

Temperature dependence of the recombination rate constant of hydrogen atoms in solid H₂ at 1.5 K < T < 5.5 K

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A second-order recombination process occurs in the solid mixture H + H₂. At $T > 4.5$ K the rate constant for this recombination is $K(T) \sim \exp(-E_a/kT)$, with $E_a = 107 \pm 10$ K. The temperature dependence $K(T)$ in the region $1.5 \text{ K} < T < 4.3 \text{ K}$ apparently corresponds to a nonclassical diffusion of H atoms in H₂.

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The stabilization of atomic hydrogen in inert solid matrices has recently attracted interest.¹⁻³ The particular case of impurity H atoms in solid H₂ is interesting in that it is a system of a “quantum impurity in a quantum crystal” and may thus exhibit the properties of quantum crystals, e.g., quantum diffusion.⁴⁻⁶

In this letter we are reporting the first study of the recombination of atomic hydrogen in a solid H₂ matrix as a function of the matrix temperature. The H atoms in the H₂ were detected with a 3-cm EPR spectrometer.⁷

A beam consisting of a mixture of hydrogen atoms and molecules was formed in an rf dissociator, transported through a quartz tube into the high-vacuum zone of a helium cryostat, and condensed on the surface of a sapphire single crystal at $T = 1.5$ K in the microwave resonator of the EPR spectrometer. The resonator also con-

tained a calibration sample of Mn^{2+} in MgO with a known number of spins. The apparatus was thus capable of detecting the number of H atoms in the H_2 matrix and the change in this number over time through measurements of EPR spectra of the H atoms.

Let us outline the experimental procedure. The $H + H_2$ mixture was condensed for 10 min on a substrate whose temperature was about 2 K. Then the beam was cut off, and measurements were begun with the resulting $H + H_2$ sample. (During the condensation the amplitude of the EPR signal corresponding to the hydrogen atoms increased linearly, showing that the H atoms were distributed homogeneously in the H_2 matrix.)

For each of the samples we measured at least one (in several cases, both) of the hyperfine lines of the ESR spectrum of the hydrogen atoms in a series of measurements at constant time intervals. The line width (~ 1.5 G) did not change during the measurements, so that the signal amplitude A_H was proportional to the number of H atoms; since the number of molecules remained essentially constant, however, the signal amplitude was also proportional to the concentration of H atoms in the sample, n_H . The $A_H(t)$ dependence is thus equivalent to the $n_H(t)$ dependence. As an additional reference, we used the amplitude of the Mn^{2+} line.

For each sample, $n_H(t)$ was measured at several (four or five) temperatures; corrections for the temperature dependence of the sensitivity of the EPR spectrometer were made on the basis of separate measurements.

The results of one of the experiments, shown in Fig. 1 as a plot of n_H^{-1} vs t , agree well with the function $n_H^{-1} = n_{H0}^{-1} + 2Kt$. It may therefore be assumed that at these particular concentrations and temperatures the recombination rate of H atoms in an H_2 matrix is determined by the equation

$$\frac{dn_H}{dt} = -2K(T)n_H^2, \quad (1)$$

where $K(T)$ is the effective recombination rate constant, which does not depend on the concentration. The decay half-life of a sample with an initial concentration n_{H0} , measured directly in the experiments is $\tau = (2Kn_{H0})^{-1}$ according to Eq. (1). Since the concentration of H atoms could be different in the different samples, we measured $A_H(t)$ for each sample at $T = 4.3$ K. The constant $K(T)$ can thus be defined for various values of T as follows:

$$K(T) = K(4,3) \cdot \frac{(\tau n_{H0})_{4,3}}{(\tau n_{H0})_T}, \quad (2)$$

where $(\tau n_{H0})_T$ is the product of the decay half-life and the initial concentration at the temperature T . In all series of experiments we set $K(4,3) = 1$.

Figure 2 shows the results of several series of measurements in semilogarithmic scale. At temperatures $T > 4.5$ K we find $K(T) \sim \exp(-E_a/kT)$. The activation energy determined from this part of the dependence is $E_a = 107 \pm 10$ K. At $T < 4.3$ K, there is a sharp change in the behavior of $K(T)$.

The recombination of the H atoms in the H_2 matrix occurs through two succes-

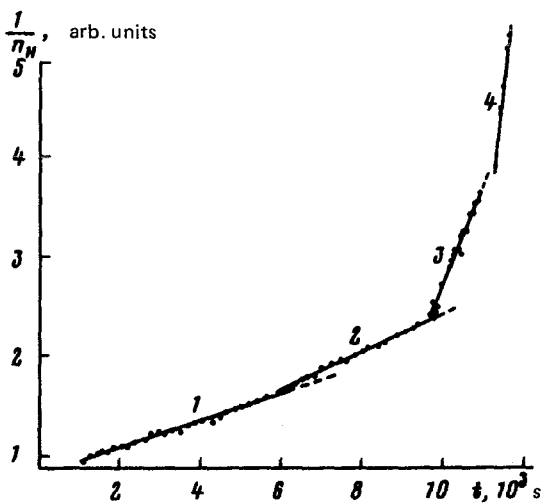


FIG. 1. Time dependence of n_H^{-1} at various matrix temperatures: 1—4.33 K; 2—4.62 K; 3—5.08 K; 4—5.27 K.

sive steps: a) Two H atoms close within a distance of the order of the lattice constant as a result of diffusion. b) A bound state of an H_2 molecule forms, and it gradually undergoes a transition to a lower-lying vibrational state, giving up energy to the lattice. Both of these processes depend on the temperature, but the temperature dependence is determined primarily by the diffusion step.

The most probable explanation for the results runs as follows: The region $T > 4.5$ K, in which $K(T) \sim \exp(-E_a/kT)$, corresponds to thermal diffusion with a diffusion activation energy of 107 ± 10 K.

If the temperature dependence $K(T)$ remained the same down to $T = 1.5$ K, we

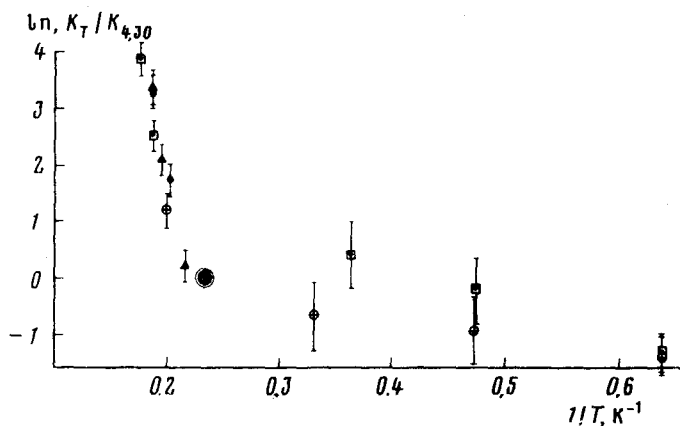


FIG. 2. Temperature dependence of the recombination rate constant $K(T)$ of H atoms in an H_2 matrix (the different symbols correspond to different samples).

could expect the characteristic decay half-lives of the system at $T=1.5$ K to be $\tau \sim 10^{24}$ s. The actual value at 1.5 K is $\tau \sim 10^4$ s. If we assumed an exponential temperature dependence at $T < 4.5$ K, we would end up with an unrealistic activation energy, $\lesssim 5$ K. The temperature dependence $K(T)$ in the region $1.5 \text{ K} < T < 4.5 \text{ K}$ thus corresponds to diffusion without an activation energy, apparently involving tunneling.

The absolute values of K are not known, since the absolute concentrations of H atoms are not known. Estimates of the concentration based on the flux density of molecules yield $n_{\text{H}} \sim 10^{-3} - 10^{-4}$. From this estimate we find $K \sim 3 \cdot 10^{-23} - 3 \cdot 10^{-24} \text{ cm}^3/\text{s}$ at $T=1.5$ K.

An estimate of the diffusion coefficient of the H atoms in H_2 under the assumption that the diffusion is far slower than the recombination yields $D(1.5 \text{ K}) \sim 10^{-17} \text{ cm}^2/\text{s}$.

Corresponding experiments with condensed mixtures of deuterium atoms in a D_2 matrix of roughly the same concentration showed that the $D+D_2$ samples are stable at $T < 5$ K. In this temperature range, the rate constant $K(T)$ for this system is smaller than for the $\text{H}+\text{H}_2$ system by a factor of at least 50.

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