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Quantum diffusion and catalyzed conversion of ortho-H_2 molecules in solid hydrogen

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The ortho-para conversion in solid hydrogen catalyzed by a small amount ($\sim 10^{-3}$) of O_2 impurities was studied to determine the temperature and concentration dependence of the ortho-H_2 diffusion coefficient. For $T > 5$ K the diffusion coefficient has the activation-type dependence on temperature $D(T) = 2\times 10^{-11} \exp(-92/T)$ cm^2 s^{-1} and is independent of the ortho-H_2 concentration C. For $T < 4$ K this coefficient substantially changes its behavior and for C in the range 0.02–0.75 it can be described by the relation $D(T,C) = 1\times 10^{-21} \cdot T/C$ cm^2 s^{-1}. The results obtained are interpreted in terms of the quantum diffusion of ortho-H_2 molecules in solid hydrogen.

I. INTRODUCTION

The conversion of ortho-H_2 molecules to the ground para-H_2 state in pure solid hydrogen occurs due to the weak magnetic dipolar interaction between ortho-H_2 neighbors. It is known to be a rather slow process.[1] However, this process can be substantially accelerated even by a small amount of paramagnetic impurities in the H_2 crystal, provided the diffusion of ortho-H_2 relative to impurities is fast enough.[2,3] The reason for the acceleration is the much stronger magnetic dipolar interaction between the paramagnetic impurities and nearby ortho-H_2 molecules than that between the ortho molecules. Yet, the catalytic effect of the paramagnetic impurity has a rather short range. Hence the diffusion process plays an important role in the case of low impurity concentrations. This makes the *catalyzed conversion* (CC) process an effective tool for the diffusion studies in solid hydrogen, actually the unique method in certain temperature ranges, where other techniques cannot be used or give ambiguous results.

The classical diffusion of ortho-H_2 in solid hydrogen has been studied previously at high temperatures by various NMR relaxation techniques.[4–6] The microscopic diffusion correlation time was found to follow the activation-type temperature dependence $\tau_d = 1\times 10^{-13} \exp(200/T)$ s. However, diffusion-independent relaxation mechanisms become dominant in solid hydrogen at relatively high temperatures (about 9 K), which puts an essential low-temperature limit for the applicability of those techniques. Cross-relaxation NMR techniques used in the experiments on HD molecules in parahydrogen[18,7] work still at substantially lower temperatures, but they cannot be used directly with ortho-H_2.

Another possibility for the ortho-H_2 diffusion studies is opened at low temperatures ($T < 4$ K) and low concentrations of ortho molecules ($C < 0.02$). Under these conditions the quantum tunneling diffusion of ortho-H_2 leads to the formation of ortho-H_2 clusters, which become favorable compared to a single ortho-H_2 due to the electric quadrupole (EQQ) interaction between ortho-H_2 neighbors. Pairs of nearest ortho-H_2 neighbors can be detected by means of NMR,[8–10] infrared,[11] and microwave[12] spectroscopy if the ortho-H_2 concentration is low enough to avoid the broadening of the pair's spectrum. The correlated change of the number of singles and pairs after the stepwise temperature change was shown to be exponential in time,[10] the rate being weakly dependent on temperature. Of course, the clustering rate observed is related to the diffusion properties of single ortho-H_2 molecules in solid parahydrogen. Still it is not clear why the process of pair formation is exponential in time instead of being second order in concentration. Furthermore, the rates of pair formation and pair decay coincide with each other. Probably it means that both of them are determined by the time of the transition of ortho-H_2 between nearest and next-to-nearest positions to another ortho molecule. Then the clustering rate observed can give only the lower limit for the macroscopic diffusion coefficient.

Recently the ortho-para conversion in solid hydrogen catalyzed by molecular oxygen impurities with concentrations $C_p \leqslant 10^{-3}$ was studied in the temperature range from 4.2 to 10.9 K.[2,3] The triplet ground state of the O_2 molecule, ${}^3\Sigma_g^-$, has the electronic spin $S = 1$ and, consequently, is a strong catalyst for the conversion of the neighboring ortho-H_2 molecules. Besides, it is heavy enough for disregarding its diffusion as compared to that of ortho-H_2, not only in the quantum tunneling regime but also in the case of classical over-barrier processes (due to smaller zero-point energy and hence a larger activation energy). Thus the CC rate should reflect mostly the diffusion of ortho-H_2. However, this is true only as far as the diffusion jump time τ_d is longer than the conversion time τ_{cc} of the ortho-H_2 neighbors nearest to an O_2 impurity. Otherwise, the CC rate becomes independent of the ortho-H_2 diffusion (and temperature) as it was observed experimentally at temperatures $T > 8$ K.[3] The obtained high-temperature limit of the CC rate gives the value $\tau_{cc} = (10.5 \pm 0.8)$ s. This imposes a high-temperature limit for the diffusion studies by the CC effect in solid hydrogen. However, such studies make it possible ''to fill the gap'' between NMR relaxation measurements and the experiments based on the ortho-H_2 clustering.

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The diffusion coefficient between 4.2 and 8 K was shown to have the activation-type temperature dependence: $D(T) = (3 \pm 2) \times 10^{-11} \exp[-(96 \pm 8)/T]$. This was interpreted in terms of the tunneling vacancy diffusion mechanism proposed in Ref. 13. According to this mechanism, the diffusion jump of an ortho-H_2 occurs by tunneling to a nearby vacancy position. In this case the effective activation energy is just the energy of the vacancy formation in H_2 crystal and hence should not depend on the type of the diffusing particle. This seems to be true at least for the two other diffusing particles, studied almost in the same temperature range. The activation energies for HD molecules and H atoms are equal to (98 ± 5) K (Refs. 18 and 7) and (103 ± 5) K,[14] respectively. However, the comparison of the pre-exponential factors in the expression of the diffusion coefficient for the different species, which should reflect the respective tunneling amplitudes Δ_0, gives an unexpected result: lighter ortho-H_2 molecules have the pre-exponential factor almost three orders of magnitude smaller than that of the heavier HD molecules. The probable explanation for this discrepancy was proposed in Ref. 2 and is based on the fact that ortho-H_2 molecules unlike HD have an electric quadrupole moment. The EQQ interaction of a tunneling ortho-H_2 with other ortho molecules can make the energy levels in the initial and final states deviate by some value δ. If $\delta \gg \Delta_0$ then tunneling becomes possible only if other lattice excitations (phonons) are taken into account to fulfill the energy conservation law. This, of course, may substantially decrease the tunneling rate of an ortho-H_2 as compared to the ''resonant'' case. In addition, the ortho-H_2 diffusion coefficient (and the CC rate) should depend on the ortho-H_2 concentration.

In the present paper we report results on the concentration and temperature dependence of the catalyzed conversion rate in solid hydrogen in the temperature range from 1.5 to 6.8 K. The concentration of O_2 impurities was $C_p = 10^{-3}$ while that of ortho molecules C varied from 0.02 to 0.75. No concentration dependence was found in the CC rate at high temperatures ($T > 4.6$ K). For T between 4.2 and 4.6 K the CC rate remains practically independent of concentration for $C < 0.1$ but decreases slowly when C increases higher than 0.1. At $T < 4.2$ K the CC rate is approximately inversely proportional to the concentration. Its temperature dependence also changes drastically when the temperature is lowered below 4 K. It becomes much slower than the activation-type dependence observed for $T > 4.2$ K and can be approximated by a linear function. In Sec. II we discuss a model, which allows the extraction of the diffusion coefficient from the experimentally measured CC rate constants. Section III contains our experimental results on the CC rate as functions of temperature and the ortho-H_2 concentration. Section IV considers the respective dependencies in the diffusion coefficient and discusses the obtained results.

II. THEORY

A detailed model of catalyzed conversion was developed previously.[2] Here we repeat the main points, required for understanding the data obtained, and also extend and modify the model to cope with additional features of the low-temperature experimental results.

In general, the process of catalyzed conversion in solid can be considered as a diffusion- controlled chemical reaction between ortho-H_2 and paramagnetic impurities.[2,3] Then the total conversion rate in the sample can be written as

$$\frac{dC}{dt} = -K_{sc}C^2 - K_{cc}CC_p, \tag{1}$$

where $K_{sc} = 1.8 \times 10^{-2}$ h^{-1} is the rate constant of the self-conversion process due to the ortho-ortho interaction[1,3] and K_{cc} is the corresponding rate for the catalyzed conversion. As far as the diffusion process remains the limiting factor in the catalyzed conversion, the CC rate constant can be written as $K_{cc} = 4\pi R_{\text{eff}} D n$, where R_{eff} is the effective conversion radius, $D = a^2/6\tau_d$ is the ortho-H_2 diffusion coefficient, $a = 3.75 \times 10^{-8}$ cm is the intermolecular distance in solid H_2, τ_d is the ortho-H_2 diffusion jump time, and $n = \sqrt{2}/a^3$ is the number density of solid H_2. The expression of K_{cc} can be modified to take into account the finite conversion time of the nearest neighbors of O_2, $\tau_{cc} = 10.5$ s.[3] Since the O_2 impurity was found to take a substitutional position in hcp lattice of solid hydrogen,[3] where each molecule has 12 nearest neighbors, the CC rate constant should be

$$K_{cc} = \left(\frac{1}{4\pi R_{\text{eff}} D n} + \frac{\tau_{cc}}{12} \right)^{-1}. \tag{2}$$

The catalyzed conversion time τ of the ortho-H_2 molecules decreases steeply with the increasing distance R from the O_2 impurity. The first factor is the declining dipolar ortho-H_2–O_2 interaction and the second one the decreasing efficiency of the emission of phonons, which are required to remove the energy released in the conversion.[1] Since the ortho-para conversion in solid hydrogen involves two phonons, τ should vary with R as

$$\tau(R) = \tau_{cc} \cdot \left(\frac{R}{a} \right)^{12}. \tag{3}$$

The effective conversion radius in Eq. (2) can be roughly estimated from the relation $\tau(R_{\text{eff}}) \approx \tau_d$. Thus the increase of R_{eff} with τ_d increasing is expected to be rather weak. Consequently, the diffusion coefficient D is roughly proportional to K_{cc} provided the latter is much less than its high-temperature limit: $K_{cc} \ll K_{cc}^{\infty} = 12/\tau_{cc}$. In order to obtain reliable quantitative data on diffusion from the measurements on catalyzed conversion, we have to find the exact dependence of R_{eff} on τ_d. This problem was solved using the Monte Carlo simulation approach, which was described in detail in paper Ref. 2. Briefly, it consists of periodical examinations of the matrix, representing the hcp lattice of a solid hydrogen sample, which contained initially randomly distributed O_2, ortho and para molecules with proper concentrations. Between the examinations three processes proceed: the ortho-H_2 diffusion, the self-conversion of the nearest ortho-H_2 neighbors and the catalyzed conversion within the nearest 11 coordination spheres of every O_2 impurity. The corresponding probabilities are governed by respective time constants τ_d, $\tau_{sc} = 12/K_{sc}$ and τ_{cc}. The main algorithm in the renewed computations was the same as described in Ref. 2. The code was speed optimized. New computing facilities allowed to double the size of the modeling lattice and to

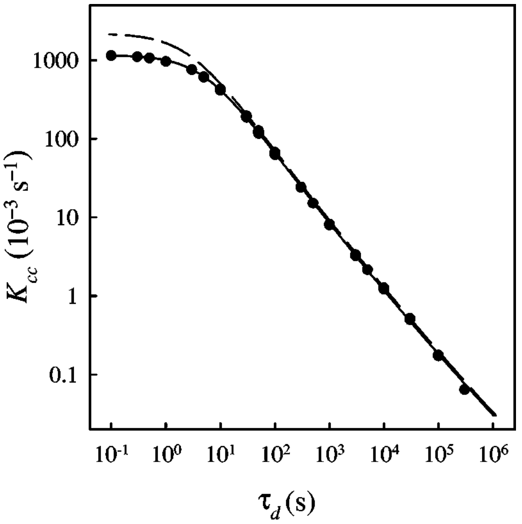

FIG. 1. The dependence of K_{cc} on τ_d, obtained by Monte Carlo simulations for the τ_{cc} values 10.4 s (circles and solid line) and 5.5 s (dashed line).

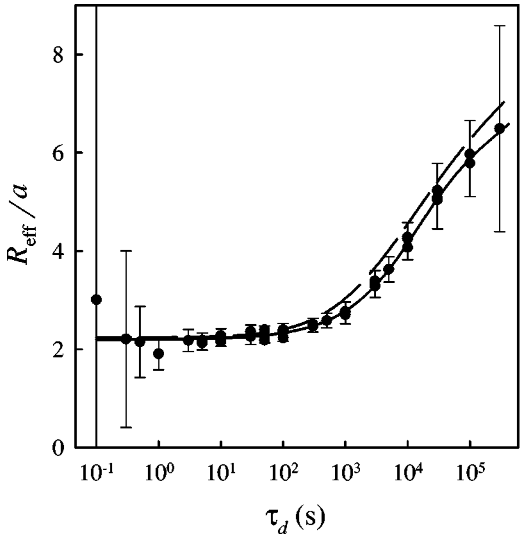

FIG. 2. The effective conversion radius R_{eff} vs τ_d, obtained from Monte Carlo simulations for various τ_{cc} values (see the legend of Fig. 1).

enhance the statistical accuracy. In addition, the experimentally determined value $\tau_{cc}=10.5$ s (Ref. 3) was used instead of $\tau_{cc}=5.5$ s estimated from the self-conversion rate constant

$$\tau_{cc}=\frac{12}{K_{sc}}\cdot\left(\frac{2\mu_{\text{p}}}{2\mu_{\text{e}}}\right)^2.$$

This estimate is rather close to the result of the calculation,[15] which gave $\tau_{cc}=5.6$ s. Yet, it is only about one half of the experimental value. Furthermore, the simulation was extended to the region of slower diffusion, which is more important for the present experiments.

The result of the simulation—the time dependence of the concentration C—is then fitted with Eq. (1) in order to extract the CC rate constant K_{cc} [similarly to the processing of the experimentally observed dependencies $C(t)$]. Figure 1 shows the obtained dependence of K_{cc} on τ_d for a few values of τ_{cc}.

The circles represent the simulated values with $\tau_{cc}=10.4$ s and the solid line is a polynomial fit to them. The dashed line is the fit to the analogous results for $\tau_{cc}=5.5$ s. A third simulation was worked out by assuming that $\tau_{cc}=5.5$ s for all the coordination spheres except the first one, for which $\tau_{cc}=10.4$ s. This is supposed to take into account the possibility of a slight distortion of the first coordination sphere by the O_2 impurity. The results of this simulation join the solid line in Fig. 1 in the fast diffusion region and the dotted line for most of the slow diffusion range. It can be noticed that the simulated results for both values of τ_{cc} are rather close to each other when $\tau_d \gg \tau_{cc}$. However, a small difference can be observed in the plot of R_{eff} vs τ_d shown in Fig. 2. The plot is obtained from the simulated data for $K_{cc}(\tau_d)$ using the relation (2). Note that R_{eff} in Ref. 2 has a different definition and hence has a different behavior in the fast diffusion limit.

The effective radius is found to increase slightly with the decreasing diffusion jumping time as it is expected from the simple relation $\tau(R_{\text{eff}})\approx\tau_d$. Still the growth is too small to affect substantially the diffusion coefficient D extracted from the experimental K_{cc} values.

III. EXPERIMENT

The general scheme of the experiment shown in Fig. 3 was practically the same as in Refs. 2 and 3. Solid hydrogen

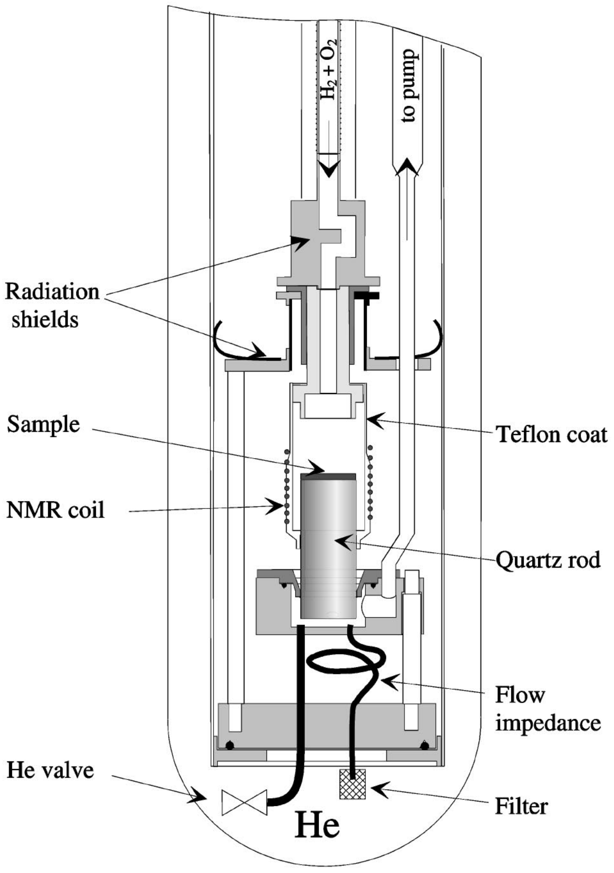

FIG. 3. The experimental setup.

samples containing about 0.1% of O_2 molecules were prepared by the matrix isolation technique inside the low-temperature, high-vacuum NMR probe, which is immersed in liquid helium inside the cryostat. The gas mixture of H_2 and O_2 was transported from the gas-handling system to the probe via a stainless steel tube. The lowest temperature of the tube was kept higher than 100 K in order to avoid possible condensation of oxygen of the gas mixture during the transportation. The substrate for the sample was made of single-crystal quartz in order to provide a sufficiently high thermal conductivity to remove the heat of condensation. The typical deposition rate was about 5×10^{17} $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ at the substrate temperature $T=(1.7\pm0.2)$ K. The sample volume was about 0.03 cm^3. Various initial ortho-H_2 concentrations ($C\leqslant0.75$) were obtained by mixing normal hydrogen gas ($C=0.75$) with almost pure parahydrogen ($C<10^{-5}$), prepared in an ortho-para converter using $\mathrm{Fe(OH)}_3$ as a heterogeneous catalyst.

In our previous experiments the temperatures $T<4.2$ K were obtained by lowering the helium vapor pressure in the whole cryostat. Then the amount of liquid helium in the cryostat limited the time for the low-temperature measurements to about 2 h. For the present studies we developed a new cooling system of the sample substrate in order to prolong the time for continuous conversion measurements at $T<4.2$ K. Liquid helium is supplied to the new cryosystem in two parallel ways: (i) through the stainless steel tube (1.2 mm i.d.) which can be tightly closed by a low-temperature valve, and (ii) through a German silver tube filled with pressed copper sinter providing for a high flow impedance. Helium vapors can be pumped out through a separate stainless steel tube, which goes through the room-temperature flange of the NMR probe (not shown in Fig. 3). When the valve is open and the pump line is connected to the recovery line, the sample space can be easily cooled down to 4.2 K. Temperatures higher than 4.2 K can be obtained by the combined action of the tunable valve and a couple of heaters, controlled by a computer. In order to obtain temperatures below 4.2 K, the valve is fully closed when the evacuation of helium vapors is on. In this way one can get temperatures as low as 1.4 K in a couple of minutes. The flow impedance chosen allowed the maximum heat load of about 30 mW at the minimum temperature. One can easily estimate that this is at least ten times higher than the heat of hydrogen condensation at the deposition rates used in the experiments. A simple mechanical membrane pressure controller stabilized the temperature between 1.5 and 4.2 K with the accuracy better than 20 mK. It is easily seen that this system allows practically unlimited time for measurements below 4.2 K.

The sample volume was almost fully isolated from the rest of the NMR probe volume with a Teflon coat (see Fig. 3). This was important for the measurements at $T>5.5$ K. Then the hydrogen vapor pressure becomes appreciable and the sample may recondense to colder walls of the NMR probe[3] if the sample volume is not isolated. The Teflon coat served also as a support for the NMR coil.

The NMR coil was wound of manganine wire to provide a perfect matching of the serial resonant circuit to the 50-Ω low-temperature coaxial cable. The distributed resistance of the coil helped also to damp a spurious parallel resonance, which was rather close to the operating frequency of 27 MHz.

The FID (free induction decay) signal of ortho-H_2 ($I=1$) was observed using the Bruker MSL-300 pulsed NMR spectrometer. The 90° pulse had the length of about 3 μs. (The paramolecules have the nuclear spin $I=0$ and do not contribute to the NMR signal.) The total number of ortho molecules in the sample is proportional to the initial amplitude of FID, A_0. Unfortunately the FID signal cannot be observed during the first few microseconds after the pulse due to the dead time of the spectrometer. So, we had to extrapolate the FID signal to its starting point by fitting the reliable part of FID with proper functions using the criteria of maximum likelihood as described in Ref. 2. Of course this may introduce some uncertainty in the result. Another approach to the measurements of the total number of ortho-H_2 molecules is based on the detection of the solid echo signal.[16] Although the echo method is obviously free from the ringing problems, it has its own disadvantages. The echo amplitude is also proportional to the number of ortho-H_2, but simultaneously it depends weakly on the transverse relaxation time, which itself varies with temperature and the ortho concentration. Thus this approach requires a precalibration of echo signals, which inevitably causes some inaccuracy. Hence the FID extrapolation seems to provide a reasonable compromise between simplicity and accuracy for the measurements of the ortho-H_2 concentrations in the sample. Since the evaporation rate was negligible for all the temperatures studied in the present investigation, the ortho-H_2 concentration $C(t)$ at any moment t can be determined from

$$C(t)=C_0\frac{A_0(t)}{A_0(0)}, \tag{4}$$

where C_0 is the ortho-H_2 concentration in the initial gas mixture. The receiver was saturated during the first 6 μs after the pulse. In addition, there were some long-term ringing components with relatively small amplitude, probably due to the ringing of the coil itself and the piezoelectric signal of the quartz crystal. They, however, degraded substantially the signal-to-noise ratio at least in samples with a low ortho-H_2 concentration. Fortunately, this long-term ringing was relatively stable and could be eliminated by measuring a correction signal from the probe without the hydrogen sample and by subtracting it from the NMR signals. Figures 4(a) and 4(b) illustrate the efficiency of the ringing elimination for a typical FID signal. The main disadvantage of this method is the long-term drift of the ringing, since the correction signal cannot be measured before the experiment is over (few days later than the respective FID's). A more effective ''ringing correction'' is achieved by using in the actual FID measurements the ''antiringing'' pulse sequence $90°-\mathrm{FID}-t_1-180°-t_2-90°-\mathrm{FID}$ with a 180° shift of the receiver phase during the acquisition of the second FID. The delay t_1 is much longer than the spin-lattice relaxation time T_1 so that the sequence corresponds to two independent FID measurements. If $T_2\ll t_2\ll T_1$, where T_2 is the transverse relaxation time, then the two FID signals of ortho-H_2 molecules are actually added, while the ringing signals, which are not sensitive to the 180° pulse, are subtracted. The resulting FID, presented in Fig. 4(c), shows at least one order of magnitude

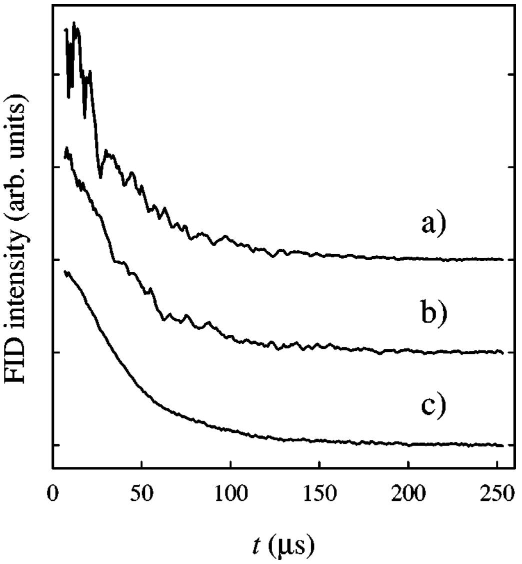

FIG. 4. FID signals of ortho-H_2 at $T=4.2$ K and $C=0.09$, corresponding to 6.3×10^{19} ortho molecules: original FID (a), FID after substracting the correction signal (b), and FID obtained with the antiringing pulse sequence (c).

better S/N ratio. The main advantage of this technique, as compared to that described above, is the possibility to obtain the ringing correction during measurements, which reduces the effect of possible long-term drifts.

The filling factor of the NMR coil for the average sample size was about 0.04. The resulting NMR sensitivity corresponds to about 10^{16} ortho-H_2 molecules observable with the S/N ratio equal to 3 at $T=4.2$ K.

IV. RESULTS

The kinetics of ortho-para conversion, studied at various temperatures and concentrations, is described well by Eq. (1). Under certain circumstances K_{cc} depends on concentration and, strictly speaking, cannot be considered as a rate constant. Nevertheless, Eq. (1) can be taken as a good approximation for the conversion kinetics since the change of concentration during each measurement is relatively small (usually less than 20% at low temperatures). Experimental data deviate somewhat from Eq. (1) during first few hours after the sample preparation at the lowest temperatures ($T<2$ K) and small ortho-H_2 concentrations. Since the deviation was accompanied by a time-dependent increase of the NMR second moment, we attributed it to the clustering process and measured the catalyzed conversion rate after the clustering was finished. Our experimental results are plots of the ortho concentration C as a function of time and they are similar to those shown in Refs. 3 and 4.

Figure 5 shows the temperature dependence of the catalyzed conversion rate constant as a function of $1/T$. The experimental points were measured on more than 40 samples with various initial concentrations. The open circles represent the data measured previously[3] using the high-temperature NMR probe. The closed symbols represent the present data. Both series of data are in a good agreement with each other. There is a drastic change in the temperature dependence around 4.2 K. The catalyzed conversion rate exhibits an activation-type temperature dependence for $T>5$ K but shows only a weak dependence on temperature below 4 K. The low-temperature part of the T dependence is shown in more detail on the linear scale in the inset to Fig. 5.

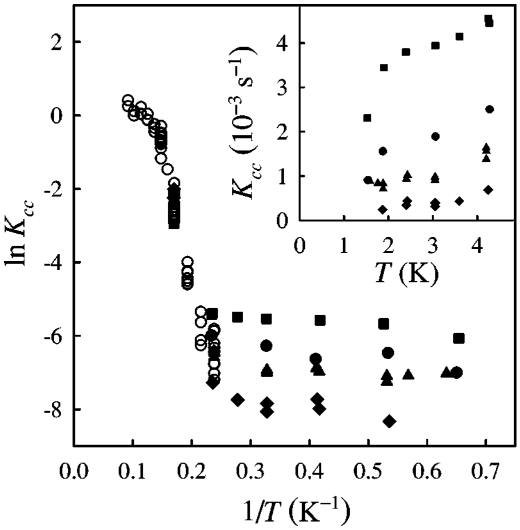

FIG. 5. The temperature dependence of the catalyzed conversion rate constant K_{cc}. The initial ortho concentrations are 0.05 (squares), 0.09 (filled circles), 0.18 (up triangles), and 0.65 (diamonds). The insert shows the low-temperature data vs T. The open circles present the data of Ref. 3.

The relatively large scatter at low temperatures reveals a certain correlation between the rate constant and the ortho-H_2 concentration. The C dependence of the rate constant is shown in Fig. 6. The concentration error bars refer not to the accuracy of the measurements, but to the change of concentration during the measurement. The shown concentration values represent the averaged concentration during the measurement.

One can observe roughly three temperature intervals with

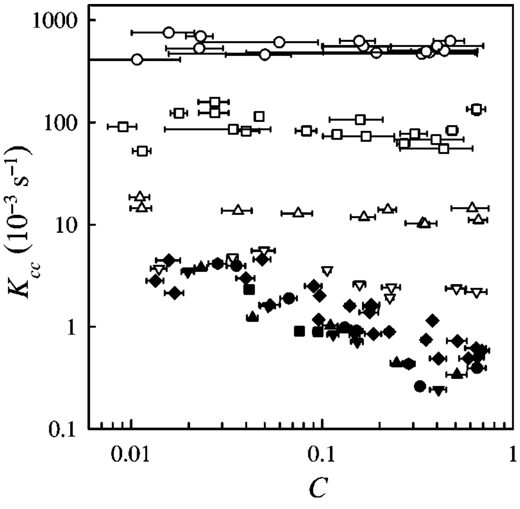

FIG. 6. The concentration dependence of the catalyzed conversion rate at various temperatures: 6.77 K (open circles), 5.87 K (open squares), 5.19 K (open up triangles), 4.64 K (open down triangles), 4.22 K (filled diamonds), 3.60 K (filled hexagons), 3.05 K (filled circles), 2.40 K (filled up triangles), 1.88 K (filled down triangles), and 1.54 K (filled squares).

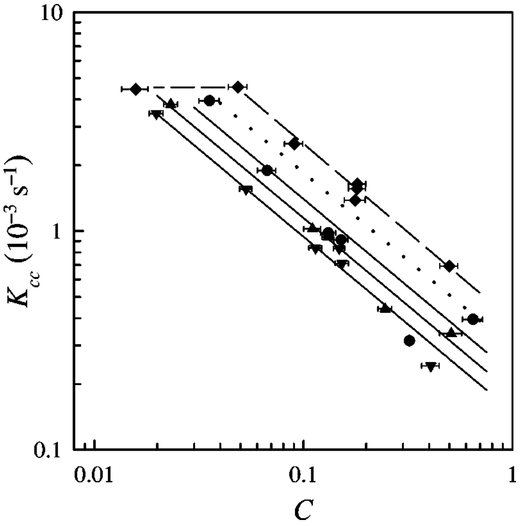

FIG. 7. The low-temperature part of the concentration dependence of K_{cc}. The symbols are the same as in Fig. 6. The dashed line is a guide for an eye for the 4.24 K points. Solid lines represent the best fit of Eq. (5) to the data for 1.88, 2.40, and 3.05 K, respectively. The dotted line is the extrapolation of the fit to 4.24 K.

a different concentration dependence of K_{cc}. At high temperatures ($T>5$ K) the rate constant does not depend on the concentration. In the temperature range between 4 and 5 K some concentration dependence is observed only at high concentrations ($C>0.1$). And, finally, below 4 K K_{cc} depends on concentration in the whole concentration range studied (0.01–0.75).

Figure 7 replots the lowest temperature data of Fig. 6 on a larger scale. They were obtained with the new probe and show thus less experimental scatter. The concentration dependence can be approximated by a power function. The weak temperature dependence at low temperatures, which can be observed in the inset of Fig. 5, also lead us to choose a power function for the description of the temperature dependence:

$$K_{cc}(T,C)=AT^{n}C^{m}. \tag{5}$$

If one omits the points at $T\geqslant 4.2$ K, which clearly have the concentration-independent region for $C<0.1$ (dashed line in Fig. 7), then the best fit parameters are

$$A=(8.7\pm 0.1)\times 10^{-5},$$

$$n=(0.84\pm 0.13),$$

$$m=(-0.80\pm 0.03).$$

The solid lines in Fig. 7 represent the best fits of Eq. (5) to the data for the temperatures 3.05, 2.40, and 1.90 K. The extrapolation of the fit to $T=4.24$ K (dotted line in Fig. 7) lies almost parallel to but lower than the experimental points for $C>0.1$.

In order to clarify the temperature dependence of the catalyzed conversion rate constant, the temperature dependence of the product $K_{cc}C^{0.8}$ is shown in Fig. 8. It can be compared with the insert of Fig. 5, which presents the T dependence of K_{cc} itself on the same scale. Almost linear temperature dependence can be observed in Fig. 8.

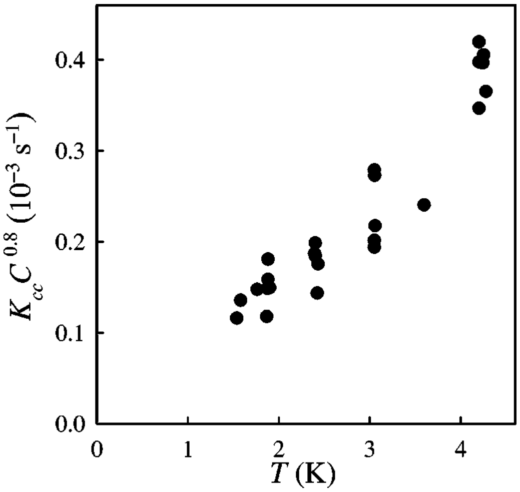

FIG. 8. The temperature dependence of the concentration-corrected catalyzed conversion rate constant $K_{cc}C^{0.8}$.

V. DISCUSSION

A. Ortho-H_2 diffusion coefficient

The results of the Monte-Carlo simulation, presented in Fig. 1, can be used to extract the diffusion coefficient of ortho-H_2 molecules in solid hydrogen from the experimental results on the catalyzed conversion rate constant presented above. The Arrhenius plot of the obtained D data is shown in Fig. 9. A major difference between Figs. 9 and 5 can be observed only at high temperatures, where the catalyzed conversion rate becomes almost independent of temperature. This causes larger error bars in the high-temperature values of D than those of K_{cc} in Fig. 5. Although $D(T)$ follows the Arrhenius dependence down to 4.2 K, the activation parameters of the diffusion coefficient were determined using the data points for $T>5$ K only, since they seem to have no

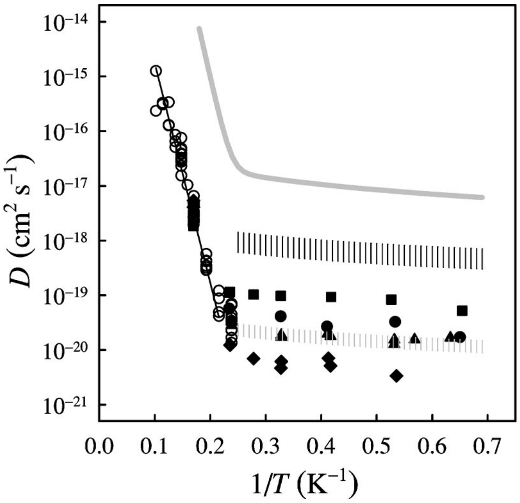

FIG. 9. The temperature dependence of the ortho-H_2 diffusion coefficient in solid hydrogen (the symbols are the same as in Fig. 5). The solid line represents Eq. (6). The gray bars were obtained from the clustering rate of ortho molecules for C between 0.002 and 0.01 (Refs. 8–10) by multiplication with $a^2/6$. The black bars show our estimate of D based on the data (Refs. 8–10). The thick gray line describes the diffusion coefficient of H atoms in solid H_2 (Ref. 14).

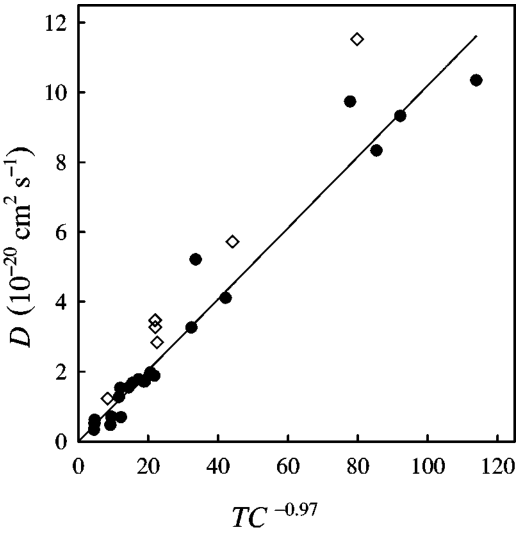

FIG. 10. The dependence of D on temperature and concentration at 4.24 K (open diamonds) and $T<4$ K (solid circles).

dependence on the concentration. The solid line in Fig. 9 represents Eq. (6), which is the best fit to the high-temperature points

$$D(T)=(2\pm1)\times10^{-11}\exp\left[-\frac{(92\pm4)}{T}\right]\ \mathrm{cm}^2\,\mathrm{s}^{-1}. \quad (6)$$

Equation (6) seems to be more accurate than the results of the previous measurements[2,3] and agrees with them within the experimental accuracy. Since R_{eff} varies only weakly with τ_d, both the diffusion coefficient $D(T,C)$ and the CC rate constant $K_{cc}(T,C)$ have qualitatively the same dependence on temperature and ortho concentration. However, minor quantitative differences are observed. The dependencies of the diffusion coefficient are slightly stronger than those of the rate constant. The linear dependence of the diffusion coefficient on temperature is observed at slightly lower temperatures than in the case of K_{cc}. This occurs due to a nonlinear variation of R_{eff} with τ_d. Fitting functions analogous to Eq. (5) were used to approximate the data for the diffusion coefficient in the low temperature range ($T<4$ K). The best fit is

$$D(T,C)=(1.02\pm0.16)\times10^{-21}T^{1.00\pm0.15}C^{-0.97\pm0.04}\ \mathrm{cm}^2\,\mathrm{s}^{-1}. \quad (7)$$

Figure 10 shows the diffusion coefficient vs the product $TC^{-0.97}$ for $T\leqslant4.3$ K. The solid line represents Eq. (7) and the closed circles the experimental points for $T<4$ K. One can see that all the points for $T=4.2$ K are clearly higher than the others. This probably means that the contribution of the high-temperature diffusion processes is not yet fully frozen out at 4.2 K.

B. Comparison with other diffusion data

Figure 9 contains also the data describing the ortho-H_2 clustering experiments.[8–10,17] The clustering time τ_c was reported[8–10] to have a shallow maximum around 0.3 K: $\tau_c^{-1}=0.14\,T^{0.7}+2.2\times10^{-3}T^{-2}$ h^{-1} and to have rather weak (if any) concentration dependence in the range of concentrations between 0.002 and 0.01. In the vapor pressure experiments[17] at $T>0.8$ K the concentration and temperature dependence were found to follow the equation $\tau_c=0.3\,C^{-0.7}T^{-0.7}$ h. As mentioned before, it is difficult to obtain the diffusion coefficient directly from the clustering time τ_c. Thus the stripes of bars in Fig. 9 are just our attempts to represent the clustering rate in the diffusion domain. The gray bars show the clustering rate $1/\tau_c$ multiplied by $a^2/6$. The black bars represent the estimate of the diffusion coefficient D_c obtained from the relation $\tau_c^{-1}\approx2(4\pi aD_c)C(\sqrt{2}/a^3)$, which takes into account the number of diffusion jumps, required for the two ortho-H_2 molecules to become nearest neighbors to each other. This is a rather rough evaluation, since the clustering process does not seem to obey the second order kinetics law. If the clustering time is determined by the last jump of two ortho-H_2 molecules towards each other, then the estimate is incorrect. Yet it can be observed that the temperature dependence of the clustering process and of the diffusion, obtained from the catalyzed conversion measurements, are rather close to each other below 4 K. The weak concentration dependence of τ_c reported in Refs. 8–10 does not contradict our data either, because for a concentration-independent τ_c one might expect the diffusion coefficient to be inversely proportional to the concentration: $D_c\propto1/C$. However, one should keep in mind the above-mentioned reservations on the estimate of D_c.

The thick gray line in Fig. 9 represent the diffusion data for H atoms in solid H_2, obtained from the recombination measurements:[14] $D_H=10^{-6}\exp(-103/T)+4\times10^{-18}T$. This curve is practically parallel to the ortho-H_2 diffusion data both in the high-temperature and low-temperature ranges. The only difference is that D_H is independent of the concentration of atoms and ortho-H_2 molecules.

The linear temperature dependence of the ortho-H_2 diffusion coefficient observed in the present study correlates also with the linear temperature dependence of the nuclear spin-lattice relaxation of HD molecules in the temperature range 1–6 K.[18,19] The spin-lattice relaxation in that case is determined mainly by the cross relaxation between HD and ortho-H_2 molecules and, hence, should be affected by the mobility of ortho-H_2.

C. Discussion of the temperature and concentration dependence

The concentration dependence of the observed CC rate is different from the expected behavior in the case of the tunneling vacancy diffusion mechanism hindered by the EQQ interaction between ortho-H_2 molecules. Some hindrance should occur since the EQQ interaction of the tunneling ortho-H_2 molecule with other ortho molecules shifts its energy levels in the neighboring lattice positions by the value $\delta\gg\Delta_0$, where Δ_0 is the tunneling amplitude, which couples the nearest ortho-H_2 positions in the lattice. The shift δ depends on the concentration. At high concentrations it is determined by the varying number of the nearest ortho-H_2 molecules resulting in $\delta\propto\sqrt{C}$.[20] At small concentrations ($C\gg1$) one may expect that $\delta\propto C^{5/3}$. Since only a small portion $\propto\Delta_0/\delta$ of all possible tunneling transitions can satisfy the energy conservation law, the concentration dependence of the diffusion coefficient and the CC rate constant should vary as C^{-n} with n between 0.5 and 5/3. Actually, the experimental CC rate constant does not depend on concentration at all above 5 K. A concentration dependence (with $n \sim 1$) is observed only when $C > 0.1$ and T is close to or below 4.2 K.

Since the temperature dependence also changes near 4.2 K, one might suppose that the concentration dependence starts to appear due to another diffusion mechanism becoming dominant. However, this is not necessarily true, because a weak concentration dependence can be observed already at 4.6 K.

A more probable explanation consists of a competition of two different interactions, resulting in the shifts δ_1 and δ_2 with only one of them depending on the concentration. For example, the first interaction is the EQQ interaction between ortho molecules with a concentration dependent shift $\delta_1 = \delta(C)$ and the second interaction, with a concentration independent δ_2, is probably the EQQ interaction between ortho-H_2 and O_2 molecules (the quadrupole moment of the O_2 molecule is about 60% of that of the ortho-H_2 molecule). The O_2 and ortho-H_2 molecules can also interact via strain fields due to lattice deformation around both O_2 and ortho-H_2. This interaction is proportional to R^{-3}, where R is the ortho-H_2–O_2 distance. It has a longer range than that of the EQQ interaction, which is proportional to R^{-5}. However, at short distances it is unlikely to exceed the EQQ interaction since the deformation around ortho-H_2 molecule is very small. One should note that despite the small concentration of oxygen, the ortho-H_2–O_2 interaction plays an important role because the catalyzed conversion process inevitably requires ortho-H_2 to approach O_2.

The only problem is why the relation between δ_1 and δ_2 changes with temperature. The reason for this can be found in the temperature dependence of the effective conversion radius R_{eff} discussed in Sec. II. Obviously the ortho-H_2–O_2 EQQ interaction is most important at $R = R_{\mathrm{eff}}$, since at closer distances the ortho-H_2 converts rapidly to para-H_2 while at larger distances the EQQ energy falls down substantially. Since $\delta_1 \propto C^n$ and $\delta_2 \propto R^{-6}$, a transition temperature $T_0(C)$ should exist corresponding to $\delta_1(C) = \delta_2(R_{\mathrm{eff}}[\tau_d(T_0)])$. Thus above $T_0(0.75)$ the ortho-H_2–O_2 EQQ interaction gives the main contribution to δ and diffusion is independent of the ortho concentration. The experiments indicate that $T_0(0.1) \approx 4.2$ K. Thus for $C > 0.1$ at 4.2 K the interaction between ortho molecules prevails resulting in a clear concentration dependence of K_{cc}. Since the dependence of δ_2 on R is rather strong, then, despite the relatively weak variation of R_{eff} with τ_d, the transition temperature range, where both δ_1 and δ_2 really compete, is rather narrow (in our case 4.2–4.6 K).

Still the most reasonable explanation for the high-temperature activation-type dependence of D on T is based on the tunneling vacancy model,[13] where the diffusion of ortho-H_2 molecules occurs by tunneling to the nearby vacant lattice positions. Such a process is consistent with the ''particle''-independent activation energy equal to the energy of the vacancy formation. However, the pre-exponential factor, containing the effect of tunneling, seems to be limited by the EQQ interaction between O_2 and ortho-H_2 molecules. Thus diffusion can be faster far from oxygen molecules, where the pre-exponential factor is limited by the ortho-ortho interaction. This may give also an alternative explanation for the fact that D in our experiments near 7 K is smaller than the value extrapolated from the high-temperature classical diffusion data for ortho-H_2 (Refs. 4 and 5) (see discussion in Ref. 3). The power-type dependence of the catalyzed conversion rate on T at low temperatures is a direct evidence for the quantum diffusion of ortho-H_2 molecules in solid hydrogen at $T < 4$ K and C between 0.02 and 0.75. The concentration dependence indicates that it is the ortho–ortho interaction that affects the tunneling rate. Hence the diffusion of ortho-H_2 molecules can be considered as uniform in the sample (at least in the macroscopic scale).

According to the theory of quantum diffusion in irregular systems,[21,22] the linear temperature dependence of the diffusion coefficient indicates that one-phonon interactions are involved in the tunneling process to compensate the energy mismatch δ. The general expression for the coherent quantum diffusion coefficient can be written as

$$D \propto \frac{\Delta_0^2 a^2}{\hbar} \frac{\Omega}{\Omega^2 + \delta^2},$$

where $\Omega(T,\delta)$ is the phase relaxation rate in the tunneling transition determined by interactions with phonons. If the one-phonon interaction dominates, then $\Omega \propto \delta^2 T/\theta_D^2$, where θ_D is the Debye temperature. In the case of large shifts $\delta \gg \Omega$, the diffusion rate becomes proportional to temperature:

$$D \propto \frac{\Delta_0^2 a^2}{\hbar} \frac{T}{\theta_D^2}.$$

This expression has certain difficulties to interpret all the features of the experimental data. It gives a good explanation to the temperature dependence of the diffusion coefficient of ortho-H_2 for $T < 4$ K, but has no explicit dependence on the shift δ to explain the observed concentration dependence.

Previously the $1/C$ dependence for the diffusion coefficient was observed in the case of very dilute impurities with rather weak interactions between them (^{3}He in ^{4}He). This kind of dependence appears due to the scattering of the ''impuriton'' quasiparticles from each other. However, this is not the case in our system, since it has rather strong interactions between diffusing particles especially at $C \sim 1$, which destroys any possibility of a quasiparticle behavior. For $C \ll 1$ the dependence of the CC rate on the ortho concentration may originate from the effect of ortho-H_2 clustering on diffusion. Let us suppose that the time t_{tr}, which an ortho-H_2 spends in a cluster, is much longer than the diffusion time to another trapping site (ortho-H_2). Then the diffusion time to the nearest O_2 molecule should be proportional to Ct_{tr} and the effective diffusion coefficient should be $\propto R_{O_2}^2/(Ct_{tr}) \propto 1/C$, where R_{O_2} is the mean distance between O_2 molecules. However, this model can not be applied to samples with high ortho-H_2 concentrations.

One possible reason for the failure to explain the experimentally observed concentration dependence is that the original theory[21,22] considers essentially a two-level system. The real tunneling system in solid hydrogen is much more complex and includes many quadrupole levels of interacting ortho-H_2 neighbors affected by the crystal field, the splitting between them being sometimes close to Δ_0. This may require the theory to be generalized to multiple-level systems. In any case the linear dependence of the diffusion coefficient on temperature indicates that one-phonon processes are involved in the tunneling process.

VI. CONCLUSIONS

We may summarize as follows the main results and conclusions reached by our study of the ortho-para conversion in solid hydrogen catalyzed by a small amount ($\sim 10^{-3}$) of O_2 impurities:

1. The catalyzed conversion rate is determined by the diffusion of ortho-H_2 molecules at temperatures between 1.5 and 8 K. Above 8 K the diffusion is faster than the conversion rate of the nearest neighbors of O_2 molecules, which restricts the total conversion rate.
2. The relation between the catalyzed conversion rate constant K_{cc} and the diffusion coefficient D was obtained by a Monte Carlo simulation using the experimentally determined conversion time of the ortho-H_2 neighbors nearest to the O_2 molecule.
3. The dependence of both K_{cc} and D on temperature and the ortho-H_2 concentration was determined in the region 1.5–10.6 K and 0.02–0.75, respectively. The ortho-H_2 diffusion data are presented for the temperature range $T < 4$ K at ortho-H_2 concentrations $C > 0.04$.
4. K_{cc} does not depend on the concentration when $T > 5$ K. In the intermediate temperature range 4–5 K K_{cc} begins to decrease with C increasing at high concentrations. And, finally, at $T < 4$ K the rate constant is roughly inversely proportional to the concentration. This concentration dependence was explained by the competition of the ortho-ortho and ortho-H_2–O_2 EQQ interactions, affecting the tunneling of ortho-H_2 molecules in solid hydrogen.
5. The temperature dependence of D above 5 K is described by the Arrhenius relation $D(T) = 2 \times 10^{-11} \exp(-92/T)$ cm^2 s^{-1}. The diffusion of ortho molecules in this region occurs, probably, via tunneling to a neighboring vacancy position in the lattice. The tunneling rate can be substantially hindered by the ortho-H_2–O_2 EQQ interaction.
6. The diffusion coefficient at low temperatures ($T < 4$ K) can be approximately written as $D(T,C) = 1 \times 10^{-21} T/C$ cm^2 s^{-1}. The linear temperature dependence can be explained by a quantum diffusion model involving one-phonon interactions to compensate the mismatch of the energy levels of the tunneling molecule.

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