 3.5 molecules, in good agreement with association numbers determined by other techniques.

The simple diffusion model fits the data for CH$_3$SH with a diffusion constant of 6.5×10^{-5} cm^2 sec^{-1}. This should be considered to be an upper limit for the diffusion coefficient of CH$_3$SH because of the limitations of the model used.

[25] B. Jacobson, Acta Chem. Scand. **9**, 997 (1955).
[26] E. D. Becker, J. Chem. Phys. **31**, 269 (1959).
[27] A. Ens and F. E. Murray, Can. J. Chem. **35**, 170 (1957).
[28] K. E. Larsson, L. Q. do Amaral, N. Ivanchev, S. Ripeanu, L. Bergstedt, and U. Dahlborg, Phys. Rev. **151**, 126 (1966).
[29] K. E. Larsson, Phys. Rev. **167**, 171 (1968).