THE EFFECT OF SURFACE INHIBITORS ON THE RELAXATION TIME OF ORIENTED ATOMS

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Almost all the numerous applications of the method of double radio–optical resonance, intensively developed in recent years, are very closely connected with the problem of increasing the longitudinal relaxation time of the system. This problem is solved by investigators in two ways. The first consists in the choice of optimum buffer components with a small effective disorientation cross section that impede contact between the oriented atoms and the cell wall. The second consists in the use of organic inhibitors (chiefly long-chain hydrocarbons) deposited internally on the cell wall.

So far no one has proposed a satisfactory theory capable of taking account simultaneously of the effect on relaxation time of both the buffer gas characteristics and those of the surface inhibitor, although the need for such a theory is perfectly obvious. The authors of the present paper have already taken a first step in this direction [1]; however, the inadequacy of the experimental data did not then permit progress beyond purely empirical structures. As a result of the appearance of the interesting papers by Brewer [2–4], it is now possible to return to this question on a new basis.

In solving in [1] the problem of the diffusion of oriented atoms in a cylindrical or spherical cell it was found that the process of "dark" longitudinal relaxation is characterized in the general case by a matrix whose elements have the form

a) cylindrical cell (length L, radius a)

$$\tau_{mn} = \left[\gamma^2 D_0 \frac{p_0}{p} \left(\mu_m^2 + \frac{\pi^2}{L^2} (2n - 1)^2 + N_0 \frac{p}{p_0} \sigma \bar{v} \right) \right]^{-1}; \quad (1)$$

b) spherical cell (radius R)

$$\tau_{mn} = \left[\gamma^2 D_0 \frac{p_0}{p} \left(\frac{\pi m}{R} \right)^2 + N_0 \frac{p}{p_0} \sigma \bar{v} \right]^{-1}. \quad (2)$$

Here D_0 is the diffusion coefficient of oriented atoms relative to the atmospheric pressure of the buffer gas p_0 (or of the density N_0), σ is the effective cross section of the disorientating collisions, $\bar{v}$ is the mean relative velocity of the colliding atoms, p is the working pressure of the buffer gas in the cell, and μ_m are the successive roots of the equation

$$J_0 (\mu_m a) = 0. \quad (3)$$

The parameter γ which appears in (1) and (2) represents the probability of disorientation resulting from the collision of an atom with the wall. If no surface inhibitor is used, it is safe to assume that $\gamma = 1$. Instead of σ the corresponding probability γ' may also be introduced by putting $\gamma' = \sigma/\sigma_0$, where σ_0 is the gas-kinetic cross section for the collision of buffer gas atoms. It should be noted that γ and γ' are of substantially different orders of magnitude; the ratio of them, γ/γ', may vary between 10^5 and 10^9 [3,5], depending on the type of buffer gas and inhibitor.

The investigations of Bernheim [16] and McNeal [7], which established the third-power dependence of σ on the atomic number of the buffer component, and, in particular, the refined experiment by Brewer with ordinary and heavy molecular hydrogen [2] all indicate convincingly enough that spin-orbital interaction is the main "disorientating mechanism" within the cell. As for the interaction of an oriented atom with a surface protected by an inhibitor, it follows from [3, 4] that the chief difficulties in calculation may be avoided by reducing the calculation to determining the mean time Δt of contact of the atom with the surface molecular layer. This time may also be expressed by the number of vibrations of the atom in a potential well of predetermined depth [8].

The probability γ' is proportional to the square of the matrix element of the "effective" Hamiltonian $\hat{H}$:

$$\gamma' \sim | \langle 0\beta | \hat{H} | 0\alpha \rangle |^2, \quad (4)$$

where α and β are the initial and final spin states of the oriented atom [6].

The theory developed by Van Vleck [9] enables us to distinguish two main components of $\hat{H}$, which it is convenient to maintain in (4). The principal contribution to the interaction is made by the term $\hat{H}_1$, due to the movement of the nuclei with coordinates r_K relative to the center of mass of the adjacent atoms and the moment of inertia I,

$$\hat{H}_1 = -\frac{g\beta e}{Ic} \sum_\kappa \sum_j \frac{Z_\kappa}{r_{j\kappa}^3} [r_j r_\kappa - r_\kappa^2] J S_j. \quad (5)$$

Here r_j and S_j are the radius vector and spin of the j-th electron (relative to the center of mass), $Z_K e$ is the nuclear charge, $J = l\omega$ is the rotational angular moment, g and β are respectively the Lande factor and the Bohr magneton.

In the second approximation account must be taken of the electron part of the interaction containing the cross term $\frac{1}{I} \sum_j l_j J$, where $l_j = m_j [r_j V_j]$.

This term relates to the fact that the rotational energy of the "quasimolecule" formed by the collision

of the atoms is in fact proportional not to J^2 but to $(J - L)^2$. Further, by using the ordinary formula of perturbation theory and Van Vleck's proportionality theorem,* we obtain

$$\hat{H}_2 = \frac{e^3 c}{Ic} \sum_j \sum_n \left\langle n \,|\, l_j \,|\, 0 \right\rangle J S_j \times \quad (6)$$

$$\times \frac{\left\langle 0 \,\left|\, \sum_\kappa \left(-\frac{Z_\kappa}{m_j r_{j\kappa}^3}\right) l_j - \sum_{p>j} \left(\frac{1}{r_{jp}^3}\right) l_j \,\right|\, n \right\rangle}{E_0 - E_n}$$

where the summation is carried out with respect to all excited states n of the interacting atoms.

Thus, by writing the Hamiltonian $\hat{H}$ in the form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \quad (7)$$

and substituting (7) in (4), it is possible in principle to find γ' within the framework of nonstationary perturbation theory.

For our purposes, however, the direct method of calculation given here can hardly be regarded as justified, since the change from γ' to γ in accordance with Brewer's hypothesis leads in practice to an insufficient degree of accuracy. Consequently it is convenient to use the method proposed by Bernheim [6], introducing the effective magnetic field H′(t) which interacts with the moment μ of the oriented atom in accordance with the Gauss law

$$\mu H'(t) = \mu H \exp\left(-t^2/(\Delta t_0)^2\right), \quad (8)$$

where Δt_0 is the mean collision time.

In the first order of perturbation theory we have

$$\gamma' = \left| \frac{1}{i\hbar} \int_{-\infty}^{\infty} \langle 0\beta \,|\, \mu H'(t') \,|\, 0\alpha \rangle \exp(i\omega't')\, dt' \right|^2 \simeq$$

$$\simeq \left| \frac{1}{i\hbar} \int_{-\infty}^{\infty} \langle 0\beta \,|\, \mu H \,|\, 0\alpha \rangle \exp\left[i\omega't' - \left(\frac{t'}{\Delta t_0}\right)^2 \right] dt' \right|^2 \simeq$$

$$\simeq \frac{\pi \mu^2 H^2 (\Delta t_0)^2}{\hbar^2}. \quad (9)$$

In further estimates of the field strength $\hat{H}$ it is possible to take values corresponding to hyperfine interaction; the concept of Bernheim's method is also included in this.

Let us now turn to the probability γ. According to [3] it is necessary to put

$$\gamma = \gamma' \left(\varkappa \frac{\Delta t}{\Delta t_0} \right)^2, \quad (10)$$

where the correction factor $\varkappa$ is introduced for the purpose of simulating the surface potential well with the help of several atoms of the buffer gas; Brewer, in particular, takes $\varkappa = 4$. If η is the period of vibration of an atom in the potential well, then from Frenkel's well-known formula [10]

$$\Delta t = \eta \exp(E_a/\kappa T), \quad (11)$$

where E_a is the adsorption energy and T is the temperature of the cell wall. Thus, taking account of (9)

$$\gamma = \pi \left(\frac{\mu \eta \varkappa H}{\hbar} \right)^2 \exp(2E_a/\kappa T). \quad (12)$$

We will make a simple estimate by putting $\mu = 10^{-20}$ erg/G, $\eta = 10^{-12}$ sec, $\varkappa = 5$, H = 10G, $E_a = 0.1$ eV, T = 350° K. Substituting these values in (12) gives $\gamma \simeq 1.5 \times 10^{-2}$, which corresponds to typical experimental conditions. The specific properties of the inhibitor mainly enter into γ through the parameter $\varkappa$ and also to a lesser degree through η and E_a.

In investigating the relaxation characteristics of a system of optically oriented atoms, account must be taken of the marked dependence of γ on T which emerges from formula (12). This in particular forces us to reconsider Franzen's conclusions [11] relating to the change in longitudinal relaxation time with concentration of oriented atoms, since in this experiment a protective coating of tetracontane was used. It is also essential to bear in mind that Frenkel's formula [10] and consequently also the exponential dependence of γ on temperature may not be valid for a change in the inhibitor from the crystalline to the amorphous state, i.e. above a certain upper limit of T [4, 12].

In a number of cases another formula for the probability γ may be useful; in this formula there is the experimentally measured shift (usually red) of the frequency of the hyperfine transition $\Delta \nu_0$ which is insensitive to changes in field strength. On the basis of [13, 14] we can write

$$\frac{\Delta t}{\Delta t_0} = \frac{\Delta \nu_0}{\nu_0 E_w \left[\frac{1}{\Delta E + V_1} + \frac{2}{V_2} \right]}, \quad (13)$$

where, instead of the van der Waals interaction energy E_ω, it is possible to use the approximate value E_a. In (13) ΔE corresponds to the resonance energy interval in the spectrum of an oriented atom with an ionization potential V_2; V_1 is the mean ionization potential for the inhibitor. From this

$$\gamma = \pi \left[\frac{\mu \varkappa H \cdot \Delta \nu_0 \cdot \Delta t_0}{\hbar \nu_0 E_w \left(\frac{1}{\Delta E + V_1} + \frac{2}{V_2} \right)} \right]^2. \quad (14)$$

Equation (14) is well illustrated by Alley's experiments [5], in which he recorded an anomalously large shift in the frequency of the hyperfine transition Rb^{87}.

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*Details of the calculations can be found in the monograph by A. Abraham, Nuclear Magnetism [Russian translation] Chap. 6, IL, Moscow, 1963.

The probability of disorientation with the approach of an atom to the wall was also considerably greater than usual in this work: $\gamma = 0.1 - 0.2$.

The considerations developed in the present paper cannot, of course, yet be regarded as a theory of relaxation that takes account of the action of both the buffer gas and the inhibitor. However, they already enable us to understand many important aspects of interaction which until recently were often described by the term "black art" [5].

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