

## OVERHAUSER EFFECT EXPERIMENTS ON THE ONE-DIMENSIONAL CONDUCTOR (PERYLENE)<sub>2</sub>PF<sub>6</sub>·2/3THF

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We have measured the Overhauser enhancement of the protons and the <sup>19</sup>F-nuclei of the one-dimensional conductor (perylene)<sub>2</sub>PF<sub>6</sub>·2/3THF in its metallic phase at room temperature. The enhancement factor *V* was found to be  $V_P = +320 \pm 20$  for the protons and  $V_F = +175 \pm 40$  for the <sup>19</sup>F-nuclei indicating a predominantly scalar interaction with the conduction electrons in both cases.

IN THE LAST YEARS a new class of one-dimensional conductors was discovered, the hydrocarbon radical cation salts [1–4]. Several investigations including conductivity measurements [1, 3], optical reflectance studies [3, 5], electron spin resonance (ESR) experiments [3, 6, 7] and nuclear magnetic resonance (NMR) relaxation studies [8] gave evidence of low dimensional electronic conductors. More recently, an electron spin echo (ESE) experiment performed with the radical cation salt (fluoranthene)<sub>2</sub>(PF<sub>6</sub>)<sub>x</sub>(SbF<sub>6</sub>)<sub>1-x</sub> ( $x \approx 0.5$ ) [9] showed quantitatively that the intrastack diffusion rate is by a factor of 10<sup>7</sup> to 10<sup>8</sup> higher than the interstack diffusion rate.

In this paper we report the first Overhauser experiments [10] with the protons and the <sup>19</sup>F-nuclei of another quasi one-dimensional organic metal, the (perylene)<sub>2</sub>PF<sub>6</sub>·2/3THF radical cation salt (*pe* = perylene, THF = tetrahydrofuran). The experiments were performed at room temperature in a magnetic field of 3300 Gauss using an apparatus which consisted of a combination of an X-band ESR-spectrometer and a NMR-pulse-spectrometer. Instead of the conventional cavity we used a loop-gap-resonator developed in our Institute which is similar to the one described by Froncisz and Hyde [11], but contains in addition a NMR-coil. The single ESR absorption line was very narrow with a peak to peak linewidth  $\Delta\gamma < 30$  mG; using this resonator it could be saturated almost completely with the power of 100 mW of the microwave bridge. The sample was oriented with the needle axis (crystalline *c*-axis) parallel to the microwave field and perpendicular to the static magnetic field *B*<sub>0</sub>; the saturation behaviour of the ESR absorption and hence the

Overhauser enhancement was found to be independent of the orientation within experimental error. The quantity to be measured was the amplitude of the FID signal which was fed into a BIOMATION transient recorder and a TEXAS INSTRUMENTS microprocessor system for averaging and registering the signal. A single crystal weighing 8 mg was used for measuring the Overhauser enhancement while the measurement of the unenhanced FID of the protons and the <sup>19</sup>F-nuclei was performed using a sample of several crystals weighing 80 mg. The monoclinic (*pe*)<sub>2</sub>PF<sub>6</sub>·2/3THF radical crystals, (*P2/m*,  $a = 13.04$ ,  $b = 14.12$ ,  $c = 13.75$  Å,  $\alpha = 110.8^\circ$ ) were prepared electrochemically. The structure and the preparation of the crystals are described separately [12].

In Fig. 1 the reciprocal Overhauser enhancement factors at room temperature both of the protons and of the <sup>19</sup>F-nuclei of (perylene)<sub>2</sub>PF<sub>6</sub>·2/3THF are plotted as a function of the reciprocal power. The extrapolation to infinite power renders a maximum enhancement factor  $V_P = +320 \pm 20$  for the protons and  $V_F = +175 \pm 40$  for the <sup>19</sup>F-nuclei. Since the saturation was almost complete, saturation parameter  $s \approx 1$ , with the maximum power of 100 mW, the difference between the highest measured enhancement factor and the one obtained by extrapolation to infinite power was within the experimental error.

The theory of the Overhauser effect is described in Abragam's book [13]. In the following discussion we shall use the nomenclature of a review article [14] on dynamic nuclear polarization which follows closely the nomenclature used by Abragam [13]. Although this article deals primarily with liquid solutions of radicals, it should be stressed that in Table I all possible interactions between the unpaired electrons and the nuclei and their time dependences are included. Hence it is fully applicable to our case of radicals in a solid matrix if we set the time constants which depend on the molecular mobility

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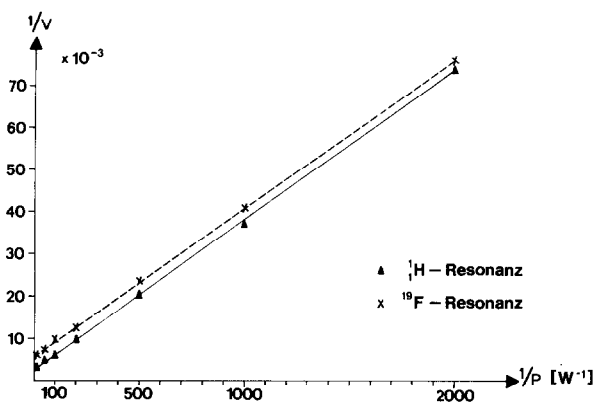


Fig. 1. Reciprocal Overhauser enhancement factor  $1/V$  of the protons ( $\blacktriangle$ — $\blacktriangle$ ) and of the  $^{19}\text{F}$ -nuclei ( $\times$ — $\times$ ) of  $(pe)_2^+\text{PF}_6^- \cdot 2/3\text{THF}$  as a function of the reciprocal power  $1/P$  in a magnetic field  $B_0$  3300 G at room temperature.

equal to infinity, i.e., the rotational ( $\tau_r$ ) and translational ( $\tau_t$ ) correlation time and the molecular exchange time  $\tau_h$ . In this case the interaction between the electronic spin  $S$  and the nuclear spin  $I$  which may be scalar or dipolar are modulated by two time dependences: The electron spin relaxation times  $\tau_1$  and  $\tau_2$  and the electron spin exchange time  $\tau_e$  which can be described by a jump function  $f_{IS}(t)$  that has the value one or zero if the nuclear spin  $I$  and the electronic spin  $S$  interact or do not. In the case of  $(pe)_2^+\text{PF}_6^- \cdot 2/3\text{THF}$  discussed here the exchange time constant  $\tau_e$  which measures the average lifetime of an electronic spin in one perylene molecule is  $\tau_e \leq 10^{-14}$  sec [5], while the electronic relaxation times  $\tau_1$  and  $\tau_2$  are  $\tau_1 = \tau_2 = 5 \times 10^{-6}$  sec [15]. Hence the condition  $\tau_e \ll \tau_1, \tau_2$  is fulfilled very well and the relevant time dependence both for the scalar and for the dipolar interaction is given by the exchange time constant  $\tau_e$  or, using the nomenclature of [14], the parameter  $\beta = 0$ .

In the next section we shall discuss the origin of the enhancement factors  $V_P = +320 \pm 20$  and  $V_F = +175 \pm 40$  extrapolated for finite power. The enhancement factor  $V$  is given by [14]

$$V = \xi f s \gamma_S / \gamma_I, \quad (1)$$

where  $\xi$  is the coupling parameter,  $f$  is the leakage factor and  $s$  is the saturation parameter which must be set equal to  $s = 1$  for extrapolation to infinite power. In our case the condition for the extreme narrowing  $\tau_e \omega_S \ll 1$  is very well fulfilled; hence the coupling parameter is equal to  $\xi = -1$  for pure scalar interaction and  $\xi = +1/2$  for pure dipolar interaction. In connection with the negative sign of the magnetogyric ratio  $\gamma_S$  of the electronic spin and the positive signs of the magnetogyric ratios  $\gamma_I$  of both the protons and the  $^{19}\text{F}$ -nuclei,

equation (1) renders a positive enhancement factor for scalar interaction and a negative enhancement factor for dipolar interaction. Our experimental results show unambiguously that the interactions of the electronic spins both with the protons and with the fluorine nuclei are predominantly scalar.

The maximum possible enhancement for pure scalar interaction is given by the ratio  $\gamma_S / \gamma_I$  which is 657 for the protons and 700 for  $^{19}\text{F}$ -nuclei. The considerably smaller enhancement found experimentally can be due to a mixed scalar and dipolar coupling and to the leakage factor which originates from other relaxation mechanisms not involving the electronic spins. For mixed scalar and dipolar interaction with a white noise spectrum ( $\Omega_S \tau \ll 1$ ) and with the simplification that the time dependence is  $\tau_e \ll \tau_1, \tau_2$  both for the scalar and dipolar interaction, the coupling parameter is given by [16]

$$\xi = (1 - M) / (2 + M), \quad (2)$$

where  $M$  is a measure for the ratio of the scalar to the dipolar interaction. The relaxation of the protons is mainly due to their interaction with the unpaired electrons in distinction to the  $^{19}\text{F}$ -nuclei for which the dipolar coupling within the  $\text{PF}_6^-$ -unit in connection with the hindered rotation of this unit provides an additional relaxation mechanism [8]. Our experimental results for the protons render using equation (1) and  $f \approx 1$  for the coupling parameter  $\xi = -1/2$ . Using equation (2) we find for the mixing parameter  $M = 4$  or, in other words, the scalar part of the hyperfine interaction seems to be twice as large as the dipolar part, (the factor four is due to the fact that the mixing parameter  $M$  is proportional to the square of the coupling constants), a ratio which is within the limits to be expected for an aromatic radical ion.

For the  $^{19}\text{F}$ -nuclei our experimental result  $V_F = +175 \pm 40$  means that the product  $\xi f = 1/4$ , but we cannot distinguish whether this is due to a smaller value of  $\xi$  or  $f$  or both as compared to the protons. A smaller  $\xi$  would be plausible since the electrons are mainly situated on the aromatic cations and hence the ratio of the scalar interaction to the dipolar one is expected to be smaller than for the protons. On the other hand, Hoepfner *et al.* [8] have stated on the basis of relaxation studies that the dipolar coupling between the  $^{19}\text{F}$ -nuclei within the  $\text{PF}_6^-$ -unit in combination with the hindered rotation of this unit are the most important relaxation mechanisms for the  $^{19}\text{F}$ -nuclei. Although this is perhaps a little overemphasized it shows that this relaxation mechanism which does not involve the unpaired electrons is not negligible as in the case of the protons and hence  $f < 1$ . Since the smaller value for  $V_F$  could originate both from a smaller  $\xi$  and from a smaller  $f$ , we

cannot calculate a ratio for the scalar to the dipolar coupling as in the case of the protons. Let us stress, however, that it is not surprising at all that  $V_F$  is smaller than  $V_P$  but that on the contrary it is surprising that we still do find a value as high as  $V_F = +175$ .

The results of our measurements of the Overhauser effect of the protons and the <sup>19</sup>F-nuclei of (pe)<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>·2/3 THF are in agreement with its character of an organic metal as shown by temperature dependent conductivity, thermopower, ESR and NMR measurements [17]. While the positive enhancement found for the protons is of the order to be expected, the surprisingly high positive enhancement of the <sup>19</sup>F-nuclei indicating a pre-dominantly scalar interaction with the conduction electrons is not understood. More information may be obtained by measuring the Overhauser enhancement of the <sup>31</sup>P-nuclei where, in distinction from the protons and the <sup>19</sup>F-nuclei, the three spin effects [18, 19] will play an important role.

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