ESRF

Experiment title: The Molecular Structure of Simple Amides

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The Molecular Structure of Simple Amides

Introduction: A characteristic property of the simple amides R_1-C=O-NHR_2 formamide FA (R_1=R_2=H), N-methylformamide NMF (R_1=H, R_2= CH3) and N-methylacetamide NMA (R_1=R_2=CH_3) is its high melting and boiling point. This is due to the intermolecular hydrogen bonding between the oxygen and the amide-hydrogen atom. This type of hydrogen bonding is omnipresent in all forms of living matter and determines the structure of the proteins. Dimethylformamide DMF ($HCO\text{-}N(CH_3)_2$) on the other hand has no possibility y to build a strong N-H. .0 hydrogen bond.

Another consequence of the hydrogen bonding is a modification of the intramolecular structure between the solid and the gaseous state [1, 2]. Hydrogen- bonding results in a increased delocalization of the n-electron system in the O=C–N moiety and hence a longer O=C and a shorter C–N bond length in the solid state. The question to pose is whether the intramolecular structure in the liquid is more gas- ore more solid like. In other words: Is long range order a necessary condition for the mentioned modification of the intramolecular structure?

Experiment: The experiments were carried out at the triple-axes diffractometer at BL 5, ID 15. The monochromator was placed on the monochromator-, the sample on the analyzer-axis. The sample-axis was unused. The energy was selected to be 100.2 keV, with an energy resolution of about 0.7%. Samples of the abovementioned amides FA, NMF, NMA and DMF have $Qi(Q)_{model}$ been investigated in a plane sample container. The sample thickness was 4 mm, the thickness of the glass windows 130 pm. The momentum transfer range covered was $3\text{Å}^{-1} < Q < 23\ \text{Å}^{-1}$ ($27\ \text{Å}^{-1}$ for NMF), with $Q = 4\pi/\lambda\sin(\theta)$ and 20 the scattering angle.

Both, the statistical accuracy and the reproducibility of the scans were at the O.l% level and thus an order of magnitude better as in the previous measurement on NMF (at BW7, HASYLAB), which is now 4 years old. This is demonstrated in Fig. 1 and 2.

Data analysis : The resulting $Qi(Q)$ of NMF is shown in Fig. 3, $Qi(Q)$ being defined by:

$$Qi(Q) = Q\frac{I_{exp} - S_{Compton} - (\sum^{uc} f_i)^2}{\sum^{uc}(f_i)^2} \qquad (1)$$

where I_{exp} is the experimental normalized intensity, corrected for dead time, absorption, multiple scattering and polarization, $S_{Compton}$ is the Compton scattering intensity taken from the respective tables, f_i are the atomic form factors equally taken from tables [3] and the sums are extended over the unit (molecular) composition. At Q values greater about 5 Å^{-1}, $Qi(Q)$ is dominated by intramolecular scattering given by:

$$Qi(Q)_{model} = \frac{1}{(\sum f_i)^2} \sum_{ij} f_i f_j \frac{\sin(Q r_{ij})}{r_{ij}} \exp(-Q^2 \gamma_{ij}/2.)$$

Fitting the C=O and the C-N distances to the experimental $Qi(Q)$ yields for NMF 1.240_9 Åand 1.299_{10} Å. This is to be compared with 1.22 Åand 1.35 Å, which were quoted for the gas phase (determined by microwave spectroscopy, gas phase electron diffraction and quantum mechanical calculations). The intramolecular scattering intensity $Qi(Q)_{model}$ corresponding to this model is compared to the experiment in Fig.3. The preliminary analysis of the other data shows that the C=O and C-N distances have a comparable length in FA and NMA, while in DMF the fit yields 1.228_3 and 1.349_2. So, all evidence accumulated so far indicates that the question posed in the introduction has to be answered with: No!

Figure 1: Reproducibility test
Relative deviation of one scan from the mean of all scans. A running average over 30 points is added as a guide of the eyes.

Figure 2: Comparison with a previous measurement on NMF
Solid line: New measurement, Diamonds: Old Measurement at BW7, HASYLAB

Figure 3: Comparison between the fitted model and the experimental data for NMF

References

[1] T. Ottersen, A. Chem Scan. A29 (1975) 939

[2] M. Kitano, K. Kuchitsu, Bull. Chem Sot. Jpn. 47 (1974) 67

[3] J. H. Hubbell et al. J. Phys. Chem. Ref. Data 4 (1975) 471

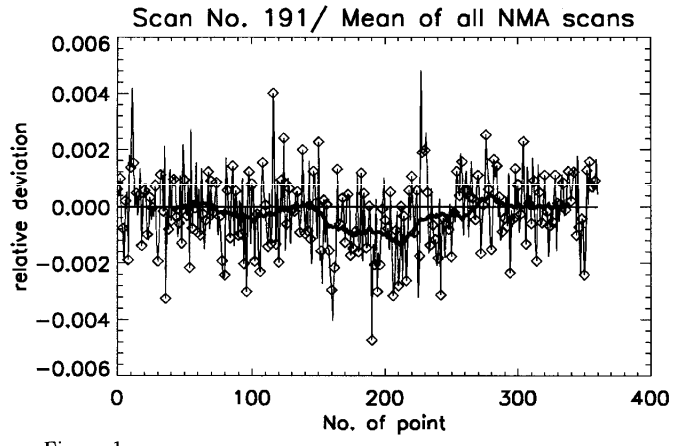

Figure 1

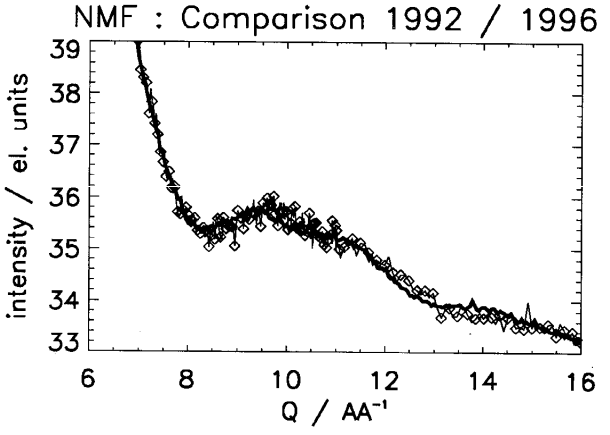

Figure 2

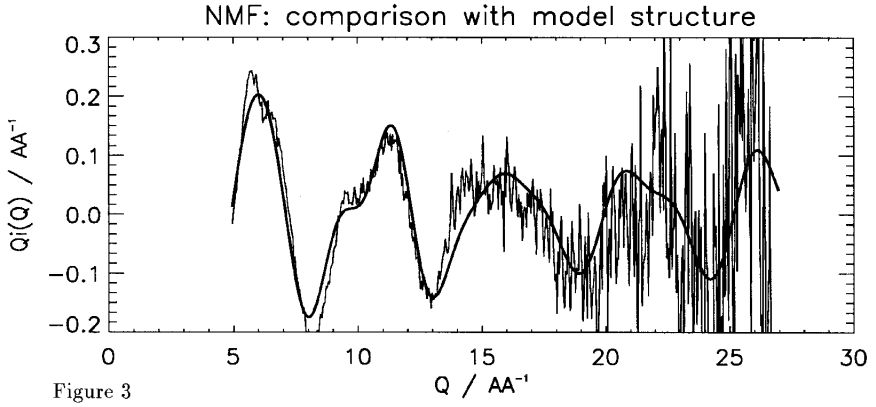

Figure 3