H_2 NMR line shapes for orientational ordering study

Kiho Kim [a,1], N. S. Sullivan [b], J. R. Bodart [c]

[a] *Department of Physics, University of South Alabama, Mobile, AL 36688, USA*
[b] *Department of Physics, University of Florida, Gainesville, FL 32611, USA*
[c] *Department of Natural Sciences, Chipola Junior College, Marianna, FL 32446, USA*

Abstract

A peculiar NMR line shape was reported [1] for a study of orientational ordering in submonolayer films of H_2 molecules adsorbed on hexagonal boron nitride. This low-temperature (below 200 mK) NMR line shape was seen for relatively high ortho-H_2 (o-H_2) concentration ($0.48 < x[o-H_2] \leq 0.69$) and was interpreted as a signature of the hindered rotor state. Preliminary results of recent computer simulations for the NMR line shapes of H_2 molecules, however, indicate that the peculiar NMR line shape may be the result of a combination of three different NMR line structures, and suggest possible well-defined clusters in two dimensions with three different order parameters dominating the orientational ordering. In addition to the hindered rotor line shape, the order-parameter dependence of the quadrupolar glass NMR line shape will be discussed.

Key words: NMR; Hydrogen; Orientational Ordering;

1. Introduction

Simple diatomic H_2 molecules form a "frustrated" system when adsorbed on BN because of the nature of the hexagonal substrate. Previous studies [1] have shown that the frustration of H_2 molecules plays a very important role in orientational ordering in 2D. In solid H_2, the two molecular species, ortho molecules (orbital angular momentum, $J = 1$) and para molecules ($J = 0$), are randomly distributed on the adsorbing sites of the BN substrate. The ortho molecules interact via the short range orientationally dependent electrostatic quadrupole–quadrupole interaction (EQQ) interaction, whereas the para molecules play the simple role of an inactive diluent. The EQQ interaction favors a "T" formation for an isolated pair, but all the pairs of quadrupoles on a BN substrate cannot reach their minimum energy state in any many body ground state. The combined effect of frustration and disorder already displayed a glassy behavior, i.e. molecular orientations frozen without any long range order at low temperatures and intermediate concentrations ($0.2 \leq x \leq 0.55$) for 3D samples [3]. Also, this glass behavior was seen in 2D in our previous studies.

2. The simulated NMR spectra

We have reported the results for NMR studies [1] of the orientational ordering in 2D for submonolayer to thick-layer samples of molecular hydrogen adsorbed on hexagonal boron nitride (BN). One of the most important observations was the appearance of an extremely unusual NMR line shape seen in submonolayer films of H_2 molecules on BN for ortho concentration($0.48 < x[o-H_2] \leq 0.69$) at low temperatures (below 200 mK). (Refer to Fig. 1.) We had qualitatively interpreted this NMR line shape as a signature of hindered rotors in 2D which agrees well with previous theoretical predictions [2]. However, we were unable to fit the submonolayer NMR line shape to any hindered rotor line with a distinct order parameter. We present our efforts to resolve the peculiar experimental NMR line shape using computer simulations which allow mixtures of different order parameters for different environments on the BN substrate. Preliminary results suggests clusters of H_2 molecules with relatively distinct order parame-

[1] E-mail:kkim@jaguar1.usouthal.edu

ters and a local distribution of order parameters in the glass state.

Consider an ortho molecule i carrying a total nuclear spin $I = 1$ whose energy levels are determined by the intramolecular dipolar Hamiltonian:

$$H_{DD} = d\sigma_i(\frac{3}{2}I_z^2 - 1)(3\cos^2\theta_i - 1) \quad (1)$$

where $d = 57.67$ kHz. The computer simulations of the NMR line shapes were based on two hypotheses:(i) the fluctuations of the molecular orientation are very fast compared to the relevant frequency for the NMR line shape measurements, i. e. the intramolecular dipolar frequency d. In this case, NMR line shapes depend only on a single particle thermodynamic average, and therefore can be used to determine the local reduced

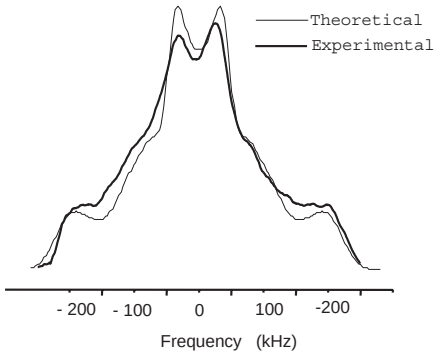

Fig. 1. The hindered rotor NMR line shape.

density matrices σ_i. (ii) The average orbital moments are all zero. The quenching of the orbital moment is a common feature of many physisorbed hydrogens as well as bulk systems [4]. In the local frame of each molecule i the matrix representing σ_i is diagonal, and therefore there is only one non-zero quadrupole moment. For a powdered sample, one can write the NMR spectrum $S(\omega)$ as:

$$S(\omega) = \{\int_{-\frac{1}{2}}^{1} dxP(x)\prod(x,\omega)\} \cdot g(\omega)\} \quad (2)$$

where $\prod(x,\omega)$ denotes the well-known Pake doublet of frequency span $6d$ and $g(\omega)$ an appropriate convolution function which takes into account the intermolecular dipolar broadening. For the sake of simplicity, we have approximated the Fourier transform as the product of a Lorentzian and a Gaussian of appropriate widths:

$$g(\omega) \propto \frac{exp(-\frac{\omega^2}{3.1\Delta^2})}{1 + (\frac{\omega}{\Delta})^2} \quad (3)$$

with $\frac{\Delta}{2\pi} = 7.2\sqrt{X}$ kHz.

A simulation program was written in such a way that for a fixed Gaussian broadening function, the order parameter was allowed to change from zero to unity and vice versa. A theoretical NMR line shapes could not be found for the hindered rotor line shape of H_2 submonolayers using a single order parameter. However, the matching simulated NMR line shape shown in Fig. 1 was obtained from the combination of three NMR line shapes with order parameters $\sigma = 0.19, 0.5, 0.95$. Also, the interesting part of these simulations occurs in the region $0.15 < \sigma < 0.4$, which is characterized by the quadrupolar glass ordering phase. The quadrupolar glass line shapes should be understood in terms of a broad distribution of the order parameters and have a noticeable shape. Fig. 2 shows simulated NMR line shapes characteristic of this region for the order parameters $\sigma = 0.2, 0.25, 0.3, 0.35, 0.4$.

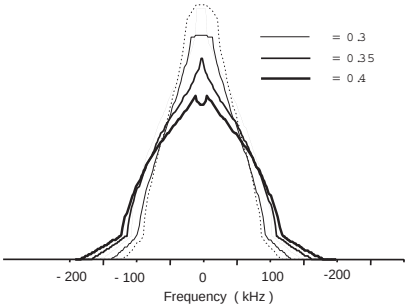

Fig. 2. The order-parameter dependent NMR line shapes for quadrupolar glass ordering.

3. Conclusion

The preliminary results given here lead to a very different interpretation of that reported previously for the hindered rotor line shape. The combination of order parameters used in the simulated NMR line shape indicates that there were clusters with well-defined order parameter for ortho concentrations $0.48 < x < 0.69$. This very complex NMR line shape is far from being completely understood. The behavior of the glass ordering is quite spectacular. The simulation indicates that the glass ordering may be extended into the very low ortho concentration regime ($x = 0.15$).

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