H and N atoms in para-H_2 crystal. 1. Microwave excitation of forbidden electron-nuclear transitions

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Excitation of forbidden electron-nuclear transitions of hydrogen and nitrogen atoms in para-H_2 crystals has been studied. Results have been obtained on the rate of diffusion of hydrogen atoms near the orthomolecules and on the rate of spin diffusion of nitrogen atoms. The rate of nuclear relaxation of ortho-H_2 near a hydrogen atom has been determined.

1. INTRODUCTION

The quantum He^3, He^4, H_2, and D_2 crystals are known to exhibit some macroscopic quantum properties. One such property is the quantum diffusion of light impurities in these crystals. For the lightest impurities, that is, hydrogen atoms, the quantum diffusion was first observed in studies of recombination of hydrogen atoms in molecular hydrogen crystals.[1] Note that this diffusion consists essentially in migration of atoms towards each other and subsequent recombination ($D_{\rm rec} \sim 10^{-17}$ cm^2/s, $T = 1.3$–4.2 K for hydrogen atoms in para-H_2). Theoretical analyses[2] of atom recombination under the conditions of quantum diffusion predicted a possible fast diffusion ($D > D_{\rm rec}$) in H_2 crystals via pathways with least misalignment of the energy levels between neighboring positions of the hydrogen atoms in the crystal lattice.

For instance, the rate of band diffusion of hydrogen atoms in para-H_2 may be rather high far from defects (in particular, far from other hydrogen atoms, orthomolecules, etc.). Since the band width for hydrogen atoms varies between 10^{-2} and 1 K this diffusion rate[2] must be not lower than 10^{-7} cm^2/s. One can find it by determining mass diffusion of atoms. This cannot be done, however, because the crystals produced from the gas phase are imperfect.[3]

Another case when diffusion may be faster (than the recombination diffusion) is the diffusion of atoms near orthomolecules in a parahydrogen crystal. Analysis of diffusion near orthohydrogen molecules can yield interesting results owing to the following factors. First, orthomolecules produce only weak distortions of the crystal lattice. Moreover, their concentration can be varied in a fairly wide range. Finally, they have a magnetic moment and thus EPR techniques may be employed to study the interaction of hydrogen atoms with ortho-H_2.

The present study is aimed primarily at measuring the rate of diffusion of hydrogen atoms near hydrogen orthomolecules in parahydrogen. This was accomplished by excitation of the forbidden electron-nuclear transitions which occur with simultaneous flipping of the electron spin of the atom and the nuclear spin of the orthomolecule. Since the probability of such transitions depends on the distance between the atom and the molecule, the migration of the atom must affect the excitation rate, as demonstrated below.

It must be noted that excitation of the forbidden electron-nuclear transitions is typically employed in the technique of dynamic nuclear polarization.[4] In addition to other factors the efficiency of dynamic polarization grows with the increase in the rate of polarization transfer from the nuclei near the paramagnetic centers to other nuclei. The rate of the transfer depends on the rate of nuclear spin diffusion. For orthomolecules in normal hydrogen it is about $3\cdot 10^{-12}$ cm^2/s (Ref. 5). If the paramagnetic centers are hydrogen atoms and their diffusion rate near orthomolecules is greater than $3\cdot 10^{-12}$ cm^2/s then the polarization of nuclei throughout the specimen can be achieved via the mechanism of quantum diffusion of hydrogen atoms in the crystal rather than nuclear spin diffusion. This opens prospects for producing polarized protons in the H-in-H_2 system.

It should be emphasized, to conclude this section, that the measurements of the rate of pumping for the forbidden electron-nuclear transitions performed in this study do not constitute direct determinations of the diffusion rate for atoms. This is why similar experiments with pumping of forbidden transitions have been made for nitrogen atoms in parahydrogen in order to verify the results for hydrogen atoms in parahydrogen. In contrast to H atoms, N atoms were found to be stationary in the process of pumping.

2. EXPERIMENTAL TECHNIQUES

2.1. Specimen preparation

Specimens of parahydrogen with atomic impurities (H, N) were produced by condensation of two beams—of atoms and paramolecules—on a cold substrate with a temperature of about 1.5 K and placed inside the operating cavity of a 3-cm EPR spectrometer ($\nu \approx 9.9$ GHz).

The beam of atoms was generated from the atom-molecule mixture produced in the microwave discharge and fed into the operation zone of the cryostat through an atom guide. The end section of the latter, known as the accommodator, had a temperature of about 5 K for H-in-para-H_2 specimens and about 8 K for N-in-para-H_2 specimens. Most molecules fed from the RF discharge were frozen on the accommodator walls.

Ortho-para conversion of hydrogen was conducted with iron hydroxide $Fe(OH)_3$ at about 15 K for 10–20 hours. The parahydrogen was then evaporated into the feeding system and in 20–30 minutes it condensed inside the cryostat. To change the ortho-para ratio in a specimen, a certain amount of normal hydrogen was added to the parahydrogen in the feeding system. The lower limit of concentration of orthomolecules in the specimens used in the experiments was determined apparently by the conversion of parahydrogen into orthohydrogen in the feeding system. The parasitic molecular flow through the accommodator could give rise to additional orthomolecules in the H-in-

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para-H_2 specimens. The minimal concentration of orthomolecules in para-H_2 specimens has been estimated to be about $(2–3)\cdot 10^{-2}$ (see below).

The specimens used in our experiments had the following compositions: H-in-par-H specimens—hydrogen atom concentration $C_H \sim 10^{-5}$ and ortho-H concentration about $3\cdot 10^{-3}–3\cdot 10^{-2}$; N-in-para-H specimens—nitrogen atom concentration $C_N \sim 10^{-6}$, ortho-H_2 concentration about $2\cdot 10^{-3}–2\cdot 10^{-2}$, and nitrogen molecule concentration $C_{N_2} \sim 5\cdot 10^{-4}$.

2.2. Detection of atoms

An electron paramagnetic resonance (EPR) technique was employed for detection of atoms. The EPR spectrum of hydrogen atoms is known to include two hyperfine structure (hfs) lines with a spacing of 1420 MHz. The EPR spectrum of nitrogen consists of three HS lines. The spacing between these lines is 11.3 MHz in solid molecular nitrogen. Both for the hydrogen and nitrogen atoms in para-H_2 the width of the unsaturated EPR line is independent of the orthomolecule concentration C_o if it does not exceed 5–10%. It is apparently determined by the instrumental broadening, and when the EPR line is detected in the modulational regime under the conditions of slow passage the width is $\delta H_{pp} = 100–120$ mG.

The spin-lattice relaxation times for H and N atoms in para-H_2 are fairly long, varying from about 10 to 100 s. A dispersion signal was therefore recorded in our experiments in the modulation regime ($f = 100$ kHz) at a fairly high microwave power $P_{\text{reg}} \sim 10^{-3}$ W. According to the classification suggested in Ref. 6, the recording conditions corresponded to the case of nonadiabatic fast line passage with complete saturation of spin packets. As a result the sensitivity of the spectrometer could be improved by approximately two orders of magnitude in comparison with the conventional recording of spectra under the conditions of slow passage. A significant observation is that the signal amplitude under these conditions remained proportional to the difference between the populations of the Zeeman sublevels of the H and N atoms.[6]

2.3. Excitation of the forbidden transitions

As mentioned in Sec. 1, this study was aimed at finding the rate of diffusion of hydrogen atoms in para-H_2 from the results on excitation of the forbidden electron-nuclear transitions which are accompanied with simultaneous flipping of the electron spin of the atom and the nuclear spin of the orthomolecule. Let us consider these transitions. The energy levels for the H atom–ortho-H_2 pair in a magnetic field are presented in Fig. 1. States with only a single projection of the nuclear spin of the H atom need be treated since the characteristic times of the processes under consideration are much shorter than the nuclear relaxation time for an H atom$^{1)}$ in para-H_2 (from 10 to 100 s).[5]

The dipole-dipole interaction in the pair mixes states with different projections of the nuclear spin of the orthomolecule. In a microwave field, therefore, not only the conventional allowed EPR transitions can occur, for which we have $\Delta M_s = \pm 1$ and $\Delta M_n = 0$, but also the forbidden satellite transitions for which $\Delta M_s = \pm 1$ and $\Delta M_n = \mp 1$ (here M_s and M_n are the components of the electron spin of the atom and the electron spin of the ortho-H_2 along the magnetic field). The splitting between the forbidden satellite transition and the normal hfs transition for the hydrogen atom expressed in magnetic-field units (for the given microwave frequency) is $\delta H = H_{\text{hfs}} (\mu_p/\mu_e)$ where H_{hfs} is the resonance field for the hfs transition, and μ_p and μ_e are the magnetic moments for the proton and electron. The probability ratio for the forbidden and normal transition is given by[4]

$$\frac{W_1}{W_0}(\vartheta) = \left(\frac{3\cdot 2^{1/2}\mu_e}{r^3 H_{\text{hfs}}} \sin\vartheta \cos\vartheta\right)^2. \qquad (1)$$

Here r is the distance between atom H and ortho-H_2 and ϑ is the angle between the vector r and the magnetic field vector.

Figure 1 demonstrates that microwave excitation of the forbidden transition causes equalization of the populations of the states with $M_s = 1/2$ and $M_s = -1/2$. This can be observed in experiment if the time between excitation and recording of the line is much shorter than the time of spin-lattice relaxation for hydrogen atoms. The amplitude of the hfs line must decrease with growing excitation time.

Since the magnetic field was weakly nonuniform (≈ 0.2 G/cm) excitation was obtained by passing linearly the magnetic field through the resonance for the forbidden transition.[4] The magnetic field near the resonance was modulated at 100 Hz and an amplitude $\Delta H = \pm 1.5$ G. A special generator comprising an avalanche-transit-time diode used for ex-

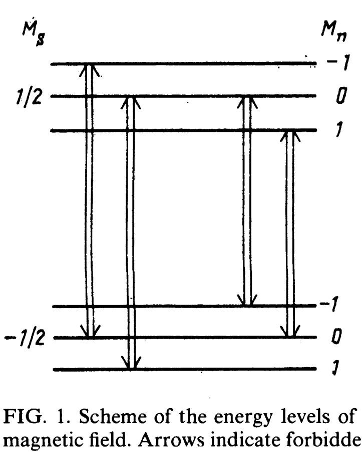

FIG. 1. Scheme of the energy levels of the H atom–ortho-H_2 pair in a magnetic field. Arrows indicate forbidden transitions.

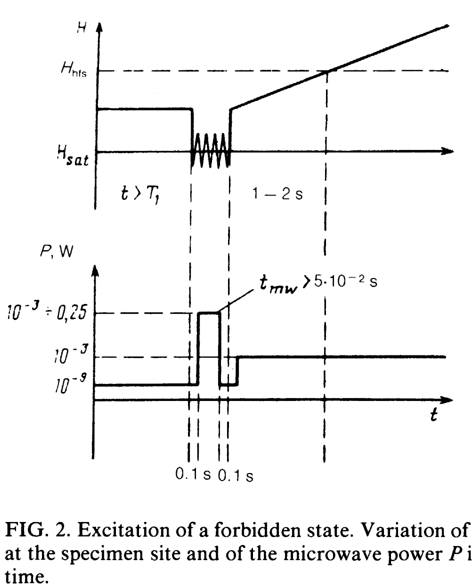

FIG. 2. Excitation of a forbidden state. Variation of the magnetic field H at the specimen site and of the microwave power P in the resonator with time.

citation had the peak power of about 2 W and the frequency stability of 10^{-4}. Figure 2 demonstrates the variation of the microwave power in the resonator and the magnetic field at the specimen during excitation and subsequent line recording. The hfs line was recorded 1–2 s after excitation of the forbidden satellite transition for this line in all experiments. This interval is always shorter than the spin-lattice relaxation time for the atoms. Figures 4 and 8 present typical saturation curves for hydrogen and nitrogen atoms.

The modulation amplitude for the magnetic field near the resonance was selected according to the following conditions. First, it must be much greater than the line width for the forbidden transition ($\delta H_{pp} \sim 100$ mG, see below). This provides for identical excitation conditions for all atoms in the specimen. Secondly, the saturation of the wings of the primary hfs line must be rather low during excitation. This condition was verified in experiments by exciting the forbidden transition but not modulating the magnetic field. While the magnetic field during excitation differed from the resonance field by ± 1.5 G, the time required for excitation of the hfs line has been found to be much longer than the spin-lattice relaxation time T_1 throughout the range of excitation power ($P_{\rm mw} \leqslant 250$ mW). Note that the spectrum width of the excitation generator expressed in terms of magnetic units is about 0.3 G which is smaller than the amplitude of modulation of the magnetic field near the resonance.

To summarize, one can say that saturation of the hfs line in this experiment is caused only by the excitation of the forbidden transition. The time of exposure, $t_{\rm mw}$, of the specimen must, though, be reduced to the real excitation time, $t_{\rm sat}$. The following assumptions have been made for that. The EPR line width for the forbidden transition is the same as that for the unsaturated primary hfs line (as supported by the data in Ref. 7) and this line has the Lorentz shape.

Under these conditions we have

$$t_{sat}=t_{mw}/10. \tag{2}$$

The time $t_{\rm mw}$ is determined with accuracy of approximately 1%. But the systematic error which may arise when we calculate $t_{\rm sat}$ from Eq. (2) is about 50%, that is,

$$t_{\rm sat} = \alpha t_{\rm mw}/10,$$

where $\alpha = 0.5$–1.5. This has been verified in experiments on excitation of the forbidden transition without modulation of the magnetic field. The lack of precision in the value of α is determined by the fact that the line shape for the forbidden transition is generally unknown. For most results derived in this study this is insignificant since it is enough that $t_{\rm sat}$ is proportional to $t_{\rm mw}$ and α independent of the concentration of orthomolecules. We shall assume therefore that Eq. (2) is exact unless stated otherwise.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

3.1. Preliminary remarks

First of all, we must qualitatively analyze the method for obtaining the data on diffusion of atoms near orthomolecules from the results on excitation of forbidden transitions.

For an impurity atom in para-H_2 the probability of a forbidden transition depends on the ortho-environment of the atom, that is, on the presence or absence of ortho-molecules around it. The ortho-environment and hence the probability of a forbidden transition, can be changed under the effect of two processes—migration of the atom and transfer of the spin state to another atom. The first process is conventional diffusion and the second is spin diffusion.

If the rates of both conventional and spin diffusion are fairly slow, each atom will have its own characteristic time of spin flip determined by the forbidden transition. If the concentration of ortho-H_2 is of the order of 10^{-2} these times for various atoms may differ by three–four orders of magnitude. The saturation curve for an hfs line following excitation of a forbidden transition will thus differ from the conventional exponential curve:[8]

$$A(t)/A(0)=\exp[-(t_{sat}/\tau_{sat})^{1/2}]. \tag{3}$$

Here $\tau_{\rm sat}^{-1} \propto C_o^2$. Slowness of the diffusion means here a diffusion hopping time $\tau_d \gg \tau_{\rm sat}$. We do not cite Eq. (3) here because it was discussed in sufficient detail in Ref. 8 for a similar case of relaxation at randomly located paramagnetic centers.

When the diffusion rate is high both conventional and spin diffusion cause averaging of the probabilities of forbidden transitions for different atoms. Under these conditions the saturation curve is described by a simple exponential:[8]

$$A(t)/A(0)=\exp(-t_{sat}/\tau_{sat}). \tag{4}$$

In this case $\tau_{\rm sat}^{-1} \propto C_o$ and $\tau_d \gg \tau_{\rm sat}$.

Let us consider in more detail fast diffusion of hydrogen atoms assuming that the atom occupies a substantial position in the lattice.[9]

1. Diffusion of atoms by themselves

Since $W_1 \propto 1/r^6$ we may assume in the first approximation that the forbidden transition occurs only when the atom has approached an orthomolecule at a distance of the lattice parameter, $r = a$. Then the characteristic time $\tau_{\rm sat}$ of hfs line saturation under excitation of a forbidden transition will be determined by the total time of the process including: a) the time needed for the hydrogen atom to approach an orthomolecule, and b) the time of spin flip caused by the forbidden transition near the orthomolecule. Thus we have

$$\tau_{sat}=W^{-1}(\tau_{mw}+\tau_\infty). \tag{5}$$

Here $W = \frac{2}{3}C_0Z$—is the probability that the hydrogen atom is near an orthomolecule with the required projection of the nuclear spin (see Fig. 1), Z is the number of molecules in the first coordination sphere, $\tau_{\rm mw} = {\rm const}/P_{\rm mw}$ is the characteristic time of a forbidden transition for a hydrogen atom near an orthomolecule H_2 (the excitation power is $P_{\rm mw}$), and $\tau_\infty = \tau_d$ is the diffusion hopping time for an atom near an orthomolecule. For $P_{\rm mw} \to \infty$ the time $\tau_{\rm sat}$ can be easily seen to be determined only by the diffusion rate for an atom near ortho-H_2.

2. Spin diffusion

A definite number of atoms in a crystal always have an orthomolecule at a distance equal to the lattice parameter. We may assume that forbidden transitions occur only for such atoms which form pairs with ortho-H_2. For all other atoms in the crystal the saturation of an hfs line occurs via spin diffusion. The fraction of the hydrogen atoms located in the vicinities of orthomolecules with the required projection of the nuclear spin is $W = \frac{2}{3}C_0Z$. As in the case of conven-

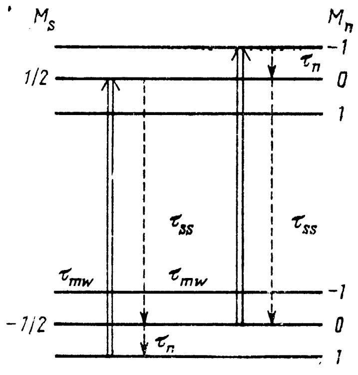

FIG. 3. Electron-nuclear transitions occurring in the H-ortho-H_2 pair in the process of excitation of the forbidden transition. τ_{mw} is the time of forbidden transition, τ_{ss} is the time of the spin state exchange with the free atom, and τ_n is the time of nuclear relaxation of ortho-H_2.

tional diffusion, we can write expression (5) where τ_∞ is the time of transfer of the spin state from an atom paired with ortho-H_2 to a free atom.

Note the following two facts. First, $W \ll 1$, that is, a large number of free atoms exist for each paired atom. This is why the subsequent process, that is, electron spin flip in the pair by a forbidden transition, the exchange of the spin state with a free atom, and others, must be cyclic. Secondly, the dipole-dipole interaction of a paired atom with ortho-H_2 is stronger than the dipole-dipole interaction of two hydrogen atoms at a mean distance (for $C_H \sim 10^{-5}$). In this case the effective spin transfer from a paired atom may occur only if the orthomolecule in the pair is in a state with $M_n = 0$.

Figure 3 illustrates two periodic processes which may occur in H-ortho-H_2 pair under excitation of a forbidden transition. Significantly, both processes include the stage of nuclear relaxation of ortho-H_2. The time of transfer of the spin state from the paired atom in these cyclic processes is

$$\tau_\infty = \tau_{ss} + \tau_n. \tag{6}$$

Here τ_{ss} is the time of exchange of the spin states and τ_n is the time of nuclear relaxation of ortho-H_2.

Under conditions of fast spin diffusion we have thus

$$\tau_{sat} = W^{-1}(\tau_{mw} + \tau_{ss} + \tau_n). \tag{7}$$

The time τ_{ss} describes the rate of spin diffusion in a system of impurity atoms and is inversely proportional to their concentration.

Note that until now we have assumed that $W = \frac{2}{3} C_0 Z$ in Eqs. (5) and (7). This assumption is a rather rough approximation for the following reasons. First of all, forbidden transitions have a certain probability to occur for all atoms in the crystal and not only for atoms in the vicinities of orthomolecules. This fact has no significant bearing on the above qualitative analysis of the excitation process but it will be taken into consideration below. More importantly, W is dependent not only on the concentration of orthomolecules in the crystal. It depends also on the ratio of the rates of two processes, namely, the diffusion of the H atom near ortho-H_2 (described by τ_d) and ortho-para conversion stimulated by the presence of a hydrogen atom near the orthomolecule. If the time $\tau_c(1)$ of conversion of ortho-H_2 in the first coordination sphere of the hydrogen atom is such that $\tau_c(1) \gg \tau_d$, then we have $W \approx 2C_o Z/3$. If, however, $\tau_c(1) \ll \tau_d$, then $W \ll 2C_o Z/3$ and excitation occurs at a much slower rate than expected from Eqs. (5) and (7). Thus the time of diffusion hopping of an atom near an orthomolecule can be found from the unknown time $\tau_c(1)$ and the absolute magnitude of τ_{sat} for low excitation powers ($P_{mw} \to 0$, $\tau_{mw} \gg \tau_\infty$).

The following conclusions can be made from the above discussion. If the rate of diffusion of hydrogen atoms is sufficiently high then we can determine the diffusion rate for atoms from the experimental results on $\tau_{sat}(P_{mw} \to \infty)$ as $D = a^2/6\tau_d$ with $\tau_d = \tau_\infty$. If it is not atom diffusion near ortho-H_2 but the transfer of the spin state that is the faster process ($\tau_d \gg \tau_{ss} + \tau_n$), then we can find τ_d by determining $\tau_{sat}(P_{mw} \to 0)$ if we know the conversion time for ortho-H_2 in the first coordination sphere of the hydrogen atom.

3.2. Experimental results for H-in-para-H_2

Figure 4 shows the amplitude of an H-atom hfs line as a function of excitation time. It is described by the expression

$$A(t)/A(0) = \exp[-(t_{sat}/\tau_{sat})^n],$$

where $n = 1.03 \pm 0.02$ (see the Table), which coincides with Eq. (4); $\tau_{sat} = 65 \pm 2$ ms.

Figure 5 gives the plot of τ_{sat}^{-1} as a function of the number x_o of orthomolecules added to the gaseous parahydrogen before condensation on a cold substrate. We have

$$\tau_{sat} = K(x_o + x_i)^n,$$

within the experimental accuracy where $n = 0.98 \pm 0.04$ and $x_i = (2.5 \pm 0.5) \cdot 10^{-3}$ (see the Table). If we assume that x_i is the lowest concentration of orthomolecules in our specimens generated by ortho-para conversion in the feed-in system we may write $C_o = x_o + x_i$. Then we have $\tau_{sat}^{-1} \propto C_o$.

Figure 6 presents the plots of the function $\tau_{sat}(1/P_{mw})$ recorded for one of the H-in-para-H_2 specimens at 4.2 and 1.5 K and a plot for a lower concentration of H atoms at 1.5 K. The plots can be seen to be described well by an expression similar to Eq. (5). In this case $W^{-1}\tau_\infty = 2.5 \pm 0.2$ ms and this time is independent of temperature and concentration of H atoms in the specimen.

The form of the saturation curve and the dependence $\tau_{sat}(C_o)$ indicate rapid diffusion of atoms. The fact that τ_∞

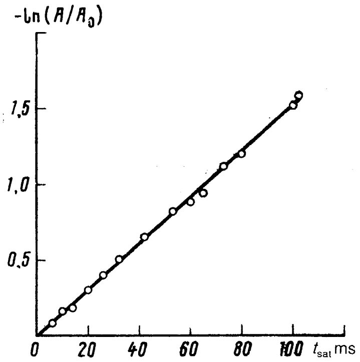

FIG. 4. Amplitude of the hfs line for hydrogen atoms as a function of the time of excitation of the forbidden satellite transition. $P_{mw} = 10$mW, $C_o = (6 \pm 1) \cdot 10^{-3}$, $T = 1.5$ K.

TABLE I. Parameters for the saturation curves (line 1) and for the dependences of the saturation times of the ortho-molecule density in the sample (lines 2–4).

Expression		H	N
$A(t)/A(0) = \exp[-(t_{sat}/\tau_{sat})]^n$	n	$1{,}03\pm0{,}02$	$0{,}52\pm0{,}02$
$\tau_{\text{sat}}^{-1} = K(x_o + x_i)^n$	K	$(3{,}3\pm0{,}3)\cdot10^3$	$(1{,}7\pm0{,}1)\cdot10^5$
$(P_{\text{mw}} = 15$ mW$)$	x_i	$(2{,}5\pm0{,}5)\cdot10^{-3}$	$(1{,}9\pm0{,}5)\cdot10^{-3}$
	n	0.98 ± 0.04	$2{,}04\pm0{,}15$

is independent of the atom concentration demonstrates that τ_∞ is not related to spin diffusion.

The results might indicate that diffusion of hydrogen atoms is a very fast rate, that is, $\tau_\infty = \tau_d$ and $D \approx 5\cdot10^{-12}$ cm^2/s. Since τ_∞ is independent of temperature at 1.5–4.2 K we can assume that band diffusion of hydrogen takes place. But then the bandwidth for diffusion of H atoms must be at least much smaller than 10^{-2} K and this result contradicts the estimates obtained from the data[1,2] on recombination of H atoms in H_2.

It remains to assume that τ_∞ is the time of nuclear relaxation of ortho-H_2 near hydrogen atoms, that is, that $\tau_\infty = \tau_n$. This means that the hydrogen atom migrates near orthomolecules at a fairly slow rate ($\tau_d \gg \tau_n$ and $D \ll 5\cdot10^{-12}$ cm^2/s) while the spin diffusion rate is high ($\tau_{\text{ss}} \ll \tau_n$).

3.4. Estimate of the diffusion rate for hydrogen atoms near ortho-H$_2$

As noted above, if the diffusion of H atoms near ortho-H_2 is slow ($\tau_d \gg \tau_n$) it can be estimated by comparing the experimental data on $\tau_{\text{sat}}(P_{\text{mw}} \to 0)$ with the results predicted for fast diffusion [$\tau_d \ll \tau_c(1)$].

From the standpoint of experiments it is more convenient to compare the calculated results not with the time $\tau_{\text{sat}}(P_{\text{mw}} \to 0)$ by itself but with the ratio of the times of hfs line saturation under excitation of the forbidden transition and of the line itself, that is, $\tau_{\text{sat}}(P_{\text{mw}} \to 0)/\tau_0$. In this case, we need not know the microwave magnetic field within the resonator[6] and need not recalculate the exposure time for the specimen in terms of the real excitation time.

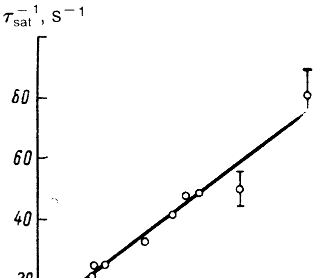

FIG. 5. The characteristic saturation time for the hfs line of H atoms in para-H_2 as a function of the number of orthomolecules added to the gaseous parahydrogen before preparation of the specimen. $P_{\text{mw}} = 15$ mW, $T = 1.5$ K.

It may be shown[8] that in the case of a low microwave power the ratio of the probability of the forbidden transition averaged over all positions of the hydrogen atom to the probability of an ordinary hfs transition is given by

$$\frac{W_1}{W_0} = \frac{\tau_0}{\tau_{sat}} = \frac{8}{5} C_o \sum_k Z_k \left(\frac{\mu_e}{r_k^3 H_{\text{hfs}}} \right)^2 . \tag{8}$$

Here summation is performed over the coordination spheres around the hydrogen atom, r_k is the radius of the k th coordination sphere, and Z_k is the number of molecules in this sphere. The greatest contribution to the sum must obviously be made by the terms with the small radius r_k, that is, by those hydrogen atoms which are in the vicinities of the orthomolecules, for instance, in the first coordination sphere.

The ratio of the saturation time (τ_{sat}) for the hfs line under excitation of a forbidden transition to the saturation time (τ_0) in the case of a low microwave power ($\tau_{\text{sat}} \gg W^{-1}\tau_\infty$) was found in experiments. When the correction for the microwave power was taken into account the result was $\tau_0/\tau_{\text{sat}} = (4.2 \pm 0.5)\cdot10^{-5}$ for the H-in-para-H_2 specimen with $C_o = (6 \pm 1)\cdot10^{-3}$. The calculated results for τ_0/τ_{sat} are tabulated below [k is the number of the coordination sphere from which summation is started in Eq. (8)].

k	1	2	3	4
$(\tau_0/\tau_{\text{sat}})\cdot10^5$	32.3	4.9	3.2	1.2 ·

The best agreement between the predicted and experimental results is achieved if summation is started from the second, rather than first, coordination sphere.[2)] Hence a very important conclusion is that forbidden transitions do not involve H-ortho-H_2 pairs for which $r_k = a$. Otherwise, the rate of saturation of the hfs line would be higher almost by an order of magnitude than that observed in experiments.

This means that the diffusion hopping time for the hydrogen atom near the orthomolecule is $\tau_d > \tau_c(1)$, that is, orthomolecules in the first coordination sphere of the hydrogen atom have the time to convert to the para state. On the other hand, since the conversion time strongly depends on the distance, the number of orthomolecules in the second coordination sphere practically does not vary in the time interval τ_d.

The conversion time for ortho-H_2 near a hydrogen atom can be estimated in the following way. In solid hydrogen the conversion rate is known[10] to vary from 1.8 to 1.9%/hour. The conversion rate for a pair of orthomolecules depends on the magnetic moment μ_n of ortho-H_2 and on the distance R between the orthomolecules as μ_n^2/R^{12}. If we assume that the hydrogen atom occupies a crystal lattice site (that is, for the first coordination sphere we have $R = a$ and for the second sphere $R = 2^{1/2}a$) and replace the magnetic moment of ortho-H_2 with the magnetic moment of the hydrogen atom we can easily find that the conversion time for ortho-H_2 in the first coordination sphere of the H atom must be $\tau_c(1) \approx 10$ s and in the second sphere $\tau_c(2) \approx 10^{-3}$ s. We obtain also the estimate 10 s $< \tau_d < 10^3$ s.

The result $\tau_d < 10^3$ s was confirmed also by the experimental determinations of the ratio $\tau_o/\tau_{\rm sat}$ as a function of the time elapsed from the preparation of the specimen. The value of this ratio measured about 20 min after preparation of the specimen was found to change by less than 5–10% at about 30 hours later.

It can be stated, therefore, that the rate $D = a^2/6\tau_d$ of diffusion of hydrogen atoms near ortho-H_2 varies from 10^{-7} to 10^{-19} cm^2/s. This implies, primarily, that atom diffusion near ortho-H_2 is much slower than the band diffusion. This is diffusion with misalignment of levels.

As noted in Sec. 1, the rate of "recombination" diffusion for hydrogen atoms in normal hydrogen at 1.5–4.2 K is about 10^{-17} cm^2/s. In para-H_2 the rate of "recombination" diffusion is of the same order of magnitude.[11] It can be readily seen that the rate of hydrogen atom diffusion near ortho-H_2 is not only much lower than the rate of the band diffusion. This rate is not much different, at least in order of magnitude, than the rate of "recombination" diffusion. This is possible if in both instances the misalignments of the energy levels caused by atom diffusion are close to each other. The misalignment of the energy levels produced when two hydrogen atoms approach each other has been estimated[12] to be about 5 K. In the conditions of diffusion of H atom near ortho-H_2 a comparable misalignment of about 1 K may be caused by the anisotropic electrostatic interaction between the hydrogen atom and the orthomolecule.[13]

3.5. Determination of the nuclear relaxation time for ortho-H_2 near a hydrogen atom

The time τ_n of nuclear relaxation of the orthomolecules can be calculated from the results on excitation of the forbidden transition and compared with the NMR data. This may yield additional verification for the interpretation of the experimental results on excitation of forbidden transitions for hydrogen atoms.

Let us average the probabilities of forbidden transitions for all H atoms under the following conditions: 1) the atom must not be in the first coordination sphere of the orthomolecule;[3)] 2) if spin flip of the atom via a forbidden transition occurs several times during saturation each of the flips cannot take a shorter time than τ_n.

We can then easily derive an expression similar to Eq. (5):

$$\tau_{sat} = \frac{\text{const}}{P_{mw}} + \alpha \frac{\tau_n}{24C_o}. \qquad (9)$$

Here $\alpha = 0.5$–1.5. As noted above, some uncertainty arises when the time of exposure of the specimen is recalculated to the real time of excitation of the forbidden transition because the shape of the absorption line of the forbidden transition is now known. Using the results given in Fig. 6 we obtain $\tau_n = 0.2$–0.6 ms for $C_o = (6 \pm 1)\cdot 10^{-3}$. In addition Fig. 6 demonstrates that τ_n is not changed upon variation of the temperature from 1.5 to 4.2 K. The dependence of τ_∞ and C_o on the orthomolecule concentration in the specimen is illustrated in Fig. 7. It coincides with the dependence of τ_n on C_o since α is independent of the orthomolecule concentration. All the above results are in a sufficiently good agreement with the NMR data on the rate of nuclear relaxation of orthomolecules in parahydrogen.[14] It has been indeed estimated that the presence of hydrogen atom cannot affect the rate of nuclear relaxation of ortho-H_2 since the time of nuclear relaxation via dipole-dipole interaction with the hydrogen atom is about 10^6 s.

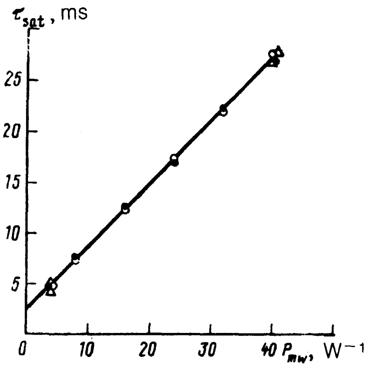

FIG. 6. The characteristic saturation time for the hfs line of hydrogen atoms as a function of the excitation power $P_{\rm mw}$. Open circles—$T = 1.5$ K, $C_{\rm H} = C_{\rm H}^0$. Dark circles—$T = 4.2$ K, $C_{\rm H} = C_{\rm H}^0$. Open triangles—$T = 1.5$ K, $C_{\rm H} = 0.25C_{\rm H}^0$.

In conclusion of this section the following observation should be made about the rate of spin diffusion of H atoms in para-H_2. For the hydrogen atom concentration $C_{\rm H} \sim 10^{-5}$ the most probable time of spin transfer from one atom to another[8] is $\tau_{\rm ss} \sim 10^{-4}$ and it agrees with the above estimate of $\tau_{\rm ss} \ll \tau_n \approx 4\cdot 10^{-4}$ s.

3.6. N-in-para-H_2 specimens

A logical continuation of the above experiments would be a study of excitation of forbidden transitions in specimens with a lower hydrogen atom concentration. In this case the spin diffusion would be slower and $\tau_{\rm ss} > \tau_n$. This would re-

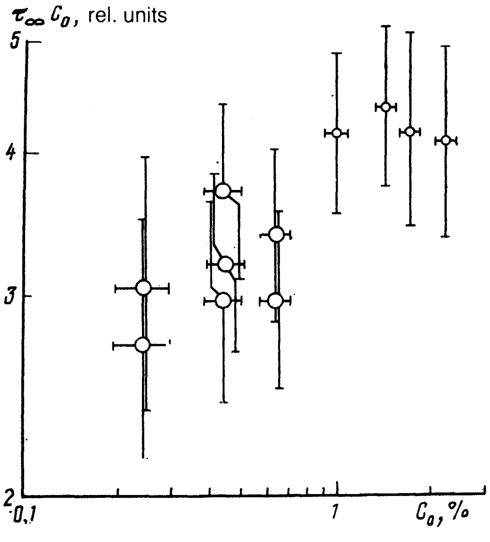

FIG. 7. Variation of $\tau_\infty C_o$ with the orthomolecule concentration in a specimen of parahydrogen.

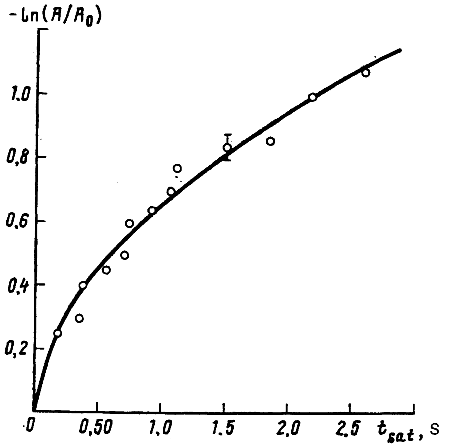

FIG. 8. The hfs line amplitude for nitrogen atoms as a function of the excitation time for the forbidden satellite transition. $P_{\text{mw}} = 20$ mW, $C_o = (2 \pm 1)\cdot 10^{-3}$, $T = 1.5$ K.

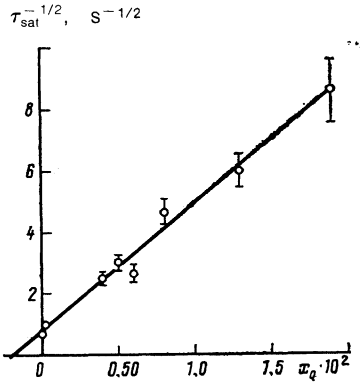

FIG. 9. Characteristic hfs line saturation time for nitrogen atoms in parahydrogen as a function of the number of orthomolecules added to the gaseous parahydrogen before preparation of the specimen. $P_{\text{mw}} = 15$ mW, $T = 1.5$ K.

sult in straggling of the excitation rates for different atoms and thus in a change of the shape of the saturation curve [which will be described by Eq. (3) rather than Eq. (4)], at least, when the excitation power is high. Experiments with specimens with hydrogen-atom concentrations about 10^{-6} demonstrate that the saturation process is also described by Eq. (4) even for $P_{\text{mw}} \sim 250$ mW. The rate of spin diffusion is still sufficiently higher than the rate of nuclear relaxation of orthomolecules.

Excitation of forbidden transitions was therefore studied in experiments with nitrogen atoms in parahydrogen. These experiments demonstrated how the excitation process is changed for stationary atoms and slow spin diffusion.

Figure 8 presents the variation of the amplitude of a hyperfine structure line as a function of the time of excitation of a satellite forbidden transition for nitrogen atoms. This function is described within the experimental accuracy by the expression

$$A(t)/A(0) = \exp[-(t_{\text{sat}}/\tau_{\text{sat}})^n],$$

where $n = 0.52 \pm 0.02$. The saturation curve for nitrogen atoms differs significantly from the saturation curve for hydrogen atoms (see Fig. 4 and the Table) and coincides with the saturation curve for the stationary atoms in the absence of spin diffusion.[3] As noted above, this means that each atom is characterized by its own rate of spin flipping caused by excitation of the forbidden transition. The most probable flipping rate[8] is $(2\tau_{\text{sat}})^{-1}$.

Let us now consider the behavior of the characteristic saturation time for nitrogen atoms as a function of the ortho-H_2 concentration in the specimen. It can be shown[8] that under these conditions

$$\left(\frac{\tau_{sat}}{\tau_0}\right)^{-1/2} = \frac{8\pi}{9}(6\pi)^{1/2} C_o \left(\frac{\mu_e}{a^3 H_{\text{hfs}}}\right) = 0.61\ C_o, \qquad (10)$$

where τ_0 is the characteristic time of the hfs line saturation under excitation of this line. As it was done for the hydrogen atom, assume that the nitrogen atom occupies a crystal site.[15]

Figure 9 illustrates the experimental results on the dependence of $\tau_{\text{sat}}^{-1/2}$ on the amount (x_o) of orthomolecules added to the gaseous para-H_2 before preparation of the specimen. This dependence is satisfactorily described by the equation

$$\tau_{\text{sat}}^{-1} = K(x_o + x_i)^n,$$

where $n = 2.04 \pm 0.15$ (see also the Table). When $C_o = x_o + x_i$ we obtain $\tau_{\text{sat}}^{-1} \propto C_o^2$.

It can be shown that the stimulated conversion of orthomolecules near the nitrogen atom under these conditions does not affect the rate of excitation. Indeed, the experimental data yield $(\tau_{\text{sat}}/\tau_0)^{-1/2} = (0.57 \pm 0.2) C_o$ (where $C_o = x_o + x_i$) which coincides with Eq. (10) to within the experimental error. This confirms the conclusion that the time τ_{sat} is essentially determined by the probability of the forbidden transition at the mean distance between the nitrogen atom and ortho-H_2.

We see that both the form of the saturation curve and the dependence of the characteristic saturation time on the ortho-H_2 concentration indicate that for nitrogen atoms the diffusion processes occur at a sufficiently slow rate. The diffusion hopping time for the nitrogen atom and the time of transfer of the spin state from one nitrogen atom to another prove to be much longer than the most probable time of spin flip for the atom caused by the forbidden transition: τ_d, $\tau_{\text{ss}} \gg 2\tau_{\text{sat}}$. From the data in Fig. 8 we obtain τ_d, $\tau_{\text{ss}} \gg 4$ s. Since the mass of the nitrogen atom is fairly large this explains why the atom does not migrate during this time. As for the spin diffusion rate, when the nitrogen atom concentration is about 10^{-6} the time τ_{ss} of transfer of the spin state[8] must be of the order of $2\cdot 10^{-4}$ s. The significant decrease in the spin diffusion rate ($\tau_{\text{ss}} > 4$ s) cannot be attributed to the dipole–dipole interaction between nitrogen atoms and ortho-H_2. But it may be related to the interaction of the nitrogen atom with the quadrupole moment of ortho-H_2 or N_2. For a nitrogen atom in the ^4S state it is difficult to evaluate theoretically the magnitude V_Q of such interaction. It may be said[8] only that V_Q must be about 10^{-5}–10^{-6} K for the spin diffusion rate to be decreased by a factor of 10^4 for the concentration $C_{\text{N}} \sim 10^{-6}$.

4. CONCLUSIONS

The following results have been obtained.

1. Exponential saturation of the hfs line for hydrogen atoms has been found to occur under excitation of a forbid-

den electron-nuclear transition involving simultaneous flipping of the electron spin of the atom and the nuclear spin of ortho-H_2. The shape of the saturation curve and the dependence of the characteristic saturation time on the ortho-H_2 concentration have been found to be determined by the relatively fast spin diffusion of hydrogen atoms ($\tau_{ss} \leqslant 4 \cdot 10^{-4}$ s for $C_H \sim 10^{-5}$). For high excitation power the saturation process is limited by the rate of the nuclear relaxation of ortho-H_2 near the hydrogen atom.

In contrast to hydrogen atoms, the spin diffusion rate for nitrogen atoms in para-H_2 has proven to be very low and $\tau_{ss} > 4$ s.

2. The diffusion jog time for the H atom near ortho-H_2 has been shown to vary between 10–10^3 s corresponding to diffusion rates from 10^{-17} to 10^{-19} cm^2/s. This means that the misalignment of the energy levels produced by diffusion of H atom near ortho-H_2 is comparable with the misalignments caused by migration of two hydrogen atoms towards each other. Hence, a rapid band diffusion of hydrogen atoms cannot occur, at least in the specimens with a large concentration of orthomolecules. In this connection it does not seem feasible to produce a significant proton polarization in a $H + H_2$ system.

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[1] All arguments and results given in this section are also applicable to the N atom–ortho-H_2 pair. As was done for the hydrogen atom, the states with different components of the nuclear spin of the N atom along a given axis can be regarded as single. According to the experimental results, the nuclear relaxation time for N atoms is much longer than the time T_1 of the electron spin-lattice relaxation for these atoms, that is, it is much longer than 10–100 s.

[2] Note that when we derive Eq. (8) for the hydrogen atom we must take into consideration the zero-point vibrations of the atom about the equilibrium position and the distortion of the crystal lattice near the atom. Estimates[9] show, however, that when these factors are taken into account the results tabulated above must be reduced by not more than 25% for $k = 1$ and by not more than 1–5% for other k values.

[3] Note that if the condition 1) is removed then the time τ_n found from the excitation results is approximately one-third of the data derived from the direct NMR measurements.[14]

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