STRUCTURE OF DISPERSION MEDIA BY NUCLEAR MAGNETIC RESONANCE

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The change of the diamagnetic shielding constant of a benzene molecule interacting with the solid phase surface is calculated.

It was shown in [1-3] that an estimate of the density of adsorbed water is based on a determination of perturbations arising in a dispersion medium at the solid phase boundary and on taking account of perturbations of the solid phase — the deformations of the crystal lattices under the action of water and organic compounds.

The effect of a change in density of a dispersion medium in a system consisting of a solid, adsorbed water, and liquid was observed in various structures by a relatively simple method [1, 2]. However, for a deeper understanding of the mechanism of this phenomenon it is necessary to employ methods of investigation differing in principle from those in [1, 2]. One such method is nuclear magnetic resonance (NMR). By using this method the state of adsorbed molecules can be investigated by the chemical shift and change of intensity of spectral lines. The chemical shift is estimated below.

In the present article we investigate the effect of the structure of the solid phase on the diamagnetic shielding constant of benzene protons. The diamagnetic shielding constants for a benzene molecule were calculated, and the effect of the solid phase structure on the diamagnetic shielding constant of benzene protons was investigated.

Figure 1 shows the location of a benzene molecule on the solid phase surface, where $a_1 = 2.64$ Bohr radii is the C—C bond length.

It follows from [4] that the diamagnetic shielding constant is calculated from the expression

$$\sigma_d = \frac{e^2}{3 m_e c^2} \left(O \left| \sum_k \frac{1}{|\mathbf{r}_k|} \right| O \right), \tag{1}$$

where the symbol $|0)$ denotes the ground state of the molecule, and $\mathbf{r}_k$ is the radius vector to the k-th electron in the molecule.

It is clear from Eq. (1) that to calculate the diamagnetic shielding constant it is necessary to know the wave function of the ground state of the benzene molecule.

By using the method of molecular orbitals expressions were obtained for the molecular π-orbitals and the corresponding energy levels of π-electrons in a benzene molecule. These are shown in Table 1. The atomic p_z-electron wave functions χ were calculated by the Slater method, which is based on the assumption that the atomic p_z-orbitals can be approximated by functions of the form $\chi_{2pz} = N_{2p} z \exp(-sr/2)$, where r is the distance to the nucleus of the carbon atom. The quantity N_{2p} is chosen from the normalization condition of the function χ, and is equal to $(s^5/(32\pi))^{1/2}$; s is the effective nuclear charge, which is equal to 3.25 for a carbon atom.

In the ground state all six p_z-electrons of the benzene molecule occupy the three lowest energy levels. Taking account of the spin, the spin-orbital wave functions have the form $\psi_i(j) = \psi_i(q_i)\varphi_i$, $\varphi_i = \alpha_0 = \binom{1}{0}$ is the wave function of the state in which the spin quantum number $I = +1/2$; $\varphi_i = \beta_0 = \binom{0}{1}$ when the quantum number $I = -1/2$.

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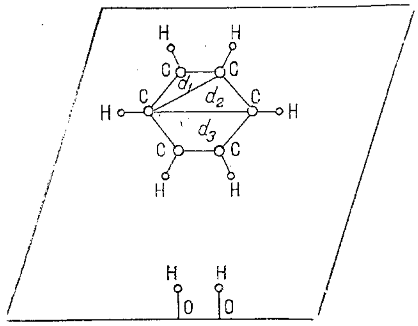

Fig. 1. Location of benzene molecule on solid phase surface.

According to the Pauli principle, only those states occur for which the total electron wave function of the atomic system is asymmetric with respect to the interchange of coordinates of any two electrons. Therefore, the molecular wave function of benzene corresponding to a given electron configuration must be written in the form of a Pauli determinant

$$\Psi_b^0(1,\ 2,\ 3,\ 4,\ 5,\ 6)=\frac{1}{\sqrt{6!}}\begin{vmatrix} \begin{pmatrix}\psi_1(1)\\0\end{pmatrix}_1 & \begin{pmatrix}0\\\psi_1(1)\end{pmatrix}_1 & \begin{pmatrix}\psi_2(1)\\0\end{pmatrix}_1 & \begin{pmatrix}0\\\psi_2(1)\end{pmatrix}_1 & \begin{pmatrix}\psi_3(1)\\0\end{pmatrix}_1 & \begin{pmatrix}0\\\psi_3(1)\end{pmatrix}_1 \\ \begin{pmatrix}\psi_1(2)\\0\end{pmatrix}_2 & \begin{pmatrix}0\\\psi_1(2)\end{pmatrix}_2 & \begin{pmatrix}\psi_2(2)\\0\end{pmatrix}_2 & \begin{pmatrix}0\\\psi_2(2)\end{pmatrix}_2 & \begin{pmatrix}\psi_3(2)\\0\end{pmatrix}_2 & \begin{pmatrix}0\\\psi_3(2)\end{pmatrix}_2 \\ \begin{pmatrix}\psi_1(3)\\0\end{pmatrix}_3 & \begin{pmatrix}0\\\psi_1(3)\end{pmatrix}_3 & \begin{pmatrix}\psi_2(3)\\0\end{pmatrix}_3 & \begin{pmatrix}0\\\psi_2(3)\end{pmatrix}_3 & \begin{pmatrix}\psi_3(3)\\0\end{pmatrix}_3 & \begin{pmatrix}0\\\psi_3(3)\end{pmatrix}_3 \\ \begin{pmatrix}\psi_1(4)\\0\end{pmatrix}_4 & \begin{pmatrix}0\\\psi_1(4)\end{pmatrix}_4 & \begin{pmatrix}\psi_2(4)\\0\end{pmatrix}_4 & \begin{pmatrix}0\\\psi_2(4)\end{pmatrix}_4 & \begin{pmatrix}\psi_3(4)\\0\end{pmatrix}_4 & \begin{pmatrix}0\\\psi_3(4)\end{pmatrix}_4 \\ \begin{pmatrix}\psi_1(5)\\0\end{pmatrix}_5 & \begin{pmatrix}0\\\psi_1(5)\end{pmatrix}_5 & \begin{pmatrix}\psi_2(5)\\0\end{pmatrix}_5 & \begin{pmatrix}0\\\psi_2(5)\end{pmatrix}_5 & \begin{pmatrix}\psi_3(5)\\0\end{pmatrix}_5 & \begin{pmatrix}0\\\psi_3(5)\end{pmatrix}_5 \\ \begin{pmatrix}\psi_1(6)\\0\end{pmatrix}_6 & \begin{pmatrix}0\\\psi_1(6)\end{pmatrix}_6 & \begin{pmatrix}\psi_2(6)\\0\end{pmatrix}_6 & \begin{pmatrix}0\\\psi_2(6)\end{pmatrix}_6 & \begin{pmatrix}\psi_3(6)\\0\end{pmatrix}_6 & \begin{pmatrix}0\\\psi_3(6)\end{pmatrix}_6 \end{vmatrix}, \qquad (2)$$

where $\begin{pmatrix}\psi_n(k)\\0\end{pmatrix}_k$ is the spin-orbital wave function of the k-th electron. The subscript k outside the parentheses indicates that the spin function refers to the k-th particle.

Taking account of (2), Eq. (1) as applied to our problem will have the form

$$\sigma_d=\frac{e^2}{3m_ec^2}\sum_{k=1}^{6}\int\Psi_6^{0*}\frac{1}{|\mathbf{r}_k|}\Psi_6^0 d\,\mathbf{r}_1\,\ldots\,d\,\mathbf{r}_6.$$

Performing the necessary mathematical operations, we obtain the following expression for the diamagnetic shielding constant of benzene protons:

$$\sigma_d=\frac{9025\,e^2\pi^2}{a_0 3m_ec^2 5!}\,[3J_1^*+4J_2^*-J_3^*],$$

where

$$J_1^*=\int\frac{r^4}{\sqrt{r^2}}\exp(-sr)\,dr;\quad J_2^*=\int\frac{r^4}{\sqrt{r^2}}\exp\left[-s\left(\sqrt{a_1^2+r^2}+\sqrt{r^2}\right)/2\right]dr;$$

$$J_3^*=\int\frac{r^4}{\sqrt{r^2}}\exp\left[-s\left(\sqrt{a_2^2+r^2}+\sqrt{r^2}\right)/2\right]dr;$$

$$J_4^*=\int\frac{r^4}{\sqrt{r^2}}\exp\left[-s\left(\sqrt{a_3^2+r^2}+\sqrt{r^2}\right)/2\right]dr.$$

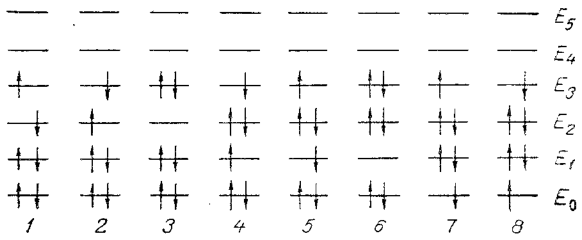

Fig. 2. Schemes of filling energy levels of excited states in a benzene molecule.

The integrals J_1^*, J_2^*, J_3^*, and J_4^* were evaluated on an ES-1022 computer. The results gave $\sigma_d = 4.59 \cdot 10^{-5}$.

In [5-8] both the experimental values of the constants σ_d and those obtained from data of model calculations were between $2.2 \cdot 10^{-5}$ and $2.9 \cdot 10^{-5}$.

In investigating the effect of the solid phase structure on the diamagnetic shielding constant of benzene protons, we assumed that the benzene molecule is located on the solid phase surface, and that the active centers of the solid phase are OH hydroxyl groups, and the molecule interacts with two OH hydroxyl groups at a distance $a = 18.87$ Bohr radii from the nearest carbon atoms (Fig. 1). The following feature appears in this interaction: within an OH hydroxyl group an oxygen atom, as a consequence of its electronegative character, attracts an electron of a hydrogen atom and thus protonates hydrogen. Consequently, a benzene molecule is in a field produced by protonated hydrogen, and the effect of this external field must be considered as a correction or perturbation, where $\hat{W} = -e^2/r$ is the perturbation operator. As is clear from [9], the wave function of the ground state of the benzene molecule in the field produced by protonated hydrogen must be written in the form

$$\Psi_6^1 = \Psi_6^0 + \sum_{m \neq 0} \frac{W_{m0}}{E_0^0 - E_m^0} \Psi_m^0, \tag{3}$$

where the matrix elements of the perturbation operator are given by

$$W_{m0} = -2e^2 \sum_{k=1}^{6} \int \Psi_m^{0*} \frac{1}{\sqrt{a^2 + r_k^2}} \Psi_6^0 d\mathbf{r}_1 \ldots d\mathbf{r}_6. \tag{4}$$

The eigenfunctions of the benzene molecule for an unperturbed problem, just as in the preceding case, are written as Pauli determinants, but it is necessary to use schemes 1-8 of Fig. 2, which shows the possible variants of filling the energy levels (the arrows in Fig. 2 show the spin directions). The two upper energy levels need not be considered, since they do not make a significant contribution to the wave function calculated by Eq. (3), because of the considerable distance between the ground and excited states. The energies of the ground state and the excited states of a benzene molecule listed in Table 2 were calculated by using schemes 1-8. By using Eq. (4) the following expressions can be derived for the matrix elements of the perturbation operator:

$$W_{10} = -\frac{540\, e^2}{6!\, a_0} [J_3 - J_4 + J_2 - J_1], \quad W_{20} = -W_{10}, \quad W_{30} = 0,$$

$$W_{40} = -\frac{1080\, e^2}{6!\, \sqrt{48}\, a_0} [J_4 - J_3 + J_1 - J_2], \quad W_{50} = -W_{40}, \quad W_{60} = 0,$$

$$W_{70} = -\frac{1080\, e^2}{6!\, \sqrt{24}\, a_0} [J_3 - J_4 + J_2 - J_1], \quad W_{80} = -W_{70},$$

where

$$J_1 = \int \frac{r^4}{\sqrt{a^2 + r^2}} \exp(-sr)\, dr; \quad J_2 = \int \frac{r^4}{\sqrt{a^2 + r^2}} \exp[-s(\sqrt{a_1^2 + r^2} + \sqrt{r^2})/2]\, dr;$$

TABLE 1. Molecular π-Orbitals and Corresponding Energy Levels of π-Electrons of a Benzene Molecule

π-Orbital	Energy level	Note
$\psi_1=\frac{1}{\sqrt{6}}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6)$	$E_0=\alpha+2\beta$	χ— atomic p_z-orbitals
$\psi_2=\frac{1}{\sqrt{12}}(\chi_1-\chi_2-2\chi_3-\chi_4+\chi_5+2\chi_6)$	$E_1=E_2=\alpha+\beta$	α— ionization potential $\alpha=2{,}56\cdot10^{-12}$ erg
$\psi_3=\frac{1}{2}(\chi_1+\chi_2-\chi_4-\chi_5)$		
$\psi_4=\frac{1}{\sqrt{12}}(-\chi_1-\chi_2+2\chi_3-\chi_4-\chi_5+2\chi_6)$	$E_3=E_4=\alpha-\beta$	β— resonance integral $\beta=-1{,}408\cdot10^{-12}$ erg
$\psi_5=\frac{1}{2}(\chi_1-\chi_2+\chi_4-\chi_5)$		
$\psi_6=\frac{1}{\sqrt{6}}(-\chi_1+\chi_2-\chi_3+\chi_4-\chi_5+\chi_6)$	$E_5=\alpha-2\beta$	

$$J_3=\int\frac{r^4}{\sqrt{a^2+r^2}}\exp\left[-s\left(\sqrt{a_2^2+r^2}+\sqrt{r^2}\right)/2\right]dr;$$

$$J_4=\int\frac{r^4}{\sqrt{a^2+r^2}}\exp\left[-s\left(\sqrt{a_3^2+r^2}+\sqrt{r^2}\right)/2\right]dr.$$

The calculations gave the following values for the matrix elements of the perturbation operator:

$$W_{10}=2{,}55\cdot10^{-13}\text{ erg};\ W_{20}=-2{,}55\cdot10^{-13}\text{ erg};\ W_{30}=0;$$
$$W_{40}=-1{,}47\cdot10^{-13}\text{ erg};\ W_{50}=1{,}47\cdot10^{-13}\text{ erg};\ W_{60}=0;$$
$$W_{70}=2{,}058\cdot10^{-13}\text{ erg};\ W_{80}=-2{,}058\cdot10^{-13}\text{ erg}.$$

We turn now to Eqs. (3) and (4) and show the validity of perturbation theory. We introduce the notation $C_m = W_{m0}/(E_0^0 - E_m^0)$, where E_m^0 is the set of energy levels of the benzene molecule. The condition for the applicability of perturbation theory, as follows from [9], is $|C_m| \ll 1$ for $m \neq 0$. In our case $C_1 = -0.096$; $C_2 = +0.096$; $C_4 = 0.0522$; $C_5 = -0.0522$; $C_7 = -0.04872$; $C_8 = 0.04872$.

Starting from Eqs. (1), (3), and (4), we obtain the following expression for the diamagnetic shielding constant of benzene in the interaction of a molecule with the solid phase surface:

$$\sigma_d=\frac{2e^2}{m_ec^2}\int\frac{1}{\sqrt{r_1^2}}\left[\frac{1}{6!}\Psi_6^{0*}\Psi_6^0+\frac{C_1}{\sqrt{6!}}\Psi_6^{0*}\Psi_1^0+\frac{C_2}{\sqrt{6!}}\Psi_6^{0*}\Psi_2^0+\right.$$
$$+\frac{C_4}{\sqrt{6!}}\Psi_6^{0*}\Psi_4^0+\frac{C_5}{\sqrt{6!}}\Psi_6^{0*}\Psi_5^0+\frac{C_7}{\sqrt{6!}}\Psi_6^{0*}\Psi_7^0+\frac{C_8}{\sqrt{6!}}\Psi_6^{0*}\Psi_8^0+$$
$$+\frac{C_1}{\sqrt{6!}}\Psi_1^{0*}\Psi_6^0+C_1C_2\Psi_1^{0*}\Psi_2^0+C_1^2\Psi_1^{0*}\Psi_1^0+C_1C_4\Psi_1^{0*}\Psi_4^0+$$
$$+C_1C_5\Psi_1^{0*}\Psi_5^0+C_1C_7\Psi_1^{0*}\Psi_7^0+C_1C_8\Psi_1^{0*}\Psi_8^0+\frac{C_2}{\sqrt{6!}}\Psi_2^{0*}\Psi_6^0+$$
$$+C_1C_2\Psi_2^{0*}\Psi_1^0+C_2^2\Psi_2^{0*}\Psi_2^0+C_2C_4\Psi_2^{0*}\Psi_4^0+C_2C_5\Psi_2^{0*}\Psi_5^0+$$
$$+C_2C_7\Psi_2^{0*}\Psi_7^0+C_2C_8\Psi_2^{0*}\Psi_8^0+\frac{C_4}{\sqrt{6!}}\Psi_4^{0*}\Psi_6^0+$$
$$+C_1C_4\Psi_4^{0*}\Psi_1^0+C_2C_4\Psi_4^{0*}\Psi_2^0+C_4^2\Psi_4^{0*}\Psi_4^0+C_4C_5\Psi_4^{0*}\Psi_5^0+$$

TABLE 2. Energies of Ground and Excited States of a Benzene Molecule, erg

Energy of ground state	Energy of excited states
$E_0^0 = 6\alpha + 8\beta = 4{,}096 \cdot 10^{-12}$	$E_1^0 = 6\alpha + 6\beta = 6{,}912 \cdot 10^{-12}$
	$E_2^0 = 6\alpha + 6\beta = 6{,}912 \cdot 10^{-12}$
	$E_3^0 = 6\alpha + 4\beta = 9{,}728 \cdot 10^{-12}$
	$E_4^0 = 6\alpha + 6\beta = 6{,}912 \cdot 10^{-12}$
	$E_5^0 = 6\alpha + 6\beta = 6{,}912 \cdot 10^{-12}$
	$E_6^0 = 6\alpha + 4\beta = 9{,}728 \cdot 10^{-12}$
	$E_7^0 = 6\alpha + 5\beta = 8{,}320 \cdot 10^{-12}$
	$E_8^0 = 6\alpha + 5\beta = 8{,}320 \cdot 10^{-12}$

$$+ C_4C_7\Psi_4^{0*}\Psi_7^0 + C_4C_8\Psi_4^{0*}\Psi_8^0 + \frac{C_5}{\sqrt{6!}}\Psi_5^{0*}\Psi_6^0 + C_1C_5\Psi_5^{0*}\Psi_1^0 +$$
$$+ C_2C_5\Psi_5^{0*}\Psi_2^0 + C_4C_5\Psi_5^{0*}\Psi_4^0 + C_5^2\Psi_5^{0*}\Psi_5^0 + C_5C_7\Psi_5^{0*}\Psi_7^0 +$$
$$+ C_5C_8\Psi_5^{0*}\Psi_8^0 + \frac{C_7}{\sqrt{6!}}\Psi_7^{0*}\Psi_6^0 + C_1C_7\Psi_7^{0*}\Psi_1^0 + C_2C_7\Psi_7^{0*}\Psi_2^0 +$$
$$+ C_4C_7\Psi_7^{0*}\Psi_4^0 + C_5C_7\Psi_7^{0*}\Psi_5^0 + C_7^2\Psi_7^{0*}\Psi_7^0 + C_7C_8\Psi_7^{0*}\Psi_8^0 +$$
$$+ \frac{C_8}{\sqrt{6!}}\Psi_8^{0*}\Psi_6^0 + C_1C_8\Psi_8^{0*}\Psi_1^0 + C_2C_8\Psi_8^{0*}\Psi_2^0 + C_4C_8\Psi_8^{0*}\Psi_4^0 +$$
$$+ C_5C_8\Psi_8^{0*}\Psi_5^0 + C_7C_8\Psi_8^{0*}\Psi_7^0 + C_8^2\Psi_8^{0*}\Psi_8^0]\, d\mathbf{r}_1 \ldots d\mathbf{r}_6.$$

The calculated value of σ_d is $9.55 \cdot 10^{-5}$.

Thus, the results obtained show that the nuclear magnetic resonance method can be used to estimate the change of structure of dispersion media perturbed by the solid phase surface.

We have begun experimental studies of the effect of the properties of the solid phase surface and adsorbed water on the change of structure of dispersion media by the nuclear magnetic resonance method.

NOTATION

σ_d, diamagnetic shielding constant; e, m_e, electron charge and mass, respectively; c, speed of light; Ψ_b°, benzene wave function; Ψ_m° and $\Psi_m^{\circ *}$, eigenfunctions of benzene molecule and their conjugates; $W_{m\circ}$, matrix elements of the perturbation operator; $E_\circ^\circ$, energy of the ground state of a benzene molecule; E_m°, energy of the excited states of a benzene molecule; $a_\circ$, Bohr radius.

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THERMAL CONDUCTIVITY OF FILLED POLYMER COMPOSITIONS

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An equation for calculating the thermal conductivity of filled polymer compositions is derived and confirmed experimentally.

In what follows, we examine the thermophysical properties of concentrated polymer solutions in hydrocarbon solvents, filled with metallic particles. In view of the high viscosity of a gel, sedimentation proceeds extremely slowly and the composition can be viewed as homogeneous and isotropic. If the volume concentration of the metal is high, the metallic particles form a branching network, encompassing practically the entire volume of the composition. In this case, the dispersed system must be viewed as consisting of two interpenetrating components: the gel and the metal. The properties of such systems are examined in detail in [1].

For relatively small volume concentrations of metallic powder, the composition can be viewed as consisting of a binding medium (gel) with randomly positioned metallic inclusions [1]. The difference between the situations can be easily observed experimentally. In the first case, the coefficient of effective thermal conductivity of the composition depends on the thermal conductivity of the metal. In the second, in view of the fact that the coefficients of thermal conductivity of metals are several orders of magnitude greater than the coefficient of thermal conductivity of a gel, the effective thermal conductivity depends on the nature of the packing, i.e., on the volume content, dispersion, etc., but not on the nature of the metal.

Quite often, the powder particles are covered by an oxide film, whose thermal conductivity in most cases exceeds the thermal conductivity of the gel by 1.5-2 orders of magnitude. As calculations of the thermal conductivity of a dispersed system with coated spherical particles have shown [2], in this case, the screening action of the coating is not great and it can be neglected. In fluidlike polymer compositions, separate particles as well as floccules, consisting of several particles, can form isolated inclusions. This is due to aggregation processes, which occur for sufficiently high specific surface of the powder. Usually, chains consisting of several particles are formed with aggregation.

In a number of works [3-5], the formation of elongated aggregates is explained by the fact that the potential barrier, which must be overcome by the particles in order to connect to an ellipsoid, is lower along the long axis of the ellipsoid than along the short axis. As is well known, with the formation of aggregates, aside from the change in the polydispersity of the inclusions, one other factor appears: the volume fraction of particles in the aggregate is greater than the average volume fraction of the dispersed phase. The effect of this factor on the dielectric permeability of the composition with spherical aggregates was analyzed in [6], where the aggregate was viewed as a system with a higher concentration of the dispersed phase. As shown in [6], this effect is significant only when the volume concentration of the dispersed phase exceeds 25%. For lower concentrations of the dispersed phase, the aggregate can be viewed approximately as a particle with a thermal conductivity of the order of the thermal conductivity of a metal.

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