Comparative study of alkali-vapour cells with alkane-, alkene- and 1-nonadecylbenzene-based antirelaxation wall coatings

M.V. Balabas, O.Yu. Tretiak

Abstract. **The dependence of both longitudinal and transverse relaxation times of ground-state magnetic polarisation in alkali atoms on the coating temperature is experimentally studied for the first time in a rubidium-vapour cell with 1-nonadecylbenzene anti-relaxation coating of inner walls. The comparison of these times with the relaxation times in a caesium-vapour cell with alkane wall coatings is presented. It is found that within the studied temperature range (294–340 K) the transverse relaxation time decreases with increasing temperature of alkene and 1-nonadecylbenzene coatings. For the alkane coating such a dependence was not explicitly found. The longitudinal relaxation time begins to decrease in all cases when passing a certain critical temperature of the coating material. It is found that the unsaturated radical structure of the coating material molecules strongly affects its antirelaxation properties.**

Keywords: antirelaxation coating, cell, alkali metal vapours, spin relaxation.

1. Introduction

Hydrocarbon antirelaxation coating of the walls of evacuated glass cells intended for the experiments on optical pumping of alkali metal vapours was first used in 1958 by Dehmelt et al. [1]. The most exhaustive study of cells with paraffin antirelaxation coatings was carried out by M.A. Bouchiat and J. Brossel [2] and J. Robinson [3]. Thorough theoretical consideration of the interaction between the alkali metal atoms and the coating, with a discussion of experimental results obtained by then, were presented in the monograph by J. Vanier [4] (unfortunately, hardly available in Russia).

The cell is an evacuated glass construction that consists of a working volume and a small volume (stem) connected to the working volume via a capillary and containing a small portion of alkali metal. The inner surface of the working volume and the capillary is coated with a transparent hydrocarbon layer that provides small probability of the quantum state change (relaxation) in the optically pumped alkali metal atoms, colliding with the wall. The smaller the probability, the better the quality of the antirelaxation coating. To achieve

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the stationary concentration of alkali metal vapour, the coated cell needs a certain time and increased temperature (about 70–80 °C). During this time, referred to as the 'curing' period of the coated cell, an active interaction of metal atoms with the coating material takes place. The character of this interaction has not been yet studied in detail.

At present, the most widespread are the cells, produced by us [5], with the coating on the basis of the low-pressure polyethylene fraction wax, consisting mainly of paraffin hydrocarbons. These cells are used in numerous experiments in the field of quantum magnetometry and quantum optics [5–17]. The characteristic relaxation times for such a coating are linearly related to the cell size and amount to $\sim$1 s cm^{-1}.

The results of the study of the relaxation characteristics for the cells, described above, are presented in [18–23]. In these cells potassium, rubidium, and caesium were used. The times of relaxation at the coating were virtually the same for different alkali metals.

In such cells the basic characteristics are the time of longitudinal (T_1) and transverse (T_2) relaxation, as well as the maximal temperature, at which the antirelaxation coating still keeps its properties, and, therefore, the maximal possible concentration of the alkali metal vapour atoms. Up to now, the material for antirelaxation coatings was traditionally based on saturated hydrocarbons – alkanes C_nH_{2n+2}, as substances, most inactive chemically with respect to alkali metal atoms, and octadecyltrichlorosilane (a saturated linear hydrocarbon with the SiCl$_3$ radical at one end of the molecule) as a sufficiently inactive and heat-resistant substance [24]. However, recently we have demonstrated high efficiency of unsaturated hydrocarbons, alkenes $CH_3-C_nH_{2n}-CH=CH_2$, as materials for antirelaxation coatings [25–28] that allowed the increase in the relaxation time of the alkali metal vapours by many times, up to 1 min, in a spherical rubidium-vapour cell with the diameter of 3 cm, which corresponds to 5×10^5 polarisation-nondestructive collisions.

This high efficiency of alkenes opens the way to searching for other materials, whose initial activity with respect to interaction with alkali metal atoms probably leads to the formation of the inert reaction product with high antirelaxation characteristics. The interaction of alkali metal atoms with saturated and unsaturated hydrocarbon is expected to yield different physical and chemical properties of the 'cured' antirelaxation coatings, prepared from these hydrocarbons. The differences may manifest themselves in the study of temperature dependences of the polarisation relaxation time in the ground states of the alkali metal atoms and the kinetics of absorption of atoms by the coating. To reveal the influence of the coating material unsaturation properties, we also studied the cell with 1-nonadecylbenzene coating.

In the present paper we report the results of the first comparative study of the temperature dependence of the longitudinal and transverse relaxation times of the alkali metal atoms ground-state polarisation in the cells with alkene, 1-nonadecylbenzene, and alkane coatings.

2. Object of the study

The experiments were performed with a spherical alkene-coated caesium-vapour cell 33 mm in diameter, with a spherical 1-nonadecylbenzene-coated $[C_6H_5(CH_2)_{18}CH_3]$ rubidium-vapour cell 32 mm in diameter, and with an alkane-coated caesium-vapour cell having cylindrical shape (length 50 mm, diameter 20 mm).

Onto the inner surface of the working volume of the alkene-coated cell the anti-relaxation coating, consisting of a mixture fraction of alpha-olefins C20-24 produced by Chevron Phillips (CAS-No 93924-10-8) was deposited. The technique of coating preparation, described in [26], consisted in preliminary vacuum distillation of light fractions from the initial material at the temperature of 80 °C, followed by deposition from the vapour in the process of cooling the cell to room temperature after heating the cell with a droplet of the prepared material to 175 °C during an hour. The 1-nonadecylbenzene coating was prepared from the material, supplied by Sigma-Aldrich (Fluka 74238, CAS-No 29136-19-4), using the same technology as for the alkene coating, but without preliminary distillation. The studies of the alkene cell were carried out after 14 months from the day of its fabrication, and for the 1-nonadecylbenzene cell after 3 years from the fabrication date. The alkane-coated cell, described in [29], was produced 6 years ago. Note that the interaction of atoms with the coating, leading to irreversible departure of atoms into the coating, possesses the activation nature.

3. Description of the experiment

The scheme of the experimental setup is presented in Fig. 1. In all experiments the cell was placed in a thermostat so that the stem with the metal was stuck out and blown with room-temperature air to keep the constant temperature $T_m \approx 21$ °C.
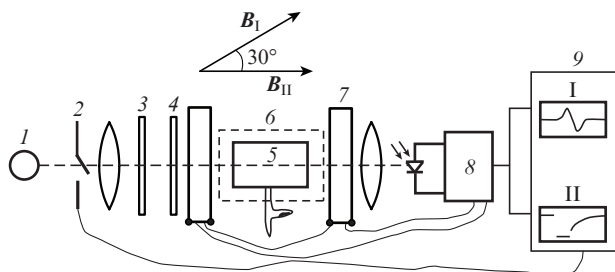

Figure 1. Scheme of the experimental setup for observing the signal of double radio-optical resonance of the M_x type (I) and the 'dark relaxation' signal (II): (B_I) magnetic induction vector directed at the angle 30° with respect to the optical axis; (B_{II}) magnetic induction vector directed along the light beam; (*1*) spectral caesium lamp; (*2*) mechanical gate; (*3*) filter for selecting caesium D_1 line; (*4*) circular polariser; (*5*) cell under study; (*6*) thermostat; (*7*) radio-frequency field coils; (*8*) digital signal processing unit; (*9*) computer.

The temperature of the cell working volume T_v was varied from 294 to 340 K and controlled by means of a calibrated thermal resistor.

The study of the longitudinal relaxation time for the ground-state polarisation in alkali metals in the cells was performed using the Fransen method ('dark relaxation') that consists in registering a series of transient processes in the passing resonant light, implementing the optical pumping, after its abrupt interruption and then opening again after a known time interval. The results of the study of the alkane-coated caesium-vapour cell are presented in Ref. [30]. The details of the experimental setup, the experimental procedure, and the character of the observed signal are also described there. The signal includes two exponentially decaying components, having essentially different decay times. The presence of two components (generally, there can be more than two of them [20]) is caused by both the contribution to the signal from two processes, the relaxation of the total electron angular momentum and the relaxation of the population difference between hyperfine structure sublevels, and the presence of several qualitatively different relaxation channels, some of them depending on the initial and final state of the atom, attained as a result of the relaxation transition (the transition between the hyperfine structure levels, involving the nuclear subsystem), while the other ones do not depend on them (irreversible departure of atoms into the appendix, referred to as the hole relaxation, or into the coating). The conventional classification of relaxation processes includes the relaxation, uniform over the states, the relaxation due to electron randomisation, and the relaxation due to spin exchange. In our case the main contribution comes from the relaxation of the total electron angular momentum, and we can neglect the spin exchange, since it does not affect the total electron angular momentum.

In contrast to Ref. [30], for the observation of the 'dark relaxation' signal in cells with alkene and 1-nonadecylbenzene coatings they were placed in the centre of Helmholtz coils with the diameter of 30 cm, creating the magnetic fields about 5 Gs parallel to the pump light beam.

To measure the transverse relaxation time, the signal of double radio-optical resonance was recorded in the stabilised magnetic field of 344 nT, which was produced by the solenoid inside the permalloy magnetic shield [31]. In this experiment the light was directed at the angle 30° to the magnetic induction vector. The thermostat with the studied cell, the optical elements, and the coil creating the alternating resonance field, was placed in the centre of the solenoid. The low-noise preamplifier with a Hamamatsu S5107 photodiode and a MagTerm digital signal processing unit, developed by A.K. Vershovskii [32], were used for signal recording. The digital processing unit implemented synchronous detection of the resonance signal. The high-frequency discharge lamp served as a light source. The pumping was implemented using circularly polarised light of the D_1 line of the principal doublet. At each value T_v of the temperature the resonance curves were recorded for 6–7 different values of light intensity and very small value of the radio-frequency field so that the contribution of the latter to the registered width could be neglected. To measure the intensity we used NS glass filters, calibrated with respect to transmission at the used light frequency. The obtained dependence of the resonance width on the intensity of light was extrapolated to zero intensity, which determined the dark line width.
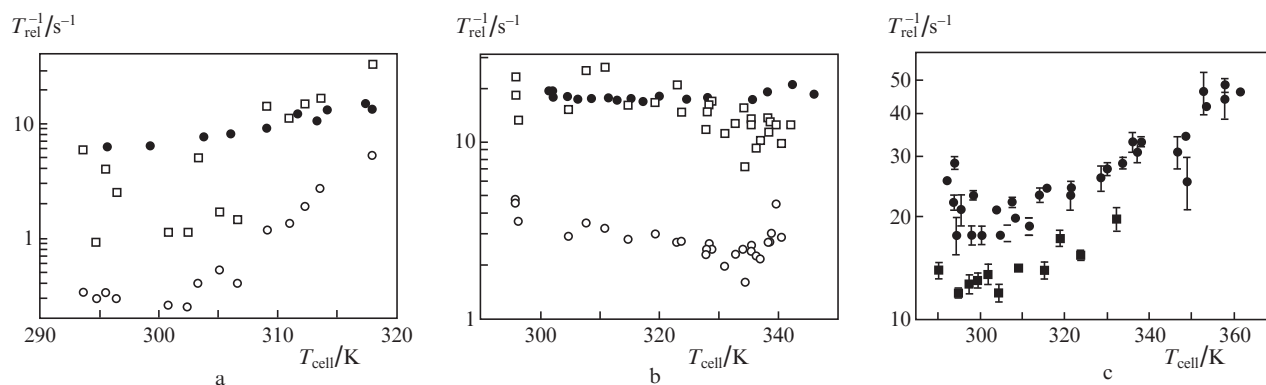
Figure 2. Dependences of the inverse time of the longitudinal relaxation $1/T_1$ (■), its slow $1/T^{\text{slow}}$ (○) and fast $1/T_1^{\text{fast}}$ (□) components, as well as the inverse time of the transverse relaxation $1/T_2$ (●), on the temperature of (a) alkene, (b) alkane, and (c) 1-nonadecylbenzene coatings.

4. Experimental results

Figure 2 presents the experimental dependence of the inverse time of transverse $1/T_2$ and longitudinal $1/T_1$ relaxation, as well as its fast $1/T_1^{\text{fast}}$ and slow $1/T_1^{\text{slow}}$ components, on the temperature for the cells with alkene, alkane, and 1-nonadecylbenzene coatings of the walls. The large scatter of the data on the time of fast longitudinal relaxation is caused by the small relative amplitude of the corresponding component, which makes it significantly affected by the low-frequency noise and allows only conclusions of the most general kind. The uncertainties in a single measurement of the inverse relaxation time for alkane and alkene coatings are within the size of the corresponding point symbol in Fig. 2.

The signal of 'dark relaxation' was explicitly double-exponential for the cells with both alkane and alkene wall coatings. For the 1-nonadecylbenzene-coated cell we could not reliably extract two components from the signal because of very fast relaxation and smaller signal-to-noise ratio.

In the 1-nonadecylbenzene-coated cell the relaxation rates appeared to be the largest and comparable with those for the octadecyltrichlorosilane coating [24]. It is seen that the time of longitudinal relaxation in the cell with the alkene coating of the walls is almost unchanged up to $T \approx 305$ K, and then abruptly decreases, similar to the cell with rubidium vapour and the same coating material, described in Ref. [8], which is probably due to the melting of the coating material. In this case, the signal amplitude is also essentially decreased. The temperatures T_{crit}, corresponding to the point of transition to fast increase in the longitudinal relaxation rate for each coating material are presented in Table 1. The melting temperature of 1-nonadecylbenzene used by us, according to the data of Sigma-Aldrich, lies within the limits $309-314$ K, which is close to the temperature T_{crit}.

Similar to Ref. [30], from the dependence of the inverse relaxation time $(1/T_1^{\text{slow}})$ on the inverse temperature $1/T$ (at $T < 305$ K) the activation energy for desorption of caesium atoms from the alkene coating surface was estimated as $E_{\text{act}} = 0.24(7)$ eV. For comparison, for the alkane coating $E_{\text{act}} = 0.13$ eV [30].

Table 1.

Coating material	T_{crit}/K
Alkane	332(2)
Alkene	306(1)
1-nonadecylbenzene	304(1)

5. Conclusions

For all coatings studied the results obtained appeared to be qualitatively similar. The temperature dependence of the inverse time of slow longitudinal relaxation has a minimum, which, apparently corresponds to the coating melting temperature. Correlation between the temperatures, corresponding to the inflection points of the temperature dependence of the relaxation rate, and the melting temperature of the coating material was mentioned in the classical papers by M.A. Bouchiat and H. Robinson [2, 3].

The inverse time of transverse relaxation for alkene and 1-nonadecylbenzene coatings grows with increasing temperature within the studied range. For alkane coatings this growth was not observed.

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