Nuclear Magnetic Resonance in Solid H₂ and D₂ under High Pressure*

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Nuclear magnetic resonance data are presented for solid H_2 and D_2 between 1.5 and 4.2°K and at pressures up to 5500 atm. For solid hydrogen, the ortho-para conversion, the transition temperature T_λ from the state of free rotation to that of a more ordered state, and the linewidth and second moment above T_λ have been measured as a function of density ρ and ortho concentration. The ortho-para conversion rate is approximately proportional to $\rho^{2.4}$ and the transition temperature T_λ for a given ortho concentration is roughly proportional to $\rho^{2.0}$. These results are compared with other experimental evidence and with theoretical expectations. The second moment for both H_2 and D_2 (the latter with an ortho concentration of 0.67) is compared to that calculated for the dipole-dipole interaction in a rigid lattice having the structure and dimensions determined from x-ray and neutron data. The experimental second moments are found to be larger than the calculated ones, and the discrepancy is discussed.

I. INTRODUCTION

BOTH solid H_2 and D_2 are interesting compounds to investigate by nuclear magnetic resonance (NMR) and such work has been reported in several papers.[1–7] Both solids are a mixture of two modifications, ortho and para, and can in principle be prepared with any ortho concentration[8] although this operation may be very difficult in some ranges of the ortho concentration. In H_2, the ortho molecule, in which both nuclear spins are parallel ($I=1$), will be the only one to give a nuclear resonance signal. In D_2, the part of the ortho modification with $I=2$ as well as the para state ($I=1$) will give a resonance signal. At low temperatures the para state is the stable one for H_2 as it has the lowest energy. For D_2 the ortho state is stable at low temperatures. Although for isolated molecules the selection rules prohibit transitions from one state to another, there is, in fact, a slow conversion when molecules interact. Such a conversion has been calculated for solid H_2 by Motizuki and Nagamiya.[9] The calculated values of the conversion rate dc/dt are in good agreement with the experimental ones,[5,7] about 1–2%/h for a 75% ortho composition. Since this conversion depends on the magnetic-dipole interaction, deuterium, which has a smaller dipole moment than hydrogen, has a conversion rate

from para to ortho which is calculated to be of the order of 0.03%/h for a 67% ortho mixture.[10] Recently this small conversion has been observed experimentally.[11]

At normal density, early NMR experiments on both isotopes showed three temperature regions to be considered:

(I) Above about 8°K, there is diffusion as well as free rotation in the solid. The line is narrow because of the molecular motion.

(II) In a certain temperature range below 8°K, the linewidth is practically constant and considerably broader than in region I. There is only rotation in the solid and the linewidth can be interpreted qualitatively in terms of the intermolecular dipole-dipole interaction.[1,2]

(III) Below a temperature T_λ there is a gradual alignment of the rotational angular momentum J in preferred directions and hence the intramolecular dipole-dipole interaction is no longer averaged out. The effect of the transition on the NMR spectrum has been analyzed quantitatively by Reif and Purcell.[2] Until recently, such a change in the line structure has been detected only for H_2, for which systematic investigations of the dependence of T_λ on the ortho concentration c at normal density have been carried out.[4,7] For D_2, evidence of a transition has recently been deduced from specific-heat[11] and NMR[12] data for low ortho concentrations.

A further step in the NMR study was to extend the measurements to high pressures. Both solids show a density increase of 60% for an applied pressure of about 6000 atm, and hence one expects to be able to observe the density dependence of many properties with relative ease. For instance the second moment M_2 of the resonance line above T_λ broadened by intermolecular dipole-dipole interaction is a strong function of intermolecular distance. The transition temperature T_λ of H_2 is also predicted to be a function of density as well as ortho

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