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An application of the deconvolution procedure in the interpretation of E.S.R. spectra

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Chimica fisica. — *An application of the deconvolution procedure in the interpretation of E.S.R. spectra.* Nota di CESARE OLIVA (*), presentata (**) dal Socio M. SIMONETTA.

RIASSUNTO. — Il metodo di Deconvoluzione qui proposto, basato sulle proprietà della Trasformata di Fourier di uno spettro ESR, si rivela un possibile mezzo per scegliere l'interpretazione corretta tra più interpretazioni apparentemente equivalenti, e per escludere la presenza di più spettri sovrapposti o di fenomeni dinamici che influenzino la larghezza delle righe.

INTRODUCTION

We often find ambiguous situations in the interpretation of ESR spectra of aromatic compounds with many hyperfine splitting constants (*hfscs*).

So, for example, if we allow 3,5-dinitrobenzonitrile (DNBN) (Fluka) to react with sodium mirror in tetrahydrofuran (THF) we obtain a complicated ESR spectrum (Fig. 1) which could be due either to the ion pair

$$\text{DNBN}^{-\bullet}, \ \text{Na}^{+} \tag{1}$$

where one sodium cation is near one nitrogroup or to the triple ion

$$\text{DNBN}^{-\bullet}, \ \text{Na}_2^{+} \tag{2}$$

where two sodium cations are near the same nitrogroup.

In fact the spectrum shows in its wings a group of seven equally spaced lines (Fig. 2 *a*) which can be attributed either to the *hfscs* of a cation and two unequivalent nitrogens (Fig. 2 *b*) or to the *hfscs* of two nearly equivalent cations (Fig. 2 *c*).

Moreover we cannot exclude the hypothesis of the presence of a second spectrum due to the radical ion superposed on the spectrum of the ion pair (or triple ion) at least at low temperature.

To decide unambiguously between these hypotheses it is possible to use the deconvolution method we propose here.

THE DECONVOLUTION METHOD

For the first order perturbation theory, the ESR spectrum is given by:

$$\beta^{-1}\,\Delta E = gH + \sum_{k=1}^{N} a_k \, I_{zk} + f(\tau) \tag{3}$$

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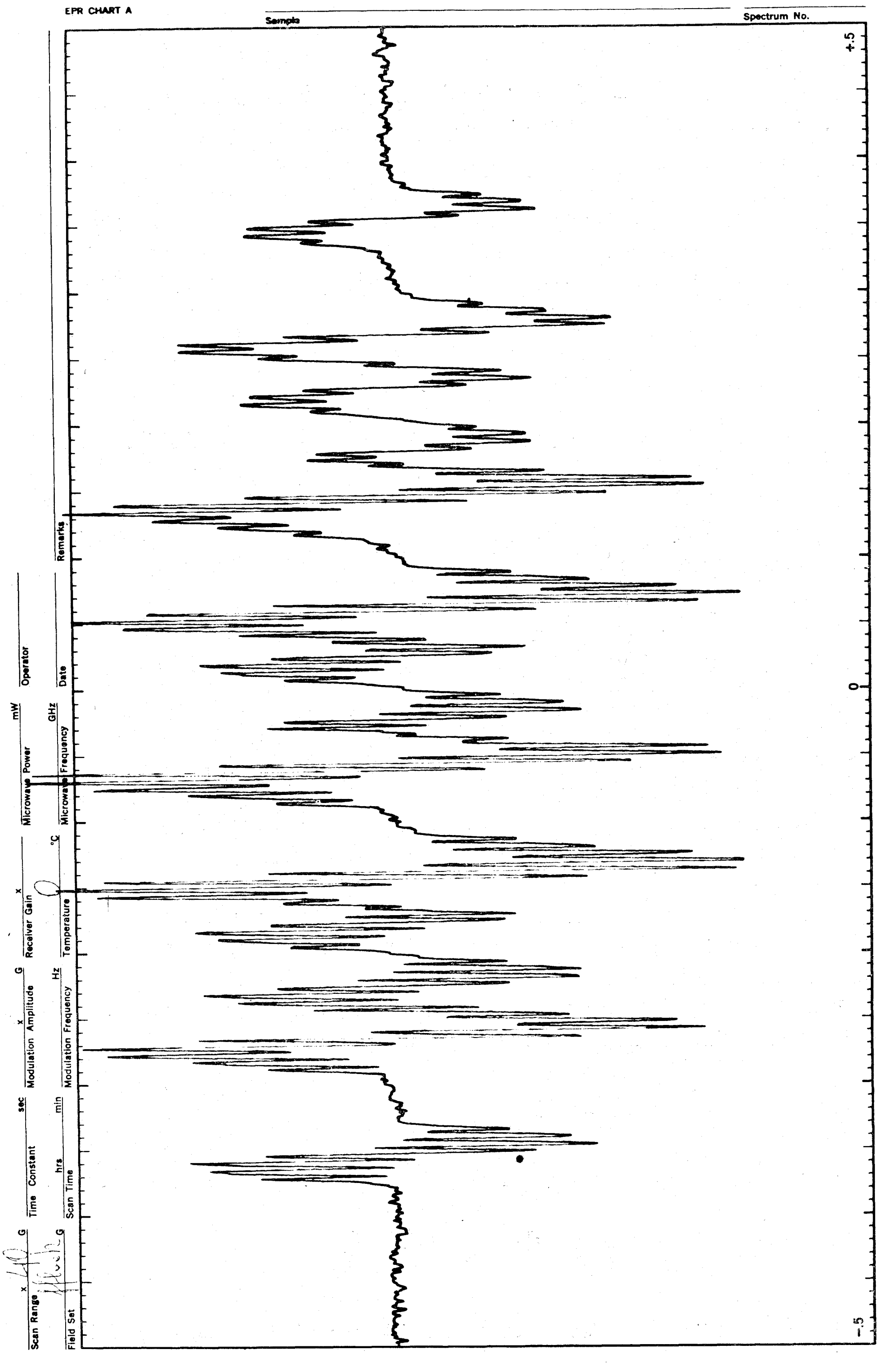

Fig. 1. – Experimental ESR spectrum of the ion pair 3,5-dinitrobenzonitrile$^-$; Na$^+$ in THF.

where ΔE is the difference between two energetic levels, β is Bohr magneton, g the Landé factor, H the magnetic field intensity, a_k the *hsfc* of nucleus k with nuclear spin I_{zk} along the z axis of the static magnetic field, N the number of paramagnetic nuclei and $f(\tau)$ a stochastic function of the time responsible for the line-width.

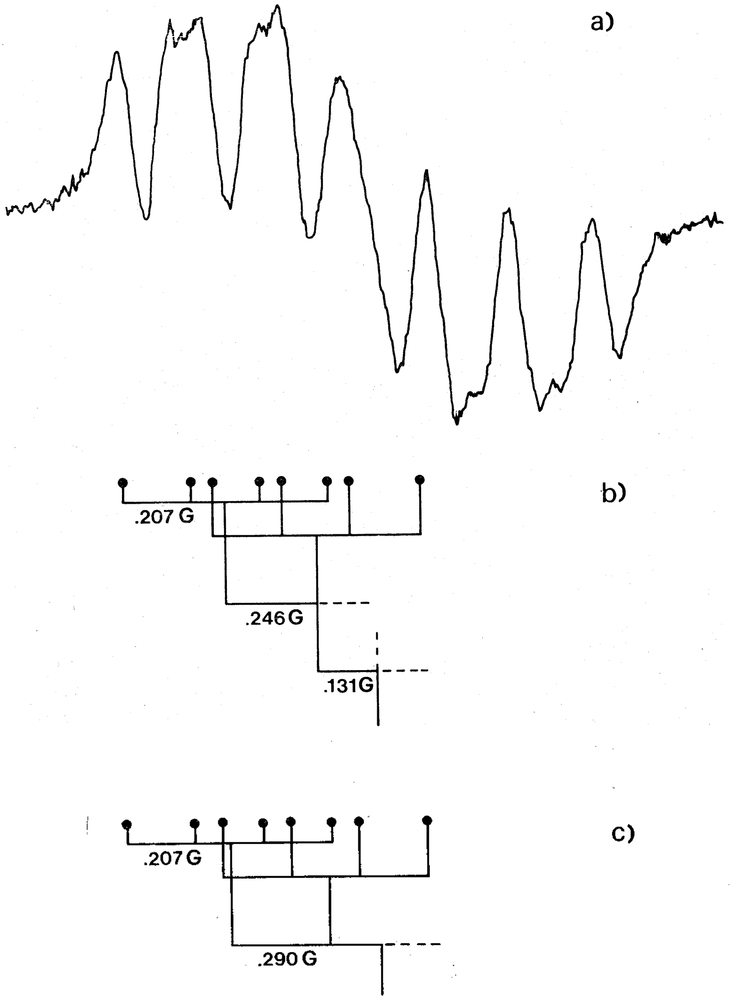

Fig. 2. – *a*) Experimental first group of the experimental spectrum shown in Fig. 1; *b*) scheme of interpretation including a *hfscs* due to a cation and two *hfscs* due to nitrogens; *c*) scheme of interpretation including two *hfscs* due to near equivalent cations.

All the hyperfine contribution $a_k\, I_{zk}$ can be seen as stochastic variables X_k of a function $G(X_k)$ characterizable by the corresponding Fourier Transform (FT):

$$\varphi_k(p) = \int_{-\infty}^{+\infty} \exp(ip\, X_k)\, dG(X_k)\,. \tag{4}$$

The line shape (lorentzian or gaussian) is proportional to dF (H)/dH where F (H) is the probability that Zeeman energy of an unpaired electron is between zero and ΔE for a given value of H, and can be characterized by the corresponding FT:

$$\varphi_{\Phi}(p) = \int_{-\infty}^{+\infty} \exp(ip\,H)\,dF(H)\,. \tag{5}$$

In the hypothesis that the shape is the same for all the lines of the spectrum, the FT of the ESR spectrum is given by[1-8]:

$$\varphi_S(p) = S_0\,\varphi_{\Phi}(p)\left\{\prod_{k=1}^{N}\varphi_k(p)\right\}\cdot\exp(ipg\,H_0) \tag{6}$$

where S_0 is a scaling factor and H_0 the center of the spectrum.

Eq. (6) is valid only if the spectrum is not affected by exchange or relaxation phenomena and if there is no superposition of more spectra.

If such restrictions are verified and we know the value $a_{k'}$ of a *hfsc* and the momentum $I_{zk'}$ of the nucleus k' to which such constant must be attributed, then we can calculate the corresponding FT $\varphi_{k'}$, divide eq. (6) for $\varphi_{k'}$ and obtain:

$$\varphi'_S(p) = \frac{\varphi_S(p)}{\varphi_{k'}(p)} \tag{7}$$

which is the FT of the ESR spectrum without the contribution arising from the nucleus k'.

Taking the Inverse Fourier Transform (IFT) of eq. (7) we obtain the ESR spectrum simplified by the *hfsc* $a_{k'}$. This procedure, termed deconvolution of the *hfsc* $a_{k'}$ from the spectrum, allows us to verify the precision of the value of $a_{k'}$ and the absolute failure of dynamic phenomena or superposition of spectra. When we are in these situations, in fact, eq. (6) is no longer valid and the result obtained by taking the IFT of eq. (7) is completely meaningless.

APPLICATION OF THE DECONVOLUTION METHOD AND ITS USEFULNESS

In the present case we digitized only the first group of the spectrum (see Fig. 2 *a*) with 1024 points by the top desk HP 9825 A and tried to do the deconvolution from this spectrum of the cationic hyperfine constant of .290 G hypothesized in Fig. 2 *c*.

In this way we obtained the meaningless result reported in Fig. 3.

The other way round, deconvolving from the experimental spectrum the nitrogen *hfsc* of .131 G (see Fig. 2 *b*) we obtained a spectrum composed of six lines (Fig. 4) interpretable as due to the nitrogen *hfsc* $a_N = .246$ G and to the cation *hfsc* $a_{Na} = .207$ G as hypothesized in Fig. 2 *b*.

Fig. 3. – Meaningless result obtained by deconvolution of the cation *hfsc* of .290 G from the spectrum of Fig. 2 *a*).

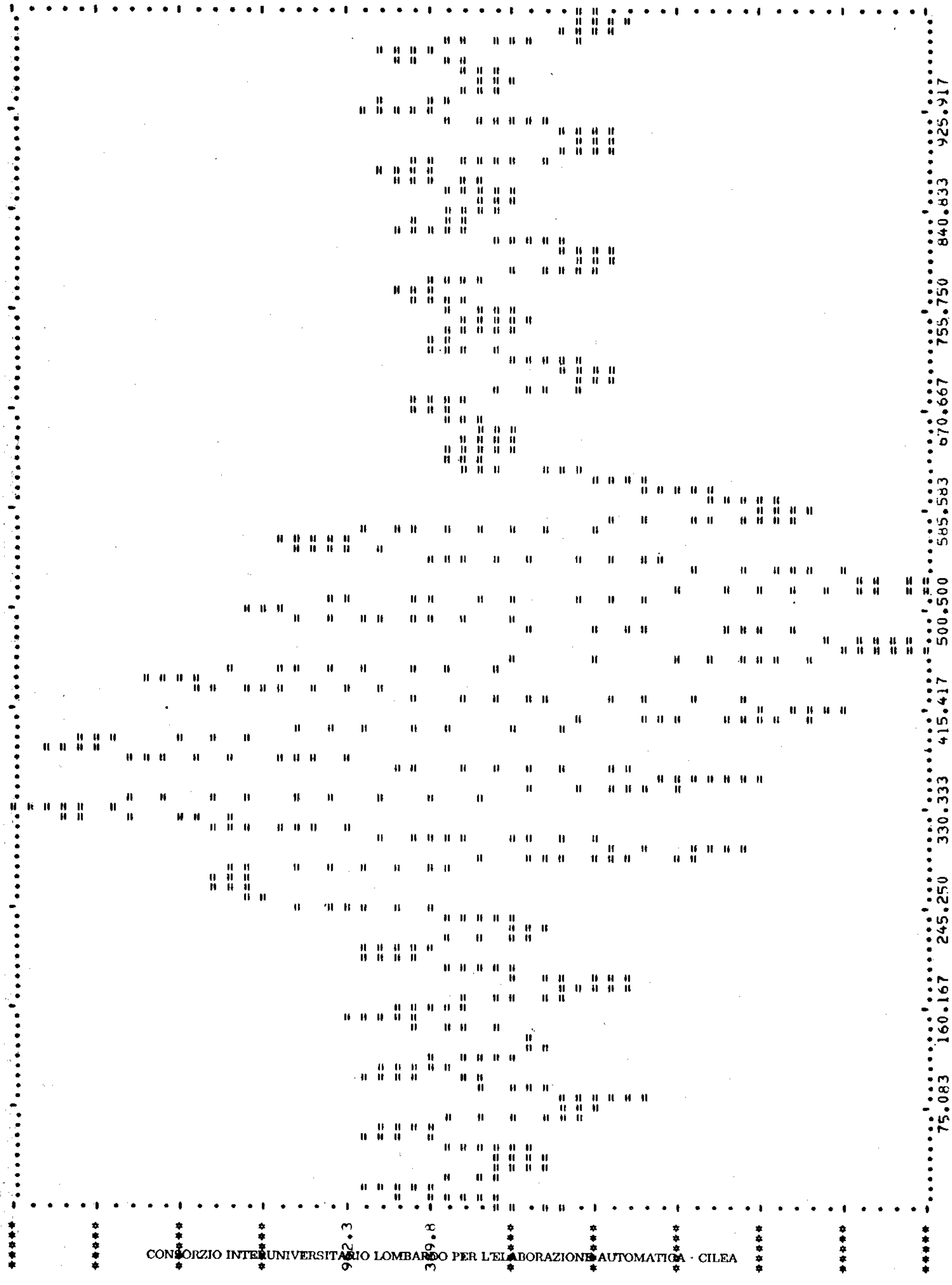

Fig. 4. – Result obtained by deconvolution of the nitrogen *hsfc* of .131 G from the spectrum of Fig. 2 *a*).

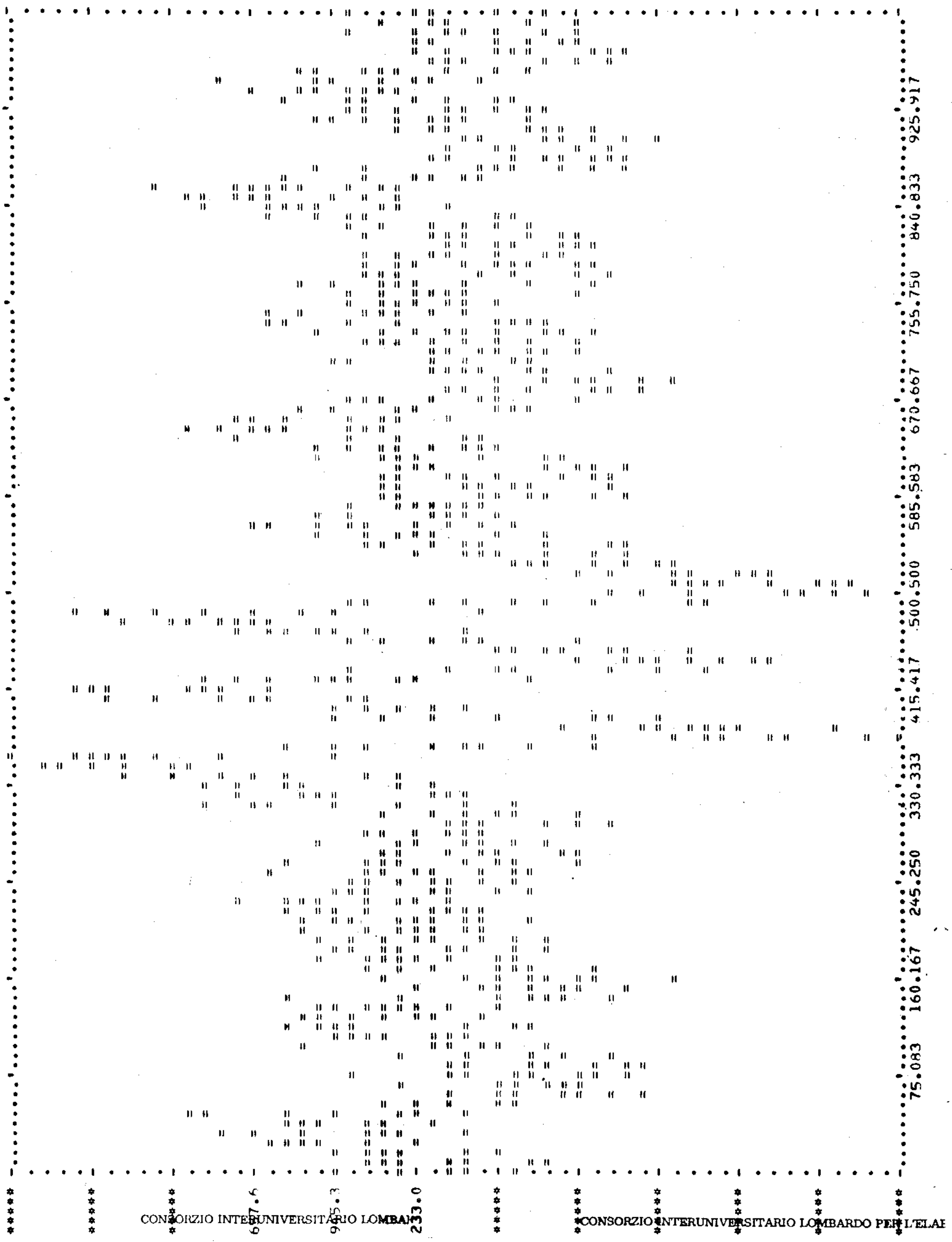

Fig. 5. - Result obtained by deconvolution from the spectrum of Fig. 2 *a*) of the nitrogen *hfsc* of .131 G and the cation *hfsc* of .207 G.

To further check this hypothesis we did the deconvolution of two *hfscs* simultaneously, substituting the following relation for eq. (7):

$$\varphi'_S(p) = \frac{\varphi_S(p)}{\varphi_{k'}(p) \cdot \varphi_{k''}(p)} \tag{8}$$

where in our case k' is a nitrogen with $a_{k'} = .131$ G and k'' is the cation characterized by $a_{k''} = .207$ G.

Again, the procedure led to the desired result and we obtained a spectrum composed of three lines equally spaced by $a_N = .246$ G (Fig. 5).

This method proved itself useful in verifying the exactness of the hypothesis drawn in Fig. 2 *b* and the absolute absence of any dynamical or equilibrium phenomena affecting the experimental spectrum.

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