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## ELECTRON SPIN POLARIZATION OF RUBIDIUM SOLUTION IN DIMETHOXYETHANE

*Helgi KOOSKORA, L. PIRN. ELEKTRONIDE SPINN-POLARISATSIOON RUBIDIUMI DIMET-  
OKSÜETAANI LAHUSES*

*Хельги КООСКОРА, Л. ПИРН. СПИНОВАЯ ПОЛЯРИЗАЦИЯ ЭЛЕКТРОНОВ В РАСТВОРЕ  
РУБИДИЯ В ДИМЕТОКСИЭТАНЕ*

*(Presented by E. Lippmaa)*

During the recent years there has been considerable activity in the studies of electron spin polarization [1-3] and photochemistry [4-6] of alkali metal solutions in organic solvents, but there is still no clear understanding about the mechanism producing the polarized photoelectrons. In this short communication we report about the observation of electron spin polarization in laser-induced photolysis of rubidium-dimethoxyethane (Rb-DME) solution.

Very careful cleaning of glassware and solvent purification were found to be essential for the formation of a stable solution. The Pyrex glassware was cleaned by a repetitive wash sequence [1] with a boiling 50/50  $H_2SO_4/HNO_3$  acid mixture and distilled water, then finally washed with bidistilled water and UV-grade acetone, followed by heating under high vacuum ( $\sim 1 \cdot 10^{-3}$  Pa), and filled with dry argon gas.

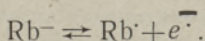
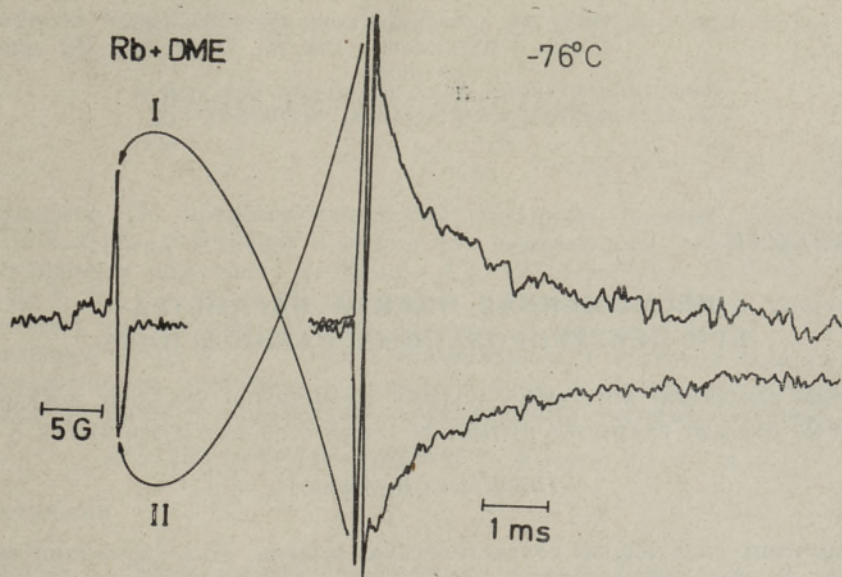
The DME solvent was purified by refluxing over  $CaH_2$  (24 h), distillation, refluxing over  $CaH_2$  (2 h), and final distillation. All these procedures were carried out under dry argon gas, and the solvent was not allowed to come into contact with atmosphere. Immediately before the use, ether was refluxed over clean vacuum melted metallic rubidium and distilled into the Rb-DME preparation glassware.

An ampoule with pure metallic rubidium was broken in argon atmosphere and put into the system prepared as described above. The argon gas was pumped out, and the purified solvent was degassed by several freeze-pump-thaw cycles. The Rb metal was distilled in high vacuum to form a fresh metal mirror surface on the glass walls of the last Rb distillation volume and thereafter allowed to react with the solvent. Five e.s.r. sample tubes were filled with the blue solution formed in the volume, sealed off the vacuum system, and stored in a dry-ice-ethanol bath.

The measurements were carried out on a modified ПЭ-1301 e.s.r. spectrometer. The light sources used were a 500 W high-pressure mercury lamp HBO-500 for continuous illumination and an ОГМ-20 ruby laser (35 ns light pulses of 20 MW pulse power at a 1 Hz repetition rate). For time averaging a fast Bruker analog-digital converter BC-104, interfaced to a spectrum analyzer LP-4840 was used. The samples were measured in a finger-type Dewar vessel filled with dry-ice-pentane mixture ( $-76^\circ C$ ).

The spectrum in the Figure was recorded under continuous illumination and shows a slightly asymmetric e.s.r. line at  $g=2.0021$  corresponding to the metal atoms  $Rb^\cdot$  and the solvated electrons  $e^-$  formed in the reaction [4]





Therefore one may expect to find at least two lines in the spectrum. As has been suggested [6], these lines will probably overlap at  $-76^\circ\text{C}$ . We believe that our spectrum supports this suggestion.

The time-dependent signal after the light pulse excitation exhibits strong polarization. Immediately after the light pulse the signal falls to emission mode, then it reverses, reaches the absorption maximum, and thereafter slowly decays to the equilibrium level. The transient polarization signals I and II have slightly different decay time constants, 120 and 150  $\mu\text{s}$ , respectively. The transient signal I most probably corresponds to electron polarization produced predominantly by the solvated electrons and the  $\text{Rb}^{\cdot-}$  counter radicals. The differences in relaxation times and the reaction rate constants are likely to produce the observed differences between the time constants of the transient signals I and II. This suggestion is supported by the observations [2] where both the solvated electrons and the alkali metal atoms at room temperature were detected. Because of the strong temperature dependence of hyperfine splitting constant ( $dA/dT = 0.13 \text{ G} \cdot \text{deg}^{-1}$  [2]), a variable temperature study is needed for final assignment of the polarization of metal atoms. If both species turn out to have the same sign of polarization, it will not be possible to interpret the results in terms of the usual radical pair mechanism, as it was supposed to be the case [2]. The temperature-dependent studies are in progress and will presumably yield additional information.

#### REFERENCES

1. Glarum, S. H., Marshall, J. H., *J. Chem. Phys.*, **52**, № 11, 5555—5565 (1970).
2. Friedenberga, A., Levanon, H., *Chem. Phys. Lett.*, **41**, № 1, 84—86 (1976).
3. Kim, S. S., Weissman, S. I., *Chem. Phys. Lett.*, **58**, № 3, 326—328 (1978).
4. Friedenberga, A., Levanon, H., *J. Phys. Chem.*, **81**, № 8, 766—771 (1977).
5. Catterall, R., Edwards, P. P., *Adv. Mol. Relax. Inter. Processes*, **13**, № 2, 123—169 (1978).
6. Catterall, R., Slater, J., Symons, M. C. R., *J. Chem. Phys.*, № 2, 1003—1004 (1970).