

THE WALL SHIFT OF FREQUENCY AND PHASE OF H-MASER
IN THE TEMPERATURE RANGE $0 \leq T \leq 420$ K

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ABSTRACT

The main theoretical prepositions of the wall shift of H-maser frequency/phase in the temperature range from 0 to 420K are given for the various coatings (PTFE, solid molecular hydrogen and liquid helium) of the storage bulb. The theory is based on the non-equilibrium statistical mechanics (classical and quantum) and includes the analysis of kinetic processes occurring on the surface of condensed matters. The various deformation mechanisms of hyperfine magnetic structure of a hydrogen atom spectrum are described and classified. The relationship between phase shift and energy accommodation coefficient is established, which allows one to give a prognosis of their temperature dependence in the investigated temperature range. The theory explains the available experimental data and predicts a new precession-inertial effect, in which a frequency of an atom radiation depends on acceleration of its mass center. It suggests a relationship of hyperfine interactions with thermal properties of a physical vacuum in non-inertial system of reading. The theory enables one also to obtain the criterion for Bose-condensation and superfluidity of a hydrogen atom in H-maser conditions. A phase shift in PTFE covering is attributed to the inelastic nature of H atom interaction with a surface becomes the adiabatic at lower temperatures. For $H_{2(sol)}$ it is a classical adsorption-desorption process after Frenkel. For He_{liq} it is a transition state and precession-inertial effect.

Key words: wall shift, H-maser, gas atom adsorption

1. INTRODUCTION

As is known, in H-maser the hydrogen atoms in exited 1S state arrived in a storage box located in a resonator where they perform the induced transition between the different levels of a magnetic hyperfine structure (MHFS): $F=1, m_F=0 \rightarrow F=0, m_F=0$, where F and m_F – quantum numbers.

Wall shift frequency $\Delta\nu_w$ of this 0-0 transition arises because of the deformation of energy levels MHFS of atoms upon their collisions with the surface of the storage bulb and is expressed via the average phase difference for one collision between precessing magnetic dipole of atom and its high frequency electromagnetic resonator field $\bar{\Phi}$:

$$\Delta\nu_w = \frac{\nu_c}{2\pi} \cdot \bar{\Phi} \quad (1)$$

$$\bar{\Phi} = \int_0^\tau \frac{\delta E_c}{\hbar} dt = \int_0^\tau \delta\nu \cdot dt, \quad (2)$$

where ν_c is the frequency of atom hydrogen collisions with a wall of storage bulb; δE_c is the deformation energy of hyperfine splitting of the levels; \hbar is the Plank constant; τ is the time of the atom interaction with a wall; $\delta\nu$ is the frequency shift; the line designates the frequency averaging. The study of the frequency and phase wall shift is a complicate experimental and theoretical task. The experiments require the solving of a number of technical and technological problems, the theory should take in account the kinetics of the processes occurring on a storage bulb surface. A significant progress is achieved, however, in this field over the past decades.

From one side, the unique experimental data have been obtained in a wide temperature range -Refs.1-6, from other side, a lot of attempts for their theoretical interpreting have

been done. They were of a semi-empirical character, as a majority of theoretical explanations accompanying the experiments. We have no intention to give a critical review of these theoretical approaches here. Our aim is to sum up the main results in this field obtained by different authors Refs.-7-9.

2.RESULTS

The model of a actual surface is introduced. It comprises a transition zone, which is limited by a thermally exited surface of semi-endless continuum from the one side, and by the layers of atoms from a disordered covering structure, absorbed atoms and mixing from the other side. As a result, a potential channel is formed, which is separated from gas by a potential barrier. The gas atoms, arriving in a transition zone, change their energy along a normal to the surface on the account of a stochastic interaction mechanism, while their tangent component remains intact. Such a model of the surface is determined as stochastic channeling.

The analysis of relationship of a change of probability of electron density of a nucleus $|\Psi_{1s}(0)|^2$ because of interaction and the additional magnetic fields on a nucleus $\sum_i \delta \vec{H}_i(0)$ leads to the following mechanisms of deformation MHFS of hydrogen atom:

Potential mechanism is caused by the hydrogen atom adsorption on a surface of a bulb. In this case, a wall shift on one interaction is described as:

$$\delta\nu_Q = R_0 \cdot \nu_0 \cdot Q \approx 1.3 \cdot \nu_0 W \quad (3)$$

where ν_0 is the frequency of non-perturbed 0-0 transition; R_0 is the constant dependent on potentials of atom ionization, as well as on the difference in the energy levels of 1S and 2P of a hydrogen atom; W is the probability of mixing of 2P state to the 1S; Q is the adsorption heat on a separate atom. Q -value is calculated using a model of semi-endless continuum and Lennard-Johns 6-12 pair interaction potential.

When calculating the average phase shift on the one interaction $\bar{\Phi} = 2\pi\delta\nu_Q \bar{\tau}$ (4)

an adsorption time τ is given by the Frenkel equation

or by the equation of the transition state of absolute reaction rates.

The orbital-dipole mechanism is associated with an appearance on a nucleus an additional magnetic field because of mixing of the exited electron state 2P to the ground state 1S. The mixing is caused by polarization of a hydrogen atom in the field of the surface forces. This shift is small, as a rule, and can be neglected in a case of H-maser.

Potential-relaxation mechanism is associated with a non-equilibrium character of hydrogen atom interactions with a covering transition zone. It is the case of H-masers, with a bulb covered with a PTFE layer. In the case of low temperature H-masers, the non-equilibrium interactions no longer dominate. For the consideration of such interactions the non-equilibrium statistical mechanics, both the classical and quantum ones, is used (I. Prigogine's technique). It allows one to establish the interrelation of a phase shift $\bar{\Phi}(T)$ and energy accommodation coefficient (EAC) $\alpha(T)$ dependent on temperature.

The energetic atom relaxation to a thermal balance with a bulb as with a thermostat is of stochastic character and can be described by uni- or bilateral process when the two counter processes are compensated, which results in the adiabatic

interaction of atoms with a surface, i.e. $\alpha(T)=0$. In the first case, the dependence of the phase shift $\Phi(T)$ on $\alpha(T)$ is given by the equation

$$\Phi_I = \frac{4\omega_0 R_0}{V_{OZ} \alpha(T)} \cdot \int_{Z_s}^{\infty} U(Z) dZ, \text{ i.e. } \Phi_I \sim 1/\alpha(T) \quad (5)$$

It is characteristic of non-elastic interactions and the higher temperatures.

In a case of bilateral process the dependence has another shape:

$$\Phi_{II} = \frac{2\omega_0 R_0 \alpha(T)}{V_{OZ}} \cdot \int_{Z_s}^{\infty} U(Z) dZ \text{ i.e. } \Phi_{II} \sim \alpha(T) \quad (6)$$

It is characteristic of elastic interaction and the lower temperatures.

The designations here are as follows: $U(Z)$ is the potential of interaction along the normal to the surface; $\alpha=1-\exp(-\beta t)$; β is the coefficient of dynamic friction; ω_0 is the frequency of the non-perturbed 0-0 transition; Z_s is the classical turn point; V_{OZ} is the initial velocity of a gas atom; t - the interaction time of the atom with a surface; $U(Z)$ and β being expressed via molecular variables.

Precession-inertial mechanism is a completely new one [8]. An additional experimental verification is then, obviously, needed. It is suggested that this mechanism operates when the elastic reflection of a polarized hydrogen atom from the bulb covering occurs. The surface should be atomic smooth, and the reflection should be unitary. Upon reflection of atom a circular precession of electronic shell appears because of acceleration of its mass center. And a reason of the precession is an action of inertia forces on the center of mass of the exited electronic shell.

The frequency of the precession is given by the equation:

$$\Omega = \frac{ma_{in} \cdot \langle R \rangle_{xy}}{\sqrt{2} \cdot \hbar \cdot W}, \quad (7)$$

where m is the mass of electron; a_{in} is the acceleration of the electron mass center upon a collision on a surface; $\langle R \rangle_{xy}$ is

the average shoulder of inertial force in a surface plane; W is a probability of an mixing of 2P state to 1S state.

The precession of the electronic shell leads to the appearance of the additional magnetic field on the atom nucleus and generates a frequency shift:

$$\Delta\nu_{PI} = \frac{8\pi\mu_I e \cdot m \cdot a_{in}}{\sqrt{2}\hbar^2 \cdot c \cdot W} \quad (8)$$

μ_I is the magnetic momentum of a nucleus; e is the charge of an electron; m is the mass of an electron; c is the light velocity in vacuum. This shift is always positive. It reaches high values and may be a cause of the transition of a negative shift to the positive region in the vicinity of the absolute zero temperature.

It is worthy to note that in this case the frequency radiation of the atom depends on its acceleration but not on its velocity as in a case of the Doppler effect. As for a phase shift, it is determined by the equation $\Phi = 2\pi\delta\nu_Q \bar{\tau} \sim \Delta\nu_z \cdot \sqrt{T_g}$,

where $\bar{\tau}$ is the average time of collision of an atom with a surface. The shift $\Delta\nu_{PI}$ correlates with an effective temperature T_{in} , which we call the inertial temperature. It is equal to $\hbar\Delta\nu_{PI}=k_B T_{in}$

$$T_{in} = \frac{8\pi\mu_I e m a_{in}}{\sqrt{2}\hbar k_B W} = 1.3 \cdot 10^{-26} \frac{a_{in}}{W} (K) \quad (9)$$

This temperature is of the same order of magnitude as so called Unru temperature (T_{un}), which characterizes of the thermal properties of physical vacuum in a non-inertial system of reading -Refs.10.

$$T_{un} = \frac{\hbar a_{in}}{2\pi k_B c} = 4 \cdot 10^{-21} a_{in} (K) \quad (10)$$

As is known, the hydrogen atoms are the bosones, and the Bose-Einstein condensation has then to take place at the gas temperature $T_g < T_d$, where T_d is the degeneration temperature.

The analysis indicates that $\Delta\nu_w \sim \Phi(T) \sqrt{T}$ if there is no Bose-Einstein condensation and is $\Delta\nu_w \sim \Phi(T) T^2$ if it occurs, where $\Delta\nu_w$ is the wall frequency shift. These interrelations are the criterion of this phenomenon, provided that the gas consists of the polarized atoms.

From the other hand, for the open boxes in the regions of super-low temperature, the superfluidity of gaseous hydrogen could take place, which didn't, however, yet observed. A criterion of superfluidity is complicate but the united criterion of bose-condensation and superfluidity is relatively simple:

$$k_B T_D \leq \hbar^2 / 2m\Delta x^2 \quad (11)$$

where Δx is the distance between the centers of adsorption; m is the mass of the hydrogen atom, k_B and \hbar are the Boltzmann and Plank constants.

3.EXPERIMENTAL

For H-masers with the PTFE coverings the phase shift changes from the negative magnitudes at the low temperatures to the positive ones at the higher temperatures passing through 0 in the temperature region from 355 to 420K (Fig.1).

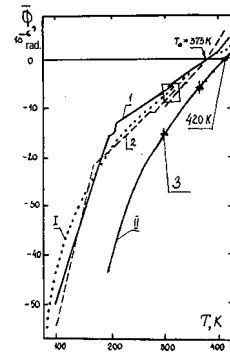


Fig.1. The comparison of experimental (1,2,3) phase shifts for copolymer FEP-120 (1), homopolymer TFE-42 (2), PTFE-4D

(3) and those shift theoretically calculated after equation (5) for 1, 2 (I) and for 3 (II).

For the comparison of the experimental and calculated values the experimental magnitude of temperature T_0 is used.

Then from the $\int U(Z) dZ = 0$, the concentration of CF_2 in the material (n_0) is determined and the adsorption heat (Q) is calculated.

The interaction time is calculated using the equation $t=L/V_{OZ}$, where L is the regulated parameter of length. The EAC is simultaneously calculated as a function of temperature $\alpha(T)$. This coefficient was not measured until now and is only predicted by a theory.

The numerical values of the main magnitudes for FEP-120 and TFE-42 (covering 1) and PTFE-4D (covering 2) are taken as:

$\rho_1=1.5 \text{ g/cm}^3$, $\rho_2=1.7 \text{ g/cm}^3$, $n_{01}=1.8 \cdot 10^{22} \text{ cm}^{-3}$, $n_{02}=2 \cdot 10^{22} \text{ cm}^{-3}$, $Q_1=0.49 \cdot 10^{-14} \text{ erg}$, $Q_2=0.55 \cdot 10^{-14} \text{ erg}$,

$\langle C \rangle = 2.6 \cdot 10^5 \text{ cm/sec}$, $L_1=13.8 \text{ \AA}$, $L_2=7.2 \text{ \AA}$, where $\langle C \rangle$ is the light velocity in the material. The parameters of the pair interaction H- CF_2 and the constant component of the friction coefficient were taken equal to: $\epsilon_0=13.15 \cdot 10^{-16} \text{ erg}$, $\sigma_0=4.57 \cdot 10^{-8} \text{ cm}$, $\beta_0=1.64 \cdot 10^{11} \text{ 1/sec}$.

Further reducing of the bulb temperature is associated with its solid polycrystalline molecular hydrogen $H_{2(sol)}$ covering. The calculation of the phase shift is based on the mechanism of the potential deformation MHFS (3) using Frenkel formula for the life time, which is only valid for relatively pure surface. The comparison of experimental and theoretical data is presented in Fig.2., where the parameters of interaction, density and concentration, are taken equal to : $\epsilon_0=4.25 \cdot 10^{15}$ erg, $\sigma_0 = 2.94 \cdot 10^{-8}$ cm, $\rho = 0.076$ g/cm³, $n_0=2.3 \cdot 10^{22}$ cm⁻³, $Q=56.7 \cdot 10^{-16}$ erg.

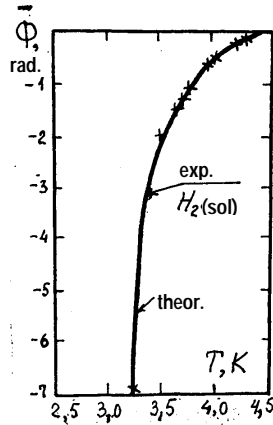


Fig.2. The comparison of the experimental and theoretically calculated phase shifts for a system $H-H_{2(sol)}$. The next stage in the development of low-temperature H-masers is associated with the coverings of a bulb by liquid helium (He^3 and He^4). The bulbs themselves can be of the open and close types. The polarized hydrogen is used here for preventing recombination the atom collisions. The theoretical calculation of the adsorption heat Q is carried out with the account of a degree of surface covering by the adsorbed gas, which is close to unit. As a result, the data close to the experimental values are obtained: $Q(He^4) = 1.59 \cdot 10^{-16}$ erg, $Q(He^3) = 0.59 \cdot 10^{-16}$ erg. For the calculation a function $\Phi(\tau)$ the potential mechanism of deformation MHFS is used. The adsorption time is determined using the method of transition state. Then the regulated parameter of potential barrier width is appeared to be equal: $\delta(He^4) = 0.56 \cdot 10^{-8}$ cm, $\delta(He^3) = 0.11 \cdot 10^{-8}$ cm. The comparison of the theoretical and experimental data are given in Fig. 3.

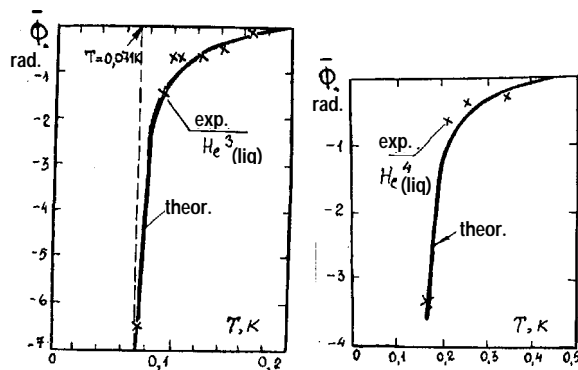


Fig.3. The comparison of experimental and theoretically calculated phase shifts for the system: $H-He^3_{(liq)}$ and $H-He^4_{(liq)}$. Thus, in a case of helium covering, one should take into account the adsorbed layer, which creates a potential barrier on a boundary with a gas phase.

4. DISCUSSION

As a result of establishing a correlation between the functions $\Phi(T)$ and $\alpha(T)$, it appeared to be possible to predict their values in the whole temperature range $0 \leq T \leq 420$ K (Fig.4).

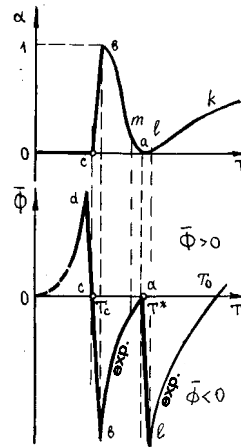


Fig.4 The qualitative representation of the correlation of functions $\Phi(T)$ and $\alpha(T)$. On a curve $\Phi(T)$ one can see the four zero phase shift points for the various covering materials. Temperature T_0 is well known and is caused by the compensation of the repulsive and attraction forces. With the temperature decrease ($T < T_0$) the inelastic reflection of the hydrogen atoms from a surface (PTFE) is observed, which becomes the adiabatic one at $T=T^*$ ($\Phi=0$, $\alpha=0$). The estimates of this temperature for different coverings are: $T^*=20-60$ K for PTFE; 4.4 K for $H_{2(sol)}$; 0.5 K for $He^4_{(liq)}$; 0.2 K for $He^3_{(liq)}$. The experiment gives 0.6 K for $He^4_{(liq)}$. At $T < T^*$ the adsorption begins, which results in the formation of an adsorbed layer in the vicinity of T_c . It is experimentally observed for the coverings $H_{2(sol)}$ and $He_{(liq)}$. The estimates for these temperatures give the following values: $T_c=0.1$ K for $He^{3,4}_{(liq)}$ (the preliminary experiment for $He^3_{(liq)}$ gives $T_c=0.07$ K; for $H_{2(sol)}$ 0.4 K; for PTFE 0.36 K). The temperature T_c corresponds to the degeneration criterion and the bose-condensation and superfluidity should occur at the $T_b \leq T_c$. In the vicinity of T_c the precession-inertial effect begins to operate and a phase shift transits from the negative to the positive values. Then, with a decay of a thermal motion, $T \rightarrow 0$ and $\Phi(T) \rightarrow 0$. Besides, the existence of the three peculiar points (1,b,d) of $\Phi(T)$ is predicted where the cessation of generation is possible. Let us compare the temperature T_{in} and T_{un} using equation (9) and (10). The calculation gives at $T=0.1$ K for $He^3_{(liq)}$ and for $He^4_{(liq)}$, respectively: $\tau=5 \cdot 10^{-11}$ s; $a_{in}=1.6 \cdot 10^{12}$ m/s²; $W_1=8 \cdot 10^{-6}$; $W_2=3 \cdot 10^{-6}$; $T_{in(1)}=2.6 \cdot 10^{-9}$ K and $T_{in(2)}=7 \cdot 10^{-9}$ K. For the same conditions we have $T_{un}=6.4 \cdot 10^{-9}$ K. Thus, $T_{in} \approx T_{un}$, which implies the exitation of the one and the same superstructure of the energetic levels of hydrogen atoms, which really exists. It also suggests the equivalency of the force inertial field and thermal field in the physical vacuum in the non-inertial systems of reading. The matter is that, in general, one can speak that the principle of equivalency of general theory of relativity to the phenomena of microworld is not valid.

Further, for the comparison of the theoretical predictions of $\Phi(T)$ for PTFE coverings in the temperature interval $T^* < T \leq T_0$ with the experiments, a relation determined by the classical turning point Z_s and an integral $\int_{Z_s}^{\infty} U(Z) dZ = 0$

$$\text{are of great importance: } \frac{n_0 \epsilon_0 \sigma_0^3}{T_0} = 6.1 \cdot 10^{-18} \text{ erg/K} \quad (12)$$

Using the experimental T_0 , one can determine from the above expression the concentration of CF_2 groups in the covering and its density. The calculation indicates that these values are very close for the different PTFE grades. This indicates to the similarity of the physical properties of various PTFE grades and the technologies of the covering production, though for PTFE-4D both the concentration and density are slightly higher than those for other grades. However, all these values are lesser than the density and concentration of CF_2 in the volume, which evidences the enhanced porosity the surface layers. The slope of the curve $\Phi(T)$ from the T_0 for the PTFE coverings depends on a parameter of the length L (the way of a hydrogen atom in the transition surface zone and the average sound velocity $\langle c \rangle$ in the coverings. The stochastic mechanism of the interaction of hydrogen atoms with a surface suggests the multiplicity of collisions in the transition zone, and then $L \gg d$, where d is the distance between CF_2 groups. That is why a slightly enhanced average sound velocity as compared to that in the volume is taken ($\langle c \rangle = 1.3 \cdot 10^5$ cm/sec for $T = 4..2K$).

This is caused, obviously, by a non-uniform chemical content of a surface structure, and a significant role of the longitudinal waves responsible for energy exchange between the atoms and a surface, i.e. for the energetic relaxation.

Knowing the n_0 and $\langle c \rangle$ - values, one can calculate the surface Debye temperature Q_{DS} , and a molar thermal capacity C_v of the covering. This value is close to the standard magnitude but slightly lesser than it. Since the samples with lower crystallinity have the higher thermal capacity, the latter can be used for qualitative estimate of a degree of crystallinity of the

PTFE coverings. The analysis indicates that FEP-120 and TFE-42 have lower crystallinity as compared to that of PTFE-4D.

Thus, the knowledge of the function $\Phi(T)$ allows one to determine the main physical properties of the covering material of the storage bulb for the traditional H-masers: the density ρ , the average sound velocity $\langle c \rangle$, the Debye temperature of a surface Q_{DS} and the molar capacity at the constant volume C_v . However, one should note that the proposed theory does not take into account the phase transitions in PTFE. As a whole, it is possible to speak about the radiospectroscopic technique for the investigation of the surface properties and of the surface processes occurring in the thin polymeric films.

5. CONCLUSIONS

-The different mechanisms of the wall deformation of MHFS of hydrogen atoms are considered and their frequency and phase shifts are determined.

-The analysis of the kinetics of the surface processes allowed to establish correlation between the phase shift function and EAC, which enables one to predict their change in a whole range of the considered temperatures.

-The theory is in a good agreement with experiments carried out with the different covering of the storage bulbs (PTFE, $H_{2(sol)}$ and $He_{(liq)}$).

-The existence of the precession-inertial effect is predicted and its relationship with the physical vacuum is established.

-The generalized criterion of bose-condensation and superfluidity of the polarized atomic hydrogen in H-masers is obtained.

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