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OBSERVATION OF MOLECULAR MOTION IN SOLID H_2 BELOW 4.2°K

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NMR measurements in solid H_2 at low ortho concentrations between 0.4 and 4.2°K show that the equilibrium distribution of ortho molecules in the lattice is temperature dependent and is approached approximately exponentially in time at a given temperature. It is suggested that the rearrangement process occurs by means of ortho-para interchange.

Studies of the "classical" thermally activated self-diffusion show that the molecular motion in solid H_2 slows drastically as the temperature decreases.[1,2] Using the well-known relation

$$\langle x^2 \rangle = 2Dt, \qquad (1)$$

where $\langle x^2 \rangle^{1/2}$ is the rms displacement in the time t and D is the diffusion constant $D = 1.3\times10^{-3} \times\exp(-190/T)$ cm^2 sec^{-1}, one can see that diffusion through three lattice spacings $3a_0$, where $a_0 = 3.76\times10^{-8}$ cm,[3] takes a time of the order of 10^4 h at 4.2°K.

We report an experiment between 0.4 and 4.2°K which shows molecular motion that is much faster and we suggest that the mechanism is the interchange of ortho and para molecules in their lattice sites. The measurements consist of recording by means of NMR the number of isolated ortho molecules as a function of time at constant temperature, after making an initial temperature change from equilibrium conditions.

This experiment can be understood as follows: Since each ortho molecule has twelve nearest neighbors, the probability that randomly distributed ortho molecules will have no nearest ortho neighbor is

$$P_s = (1-c)^{12}.$$

In samples with an ortho concentration below $c = 0.01$ and at high temperature, where the molecules are randomly distributed on the lattice, less than 1% of the ortho molecules have more than one nearest ortho neighbor. For simplicity, then, we will consider a system consisting of isolated single ortho molecules and ortho pairs in a background of para-H_2, but the argument that follows can be extended to include higher ortho configurations. All ortho molecules that are not "isolated" are assumed to be in pairs; so the random pair probability is

$$P_p = 1 - P_s. \qquad (2)$$

We make the approximation that the three rotational levels of an isolated ortho molecule are degenerate, since the crystalline field splitting is small[4] and we neglect next nearest-ortho-neighbor interaction. The partition function for a single molecule is then $Z_s = 3$. The nine energy levels of the isolated pair are split by electric quadrupole-quadrupole (EQQ) interaction[5] and the partition function of the pairs is then

$$Z_p = 2\exp(4\Gamma/kt) + 4 + 2\exp(-\Gamma/kT) + \exp(-6\Gamma/kT), \qquad (3)$$

where Γ is the EQQ coupling constant with a value $\Gamma/k = 0.82$°K in solid H_2[6,7] at zero pressure.

The equilibrium distribution between the two configurations can be calculated from the partition function per ortho molecule which is found from standard statistical methods to be

$$Z = Z_s P_s + Z_p^{1/2} P_p. \qquad (4)$$

The equilibrium numbers of single ortho molecules and isolated ortho pairs are given, respectively, by

$$N_{sE}/N = P_s Z_s/Z;\quad N_{pE} = N - N_{sE}, \tag{5}$$

where N, the total number of ortho molecules, is constant because at such low ortho concentrations the ortho-to-para conversion is very small. The system of ortho molecules will tend to redistribute so as to achieve thermodynamic stability. If there is no diffusion, the high-temperature random distribution will remain "frozen in." This situation has been tacitly assumed in previous work.[8]

The system's approach to equilibrium will in general be quite complicated. In addition to formation and dissociation of ortho pairs, triangular and even larger ortho molecule clusters must be included in the calculation since their concentration is not negligible at the lower temperatures. Hence we have sought in preliminary fashion to analyze the data according to a simple exponential expression,

$$N_s(t) - N_s(t=\infty) = [N_s(t=0) - N_s(t=\infty)]\exp(-t/\tau). \tag{6}$$

The rate constant τ^{-1} is directly related to the rates of ortho-para interchange and ortho molecule cluster formation and dissociation. The rate τ^{-1} will also be a function of ortho concentration.

Nuclear magnetic resonance allows the observation of this effect since at these low ortho concentrations, the single molecules give a sharp absorption line, while ortho pairs give a symmetric structure about this line,[6] well resolved from it, and the triangles give a broader background.[6]

In the experiment, it is observed that the width of the central line is constant at a given temperature, and therefore, the number of isolated ortho molecules N_S is taken to be proportional to the height of the maxima of the NMR line derivative. Observation of the central line as a function of time at a given T shows then the change of the number N_S until an equilibrium value N_{SE} is reached.

The NMR absorption was observed by means of a low-level Robinson[9] spectrometer, the frequency of which was slowly swept through resonance while the derivative of the line was plotted by a chart recorder. Careful checks were made on the stability of the electronics by periodically recording the intensity of the F^{19} resonance from the Kel-F sample container. Checks were also made on possible saturation effects, but these were found to be absent. Observations of the derivative of the H_2 spectrum were made over periods up to 60 h at a given temperature between 0.4 and 4.2°K. After a decrease of T, the central line was found to diminish with time, and became faint at 0.4°K as expected from Eqs. (3) and (5). The area of the NMR absorption away from the central line was found to have increased with time, as was expected. After warming the sample, the central line became more intense with time. In Fig. 1 a semilogarithmic plot shows the progress to equilibrium to be reasonably exponential in time. Figure 2 gives the value of τ^{-1} as a function of T for $c = 0.005$ and $c = 0.01$ and shows a tendency for τ^{-1} to increase

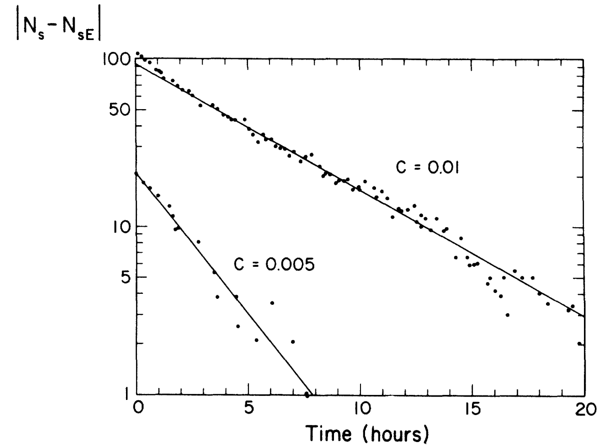

FIG. 1. Two representative examples of the exponential approach to equilibrium by means of molecular rearrangement in solid H_2. The curves at $T = 0.57$°K (upper) and $T = 3.3$°K (lower) were obtained after respectively cooling and warming the sample.

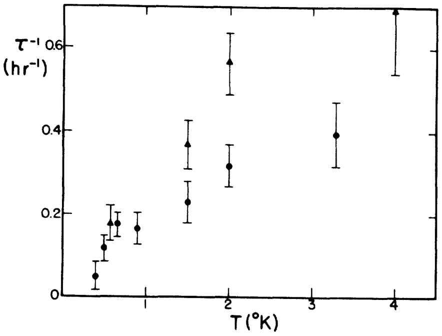

FIG. 2. The factor rate τ^{-1} that characterizes the approach to thermodynamic equilibrium. Circles: $c = 0.005$. Triangles: $c = 0.01$.

with c. Further experiments are needed to obtain a more precise limiting value as the temperature approaches 0°K.

In principle, it is possible to compare quantitatively the experimental value of N_{SE} with that obtained from theory. This is made difficult, however, by the uncertainty in several experimental parameters and by the simplifying assumptions made in deriving Eq. (4). Calculations including more complicated ortho-molecule configurations are in progress.

The ortho-cluster formation is expected to enhance the rate of ortho-to-para conversion since this rate depends on the interaction between ortho molecules. The observation of this effect is difficult. However, one can place an upper limit on it from the ortho analysis before and after the experiments and from the estimated time the samples spent below 1°K, where the equilibrium cluster concentration becomes appreciable. The upper limit was found to be $dc/dt = 2\times10^{-5}$ h^{-1} for $c = 0.005$.

The redistribution of ortho molecules with temperature will affect the thermodynamic properties, as can be expected from Eq. (4), and the implications of the present work on any measurements in solid H_2 at low ortho concentrations are obvious. Unless the temperature is changed slowly or quickly in comparison with τ, the results will not reflect an equilibrium state. For measurements short in comparison with τ, the physical properties will be representative of a "frozen in" distribution of ortho-H_2 molecules.

Measurements of pressure versus time at constant volume and temperature being carried out presently in another cryostat[7] are consistent with those presented in this paper. These same measurements[7] failed to detect any evidence of motion of para-D_2 molecules in solid D_2. Proton NMR measurements similar to those described above did not detect motion of isolated ortho-H_2 molecules in a solid mixture 1% H_2-99% D_2. This shows that, as expected, interchange of lattice position between H_2 and D_2 does not take place.

It is hoped that these experiments will stimulate theoretical calculations on the ortho-para-interchange effect and the ortho-cluster formation and dissociation rate.

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