High-Field ^{17}O NMR Investigation of Hydrogen Bond Dynamics in Benzoic Acid

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Introduction

Carboxylic acid dimers are model systems that have been used extensively to study hydrogen bond dynamics. The pair of hydrogen atoms involved in hydrogen bonding undergo quantum tunneling in a double energy well. The tunneling energy barrier and the asymmetry of the double-well system are sensitive to crystal packing and vary among different carboxylic acid compounds. This ^{17}O NMR study of benzoic acid using the 900 MHz ultra-wide bore magnet is reported. It is found that the chemical shift of the two carboxylic ^{17}O nuclei varies with temperature as a result of the hydrogen tunneling dynamics.

Experimental

Experiments were performed on a 21.1 T ultra-wide bore magnet at the NHMFL equipped with a Bruker Avance III console. A home-built 3.2 mm transmission line MAS probe with extended variable temperature range was used.

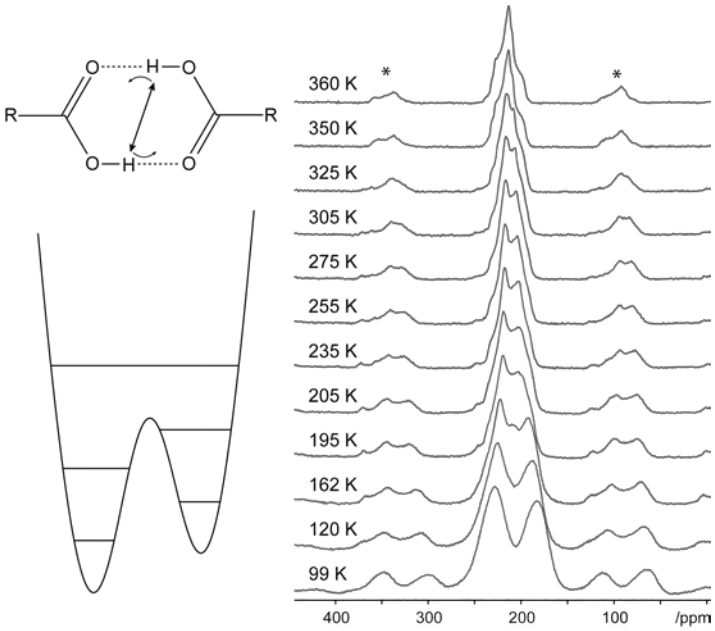

Figure 1 Carboxylic acid dimers with hydrogen pair tunneling between two asymmetric potential wells. The ^{17}O spectra of deuterated benzoic acid were acquired at 21.1 T with a 15 kHz magic-angle spinning rate at various temperatures. Asterisks (*) indicate spinning sidebands. Schematics of hydrogen bonding confirmation between carboxylic acid dimers, and asymmetric potential well associated with observed spectra.

Results and Discussion

Figure 1 shows ^{17}O magic-angle spinning spectra of deuterated benzoic acid acquired at 21.1 T with the full temperature range of the probe. At room temperature and above, the spectra seemingly consists of a single site indicating a complete average of the two carboxyl oxygen sites due to the rapid concerted tunneling of the two hydrogen atoms as indicated in the figure. The signal starts to split when lowering the temperature and the separation increases when the sample is cooled down further. The shift separation is the result of an asymmetric double potential well. The asymmetric low-energy states become more populated at low temperatures resulting in an incomplete average of the carbonyl and hydroxyl oxygen sites. Hydrogen bond dynamics in carboxylic acid dimers has been previously studied using ^{1}H, ^{2}H and ^{13}C NMR.[1] The use of ^{17}O NMR is advantageous for the study of carboxylic acids because direct measurement of the chemical shift for the two chemically non-equivalent sites is possible. Considering that spin-5/2 ^{17}O nuclei have significant quadrupolar broadening, high magnetic fields are essential for NMR measurement, since broadening is reduced while chemical shift separation is increased. Analysis of the spectral temperature dependence will afford detailed information of the asymmetric double potential well and is currently under way.

Conclusions

High field ^{17}O NMR shows that the chemical shift of the two oxygen sites in benzoic acid varies with temperature. This temperature can be explained by the tunneling of the pair of hydrogen atoms in an asymmetric potential well.

Acknowledgements

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References

[1] Stöckli, A., *et al*., J. Chem. Phys., **93**, 1502 (1990).