

# Behavior of hydrogen and deuterium atoms in a solid solution of $H_2$ in $D_2$ at liquid-helium temperature

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Only the quantum exchange reactions  $D + H_2 \rightarrow HD + H$  and D-D recombination occur at  $T < 5.9$  K in a solid solution of  $H_2$  (1-4%) in  $D_2$  with impurity H and D atoms. The experiments reveal a localization of H atoms near a molecular impurity.

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## INTRODUCTION

Impurity hydrogen atoms in a crystal of molecular hydrogen represent a case of a "quantum impurity in a quantum crystal." The quantum properties of the system become quite apparent in, for example, the quantum diffusion of H atoms in solid  $H_2$  at  $T \lesssim 4.2$  K, which gives rise to a recombination of the hydrogen atoms.<sup>1-4</sup> Also of some interest are other reactions involving hydrogen atoms: the isotope exchange reactions  $D + H_2 \rightarrow HD + H$  (a) and  $H + D_2 \rightarrow HD + D$  (b), which at  $T = 4.2$  K can occur only by tunneling because of the high activation energy (several thousand degrees<sup>5</sup>).

Reaction (a) was observed to occur at  $T = 4.25$  K in the " $D + H_2 + D_2$ " solid mixture in Ref. 6. It was shown in the same study that reaction (b) does not occur (because it is endothermic). Gordon *et al.*<sup>7</sup> have reported observing a quantum isotope-exchange reaction.

In this letter we report a study of an isotope exchange reaction in a solid phase at liquid-helium temperature. The experimental apparatus was a modification of that which we have used previously to study the recombination of H and D atoms in the corresponding molecular matrices by an ESR method.<sup>1,3,4</sup> The apparatus was modified to allow simultaneous condensation on a cold substrate of two independently transported beams (for example, a beam of D atoms and a beam consisting of a mixture of  $H_2$  and  $D_2$ ).

## EXPERIMENTAL RESULTS

I. It was shown in Ref. 6 that the exchange reaction occurs effectively even while the sample is being prepared. When a beam of D atoms and a beam of the molecular mixture  $H_2 + D_2$  are deposited simultaneously on the cold substrate, the resulting sample therefore contains both D atoms and H atoms. Figure 1 shows the ratio of the atomic concentrations  $n_H^0$  and  $n_D^0$  measured immediately after the preparation of the sample as a function of the composition of the matrix; the actual coordinates here are  $\ln [n_D^0 / (n_D^0 + n_H^0)]$  and  $\ln d$ , where  $d = n_{D_2} / (n_{D_2} + n_{H_2})$ .

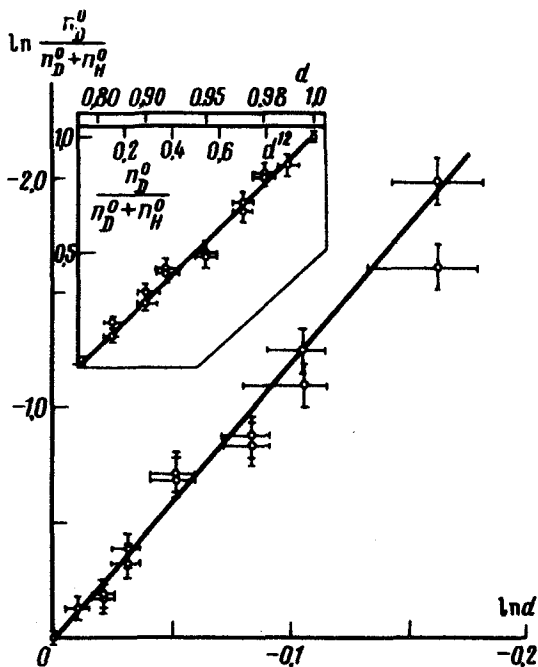


FIG. 1. Dependence of the ratio of the initial concentrations of H and D atoms on the relative number of  $D_2$  molecules in the matrix.

Let us assume that a deuterium atom at a lattice site in the crystalline matrix that forms undergoes an exchange reaction with a nearby hydrogen molecule  $H_2$  in a time shorter than the characteristic times of the preparation of the samples (on the order of a few minutes). If all the nearest neighbors are  $D_2$  molecules, the D atom survives. In this case the survival probability is  $d^Z$ , where  $Z$  is the number of nearest neighbors. We then have  $n_D^0 / (n_D^0 + n_H^0) = d^Z$ . The line in Fig. 1 corresponds to this expression with  $Z = 12$ . For clarity, the inset in Fig. 1 shows the same dependence but in terms of the coordinates  $n_D^0 / (n_D^0 + n_H^0)$  and  $d^{12}$ . For an hcp structure we would have  $Z = 12$ ; there would be an equal number of neighbors in, for example, two coordination spheres for a tetrahedral interstitial position in an hcp lattice. Accordingly, the exchange reaction which occurs when the sample is formed does so in a solid matrix, not on the growth surface and not in the gas phase.

II. Figure 2 shows the results of one of the experiments on the time evolution of the concentrations of H and D atoms in samples produced by the technique described above, with a concentration of  $H_2$  molecules in the range 1–4%. The increase in the concentration of H atoms in the sample over time at  $T = 5.23$  K is direct evidence of the quantum chemical exchange reaction (a). The concentration of H atoms eventually reaches a plateau, which then persists throughout the experiment ( $\sim 10^4$  s) at  $T < 5.9$  K. The concentration of deuterium atoms decreases even after  $n_H$  reaches the plateau. The decrease in the number of D atoms corresponds to a second-order recombination law; i.e., the decrease results from the recombination of D atoms with each other:

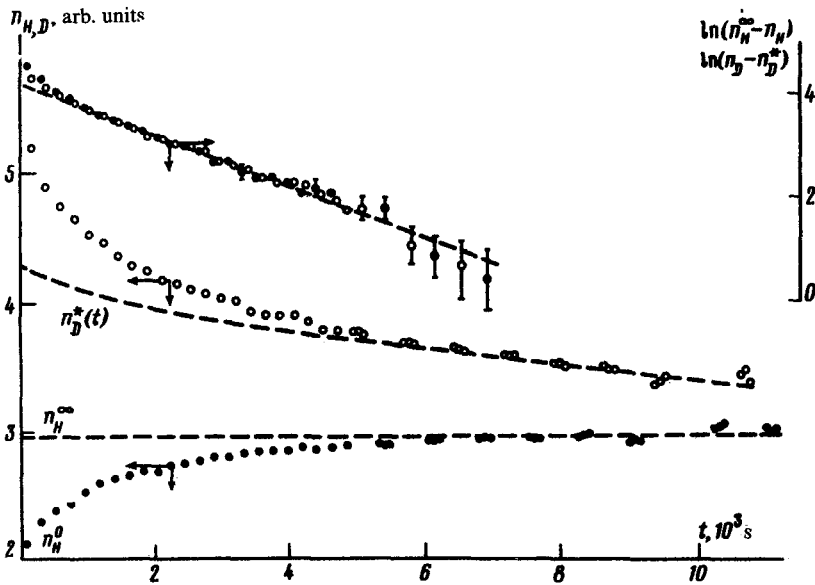


FIG. 2. Time evolution of the concentrations of H and D atoms at  $T = 5.23$  K. ● —  $n_H$ ,  $\ln[n_H^\infty - n_H(t)]$ ; ● —  $n_D$ ,  $\ln[n_D(t) - n_D^*(t)]$ .

$dn_D^*/dt = -2K_D n_D^{*2}$ . Here  $n_D^*(t)$  is the concentration of D atoms after  $n_H$  reaches the plateau. We also find  $n_D(t) - n_D^*(t) \approx n_H^\infty - n_H(t)$ ; i.e., nearly all of the D atoms which do not undergo D-D recombination take part in the exchange reaction. As Fig. 2 shows, the decrease in  $[n_D(t) - n_D^*(t)]$  {and the increase in  $[n_H(t) - n_H^\infty]$ } occurs by a first-order law:  $\frac{d}{dt}(n_D - n_D^*) = -\frac{1}{\tau}(n_D - n_D^*)$ . Accordingly, although H-H, H-D, and D-D recombination can occur along with the D-H<sub>2</sub> exchange reaction in our samples, only two reactions actually occur at  $T < 5.9$  K: the exchange reaction and the recombination of D atoms with each other. The H-H and H-D recombinations are largely suppressed.

## DISCUSSION OF RESULTS

We believe that this nontrivial circumstance can be explained as follows. A zone in which the diffusion of atoms is difficult forms around each H<sub>2</sub> (or HD) molecule in a D<sub>2</sub> crystal. The D atoms enter these zones primarily during the formation of the sample. These atoms are the ones which are responsible for the initial concentration of H atoms,  $n_H^0$  (Fig. 2), and the subsequent increase in this concentration over time. The D atoms outside these zones subsequently recombine with each other. The H atoms which are formed in the immediate vicinity of HD molecules are quasilocalized near these molecules. As a result, they become isolated from all the other atoms, so that the H-H and H-D recombinations do not occur to any great extent. The possibility of this localization of atoms follows, in particular, from the quantum theory for the diffusion of atoms in irregular crystals.<sup>8,9</sup> The strain energy of impurity H<sub>2</sub> and HD molecules in a D<sub>2</sub> crystal may substantially lower the energy levels for the H and D atoms in the

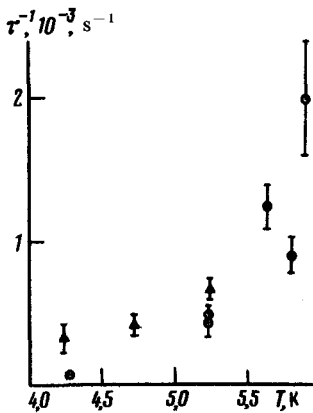


FIG. 3. Temperature dependence of the rate of the quantum isotope exchange reaction.  $\circ$ — $\text{H}_2$  concentration  $\sim 1\%$ ;  $\triangle$ — $\sim 3\%$ .

crystal. A zone which is difficult to traverse by diffusing atoms forms in the region of the pronounced lowering of levels near impurity molecules.

Figure 3 shows some preliminary results on the temperature dependence of the effective exchange rate,  $\tau^{-1}(T)$ , in  $\text{D} + \text{H} + \text{H}_2 + \text{D}_2$  samples with an  $\text{H}_2$  concentration  $\sim 1\%$  at  $T < 5.90$  K. Increasing the  $\text{H}_2$  concentration (to 3–4%) increases the rate of the exchange slightly. At temperatures above 6 K, the diffusion of atoms in the crystal becomes important (the diffusion involves an activation energy). At this point, the H-H and H-D recombination reactions “thaw,” greatly complicating the recombination kinetics in our samples and making it difficult to study the exchange reaction.

The localization of atoms near impurities observed by us in these experiments is apparently a common effect and can be exploited to increase the concentrations of atoms in inert matrices under quantum-diffusion conditions.

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