| ESRF | **Experiment title:Quantum Effects in Liquid Methanol** | **Experiment number**: SC-448 |
|---|---|---|
| **Beamline**: ID15A | **Date of experiment**: from: July 8/98 to: July 12/98 | **Date of report**: Nov.23/99 |
| **Shifts:** | **Local contact(s)**: Veijo Honkimaki | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

Bruno TOMBERLI*, Peter EGELSTAFF, Department of Physics, University of Guelph, Guelph, Ontario, Canada, N1G2W1

Chris BENMORE*, ISIS Facility, Rutherford Appleton Laboratory, Chilton,Didcot, Oxon OX11 0QX UK

Veijo HONKIMAKI*, European Synchrotron Radiation Facility BP 220, F-38043 Grenoble Cedex, France

**Report**:

Molecular fluids at room temperature are often assumed to be comprised of classical, rigid heavy molecules. However, for hydrogenous molecules, quantum corrections to this model are required. In these experiments we have compared the static structure factor, S(Q), before and after H to D substitutions at varying sites . Because the H and D isotopes have a different mass and both contribute one 1s electron, any observed change in electronic structure factors is due to quantum-induced differences.

These investigations on beamline ID15A represent the first time that such measurements have been attempted using synchrotron radiation at ESRF. Previous studies using fixed γ-ray sources [1-3] may be improved by using a higher level of precision. Firstly, $H_2O$ and $D_2O$ at 297 K were studied. Agreement with the careful X-ray measurements of S(Q) for water by Narten [4] were good in each case, but in our experiments better comparative techniques were employed. Subsequent measurements involved four isotopes of methanol: $CH_3OH$, $CD_3OD$, $CD_3OH$, and $CH_3OD$ at the same temperature.

A beam energy of approximately 116 keV was incident on liquid samples contained in small diameter (3 mm) thin walled (10 μm) silica tubes. This reduced multiple scattering and background effects considerably. Isotopically pure (total impurities less than 0.3%) samples were then carefully sealed in the vessel to prevent contamination. Beam variation effects were minimized by interleaving and averaging a number of 40 minute scans (typically 8 for each isotope). Each isotope was held in a different tube which required an individual empty vessel measurement (typically 3 runs for each tube). Due to the high intensity of the synchrotron radiation, the necessary counting statistics were acquired much more rapidly on ID15A than in previous γ-ray experiments [1-3]. Temperature variation was within ± 1 K over each difference measurement. The raw detector counts required correction for background, detector dead-time, varying beam current, beam polarization, multiple scattering and attenuation. The spectrum is then normalized to the Klein-Nishina corrected Compton spectrum plus the form factor [5] at high Q to obtain the static structure factor in absolute electron units. Slight corrections for the intramolecular structure, based on the independent atom model, were used in the high Q normalization. Unlike previous experiments of this kind [1], a separate high-scattering-angle Compton detector was not employed.

S(Q) was measured for both $H_2O$ and $D_2O$ over a range of 0.4-20.3 $Å^{-1}$ in steps of approximately 0.1 $Å^{-1}$. Methanol samples were measured over the same Q range in steps of 0.05 $Å^{-1}$ for $CH_3OH$, $CD_3OD$ and $CD_3OH$ and $CH_3OD$. Satisfactory agreement with previously published results was obtained [1,4,6]. Additional corrections for residual intramolecular structure at 15-20 $Å^{-1}$ were found to affect results by approximately 0.01 % for $H_2O$ and 0.2% for methanol. There are six possible $\Delta S_x(Q)$ isotopic differences for methanol from our measured results. The $CH_3OD$-$CD_3OH$ difference is shown in Figure 1. Our precise measurements show observable differences which are due to quantum mechanical effects.

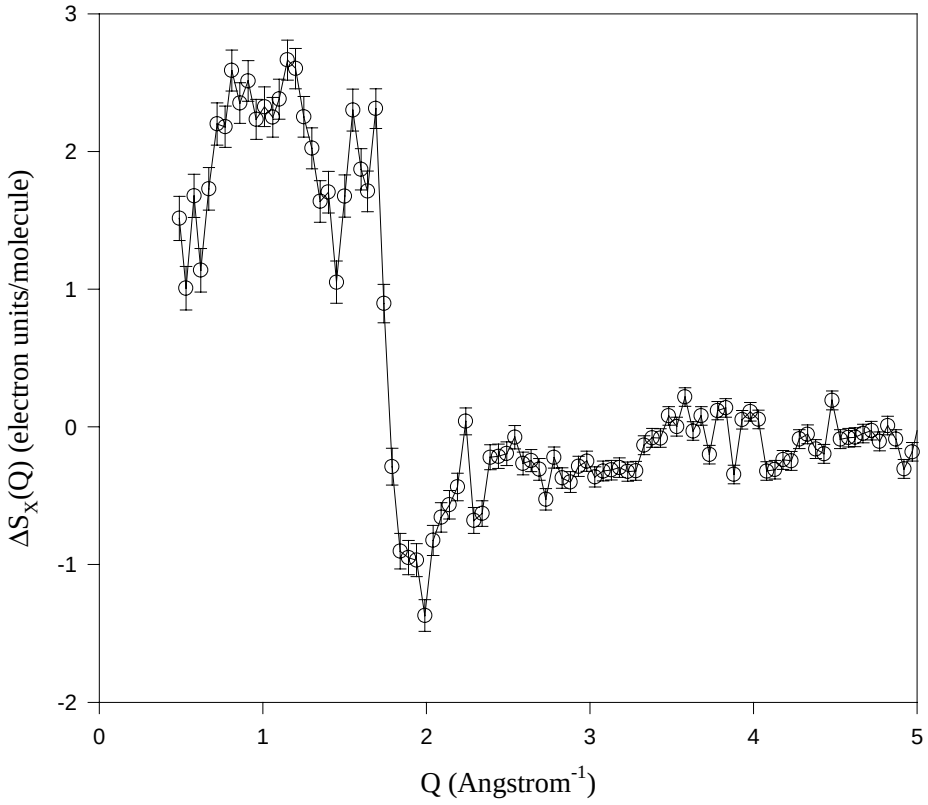


Figure 1: Isotopic substitution effect in methanol at 297 K

## Summary

The liquid structure factor data analyzed show that quantum effects may be observed in many hydrogenous liquids at room temperature. The data will provide stringent tests on theoretical intermolecular potentials used (for example) in liquid state (quantum) computer simulations. In the future, these results will be compared to other calculations based on partial nuclear correlation functions available from neutron scattering.

## References

[1] J.H. Root, P.A. Egelstaff, and A. Hime, Chem. Phys. **109**, 5164 (1986)
[2] S. Takeda, and P.A. Egelstaff, Can. J. Phys. **73**, 735 (1995)
[3] C.J. Benmore, and P.A. Egelstaff, J. Phys. Condensed Matter. **8**, 9429 (1996)
[4] A.H. Narten, ORNL Report # 4578 (1970)
[5] J.H. Hubbell, W.J. Veigele, E.A. Briggs, and R.J. Howerton, J. Phys. Chem. Ref. Data **4**, 471 (1973)
[6] A.H. Narten and A. Habenschuss, J. Chem. Phys. **80**, 3387 (1983)