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MEASUREMENT OF THE CROSS SECTIONS OF SPIN EXCHANGE OF H ATOMS (F = 1, m_F = 0) ON PARAMAGNETIC
O_2, NO, and NO_2 MOLECULES IN THE TEMPERATURE INTERVAL 310 – 390°K

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A hydrogen laser operating in the pulsed regime is used
to measure the cross sections of spin exchange of H atoms in
the hyperfine state (F = 1, m_F = 0) on the paramagnetic mole-
cules O_2, NO, and NO_2. The cross sections are equal to
0.85×10^{-15} cm^2, 1.02×10^{-15} cm^2, and 0.88×10^{-15} cm^2, respectively.

When hydrogen atoms collide with paramagnetic molecules, the spin exchange process, which
leads to a change of the hyperfine state of the hydrogen atoms, has a large cross section. On
the other hand, it is known that in this case the chemical joining reaction with subsequent
decay or collision stabilization of the complex has a high probability. The present paper is
devoted to a measurement of the cross sections of spin exchange of hydrogen atoms with the
paramagnetic molecules O_2, NO, and NO_2, to the dependence of the cross sections on the tempera-
ture, and to a comparison of the cross sections of spin exchange and of the chemical reaction
of the hydrogen atoms with these molecules.

Calculations show [1 – 3] that the spin-exchange process is coherent, i.e., the phase
information connected with the oscillating magnetic moment of the hydrogen-atom system is
conserved during the course of the interaction. The ratio of the relaxation times T_1 of the
population difference of the hyperfine levels and T_2 of the oscillating magnetic polarization
is equal to 3/4 in the case of interaction of a hydrogen atom with a paramagnetic particle.
The experimental values of the mean cross sections for the change of the hyperfine structure
in spin exchange at 300°K are $\sigma(H-O_2) = (1.9 \pm 0.2) \times 10^{-15}$ cm^2, $\sigma(H-NO) = (1.9 \pm 0.2) \times 10^{-15}$ cm^2,
and $\sigma(H-NO_2) \sim 2 \times 10^{-15}$ cm^2.

We measured the rate constants K_1^{se} and K_2^{se} of the spin exchange of a hydrogen atom in
the state (F = 1, m_F = 0) colliding in the gas phase with the molecules O_2, NO, and NO_2
in the temperature interval 310 – 390°K.

The procedure [5, 6] consisted of measuring the cross sections for the relaxation of the
hyperfine levels of the ground state of the hydrogen atoms in the collisions with the molecules
of the investigated gas with the aid of a hydrogen maser operating in the pulsed regime. The
inverted population of the levels (F = 1, m_F = 0) and (F = 0, m_F = 0) of the H atoms in the
maser accumulating flask, placed in a microwave resonator, was produced by focusing the atom
beam in an inhomogeneous magnetic field. The investigated gases were also admitted into the
flask, and their concentration was in the interval $(0.5 - 3.5) \times 10^{10}$ molecules/cm^3, while the
H-atom concentration was about 10^8 atoms/cm^3. The oscillating magnetic polarization of the
system of atoms was excited with a 90° pulse at the transition frequency, with duration that
was short in comparison with T_1 and T_2. Since the inverted population did not exceed one-tenth
of the threshold value for generation under the experimental conditions, the coherent-radiation
signal of the system of atoms varied in time like $\exp(-t/T_2)$. The absolute value of the time
was obtained from the decrease of the initial amplitude of this signal, from the time between
the instant when the flow of focused atoms into the flask stopped and the start of the 90°
pulse. The rate constants of the spin exchange were determined from the relation $T_{1,2} =
(K_{1,2}^{se} n_B)^{-1}$, where n_B is the concentration of the investigated molecules (O_2, NO, or NO_2) in
the accumulating flask.

The measurement results are listed in the table (in the case of NO_2, the obtained cross
sections were extrapolated to the instant when the gas was admitted, to exclude the influence
of its adsorption on the walls of the flask).

For all the partners, within the limits of the experimental accuracy, we obtained

Rate constants K_1^{se} of the change of the hyperfine state of the H atom and mean spin-exchange cross sections $\sigma = (n_B v T_2)^{-1}$ (n_B is the free-radical concentration, and v is the relative velocity of the colliding particles) in collisions with molecule B

B	T,°K	T_1/T_2	$K_1^{se} \cdot 10^{10}$, cm³/sec	$\sigma \cdot 10^{15}$, cm²
O_2	310		3.04 ± 0.20	0.880 ± 0.07
	315	0.72 ± 0.07	3.40 ± 0.25	0.975 ± 0.10
	350		3.03 ± 0.20	0.830 ± 0.07
	388		3.09 ± 0.20	0.80 ± 0.07
NO	310	0.73 ± 0.07	3.67 ± 0.25	1.06 ± 0.09
	373		3.79 ± 0.25	0.99 ± 0.09
NO_2	315	0.75 ± 0.07	3.06 ± 0.50	0.88 ± 0.20

$T_1/T_2 = 3/4$, and the cross sections were independent of the temperature and were about half as large as those measured by Berg at 300°K by an analogous method [4]. The discrepancy is apparently due to the low accuracy with which the pressure of the investigated gas was measured, and to Berg's failure to allow for the influence of the induced radiation.

It can be asked whether the state of the particle pair during the spin-exchange process is that intermediate compound particle which leads, in the case of stabilization by collisions, to the chemical reaction of joining the H atom to the free radical (or, in other words, there is no intermediate state as such in this reaction). The experimental results obtained by us for O_2 and NO[1] do not contradict this assumption. Indeed, the rate constant $K^{(3)}$ of the trimolecular reaction can be expressed in terms of the rate constant of the bimolecular joining reaction $K^{(1)}$, the lifetime τ of the produced compound particle, and the rate constant $K^{(2)}$ of its deactivation in collisions in the following manner: $K^{(3)} = K^{(1)} K^{(2)} \tau$ [7]. If we set τ equal to the time of flight of the particles past each other, i.e., $(4/3)(r/\bar{v})$, where r is the gas-kinetic radius of the molecule [7], $K^{(2)}$ is the rate constant of the collision of HB with Ar in the hard-sphere approximation, and $K^{(1)} = 2K^{se}$ (spin exchange leads to a change of spin with probability 1/2), then we obtain the values $K^{(3)}(H + O_2 + Ar) = 2.4 \times 10^{-32}$ cm⁶/sec and $K^{(3)}(H + NO + Ar) = 3.0 \times 10^{-32}$ cm⁶/sec, which are close to the experimentally measured [8 - 10] $K^{(3)}(H + O_2 + Ar) = (1.6 - 1.9) \times 10^{-32}$ cm⁶/sec and $K^{(3)}(H + NO + Ar) = (2 - 3) \times 10^{-32}$ cm⁶/sec.

An alternate assumption is that only a fraction of the trajectories leading to spin exchange between the particles brings about their chemical reaction. In this case, the lifetime of the compound particles should exceed the time of flight, and one can indeed speak of an intermediate state. On the other hand, the lifetime of this intermediate state should be much shorter than the characteristic times corresponding to the hyperfine frequency of the hydrogen atom ($\omega^{-1} = 10^{-10}$ sec)[2]. It is therefore quite possible that the interacting hydrogen atom can conserve the phase information connected with the oscillating magnetic polarization. We then have for the "chemical" channel $(T_1/T_2)_{chem} = 3/4$ and the contribution of this channel to the total cross section cannot be deduced in principle from spin-exchange experiments.

On the other hand, if the chemical reaction does proceed somehow in an incoherent manner (relative to the H atom) and therefore $(T_1/T_2)_{chem} = 1$, then, since the experiments revealed no contribution of this channel, we can conclude that $K^{(1)}(H + O_2) \leq 8 \times 10^{-11}$ cm³/sec and $K^{(1)}(H + NO) \leq 1 \times 10^{-10}$ cm³/sec, and consequently $\tau(H...O_2) \geq 3.3 \times 10^{-13}$ sec and $\tau(H...NO) \geq 1 \times 10^{-13}$ sec.

The question whether a chemical reaction lasting less than 10^{-10} sec can actually lead to loss of coherence by the H atoms can be answered by experiments with simple (di- and tri-

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[1] There are no published data on the trimolecular process H + NO_2, probably because it is masked by the very fast bimolecular process with formation of NO and OH.

[2] The estimate $\tau \leq 10^{-11}$ sec for O_2 and NO follows from the fact that experiment did not reveal a deviation from trimolecular behavior of the corresponding reactions of the H atom, up to a pressure of 2 atm [8 - 10].

atomic) diamagnetic molecules capable of reacting chemically with the hydrogen atom.

We note that the value of K_1^{se} obtained by us exceeds by one order of magnitude the rate constant of the chemical act $H + NO_2 \rightarrow OH + NO$ (1) known for these partners [1]. It is not excluded, however, that in addition to (1) there occurs, with large rate constants, the formation of a shorter-lived compound particle that decays into H and NO_2 via the inverse channel. From this point of view, it would be quite interesting to experiment with observation, by any method, of the trimolecular process $H + NO_2 + M \rightarrow HNO_2 + M$.

Thus, on the basis of a comparison of the characteristics of the spin-exchange processes and the chemical reaction between the H atom and a paramagnetic molecule, we have raised in this paper a number of questions, an experimental answer to which by the given method and by the means of chemical kinetics will make it possible to choose the mechanism of the elementary processes of joining of a hydrogen atom to a free radical.

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INFLUENCE OF MAGNETIC FIELD ON LIGHT SCATTERING IN NEMATIC LIQUID CRYSTALS

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The scattering of light in nematic liquid crystals was
investigated in a magnetic field up to 130 kOe and in an
electric field up to 24 kV/cm.

We have investigated the joint action of magnetic and electric fields on the scattering of light in crystals with negative ($\varepsilon_{||} < \varepsilon_{\perp}$) and positive ($\varepsilon_{||} > \varepsilon_{\perp}$) anisotropies of the dielectric constant, where $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are the dielectric constants along the elongation direction of the molecule and perpendicular to it.

The experiment consisted of measuring the intensity I(H) of the light passing through the liquid crystal. In the case $\varepsilon_{||} < \varepsilon_{\perp}$ we used the MBBA nematic liquid crystal, and in the case $\varepsilon_{||} > \varepsilon_{\perp}$ we used a mixture (6% MBBA + 30%EBBA + 10% nitryl). The liquid crystal was placed between plates of fused quartz separated by liners 125 μ thick. To apply the electric field, the plates were coated with a transparent conducting SnO_2 layer. The light source was an He-Ne laser (LG-75) with 0.63 μ wavelength. The magnetic field was produced by the "Solenoid" setup [1]. The measurements were made at 19°C.

The action of the magnetic field on the liquid crystals is due to the diamagnetism of the molecules, owing to the presence of benzene rings. In a sufficiently strong magnetic field $\vec{H}$, the molecules become aligned along $\vec{H}$. The nematic liquid crystal, which has a polycrystalline structure characterized by a set of regions with inidvidual preferred molecule directions, then becomes monocrystalline. The formation of the single crystal is revealed by the saturation of the I(H) dependence in fields H > 50 kOe at E = 0 V/cm (Figs. 1 and 2). If the electric and magnetic fields are applied simultaneously, however, the I(H) dependence will be different for $\varepsilon_{||} < \varepsilon_{\perp}$ and $\varepsilon_{||} > \varepsilon_{\perp}$.

2. If $\varepsilon < \varepsilon$ and an electric field E is applied, a static perturbation picture is produced in MBBA by the presence of residual ions in the medium [2]. With increasing E, this