Computer solution of a difficult experimental EPR spectrum hyperfine structure

O. DRAČKA

Department of Theoretical and Physical Chemistry, Faculty of Natural Sciences, Masaryk University, CS-611 37 Brno

Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The application of previously developed methods for the computer solution of the hyperfine structure of a 2-furylethenetricarbonitrile anion radical experimental EPR spectrum is presented. While for other commonly used methods the vicinity of some splitting constant values in this spectrum complicates the solution, the methods applied allow a simple and straightforward solution of this problem.

В приведенной работе показывается применение раньше развитых методов вычислительного решения структуры сверхтонкого расщепления на экспериментальный спектр 2-фурилэтилентрикарбонитрил--анионрадикала. Тогда как для остальных обычно использованных методов очень близкие величины некоторых констант расщепления в спектре вызывают при его анализе затруднения, здесь применяемый метод позволяет простое и прямое решение этой проблемы.

The development of methods for computer processing and analysis of linear isotropic EPR spectra [1] provided the possibility of a simple solution of complicated cases in this area. Software support of these methods by a system of programs [2] then permits their general use. The methods developed were tested on noise-loaded simulated spectra [1]. The result of their application to difficult experimental spectra is therefore of general interest. Such a case is reported below.

An experimental EPR spectrum of 2-furylethenetricarbonitrile anion radical [3] was selected as a suitable spectrum for this purpose. The difficulties in solution of the hyperfine structure (hfs) of this spectrum resulted from the close vicinity of values of some splitting constants. The solution of this problem by a spectrum simulation with variation of splitting constants for a known number and spin of splitting atoms, based on quantum chemistry results assuming a known molecular structure took a week of work by a skilled scientist [4].

Computer processing of the EPR spectrum starts with base line correction and a search for the spectrum symmetry centre. Computation of the function $C(x_0)$, expressing the deviation of the spectrum symmetry for a given position x_0 of the centre, serves for the last purpose. The stronger minimum on this centre

search function thus indicates the spectrum symmetry centre position. The core of the methods used further is based on computed elimination of one particular splitting from the spectrum, which is called spectrum contraction. The contraction can be achieved either for doublet or for triplet splitting (which results from atoms with spins of 1/2 and 1, respectively), and is, therefore, designated as doublet or triplet contraction accordingly. The computer spectrum analysis is then made by computing the function $F(a)$, expressing the deviation from correctness of the spectrum resulting from contraction with the particular value of the splitting constant a. Resulting $F(a)$ *vs.* $a(1/2)$ or $a(1)$ dependence, for doublet or triplet contraction, is then called the doublet or triplet analysis. Minima on those analyses thus point to the possible values of splitting constants for the doublet and triplet splitting involved in the spectrum analyzed. The smoothing of $F(a)$, giving $\tilde{F}(a)$, usually suppresses more strongly some artefacts, and thus helps to estimate the importance of different minima revealed by analysis. With a known value of a splitting constant the spectrum can be contracted and the resulting spectrum analyzed again. Application of those processes is demonstrated below. Introduced condensed notation [1], expressing the splitting and contraction by formal multiplication and division using particular splitting constant, has been used throughout.

Experimental

The EPR spectrum used was reported in paper [3] as experimental spectrum *Ia* and it will be so designated below. It was measured by *Staško* on Bruker SRC 200D spectrometer with a sweep width of 2 mT and a central field of 347.4 mT and recorded on a dedicated ASPECT 2000 computer to 8-inch floppy disc in ADAKET system digital format with 2048 points [4]. A copy of the experimental spectrum record was converted from ADAKET to CP/M system format on a SAPI-1 computer by means of a special conversion program [5]. The 8-inch floppy disc with converted record was then used as input for an EC-1033 computer, on which the system of programs [2] was implemented. The details of application of various programs to obtain functions reported below are described in paper [2]. The smoothing reported below was performed with a fixed smoothing width taking three inner points, *i.e.* with width of 0.008 mT for doublet and of 0.004 mT for triplet analysis. Note that the precise numerical values reported below are the results of computer printouts to exhibited functions. All spectra and functions plotted in the figures have the same x-scale in order to simplify comparison.

Results and discussion

The processed experimental *Ia* EPR spectrum after base-line correction is shown in Fig. 1. Under it there is the centre search function $C(x_0)$ with the same x-position. It exhibits a -0.011 mT shift of the spectrum symmetry centre with
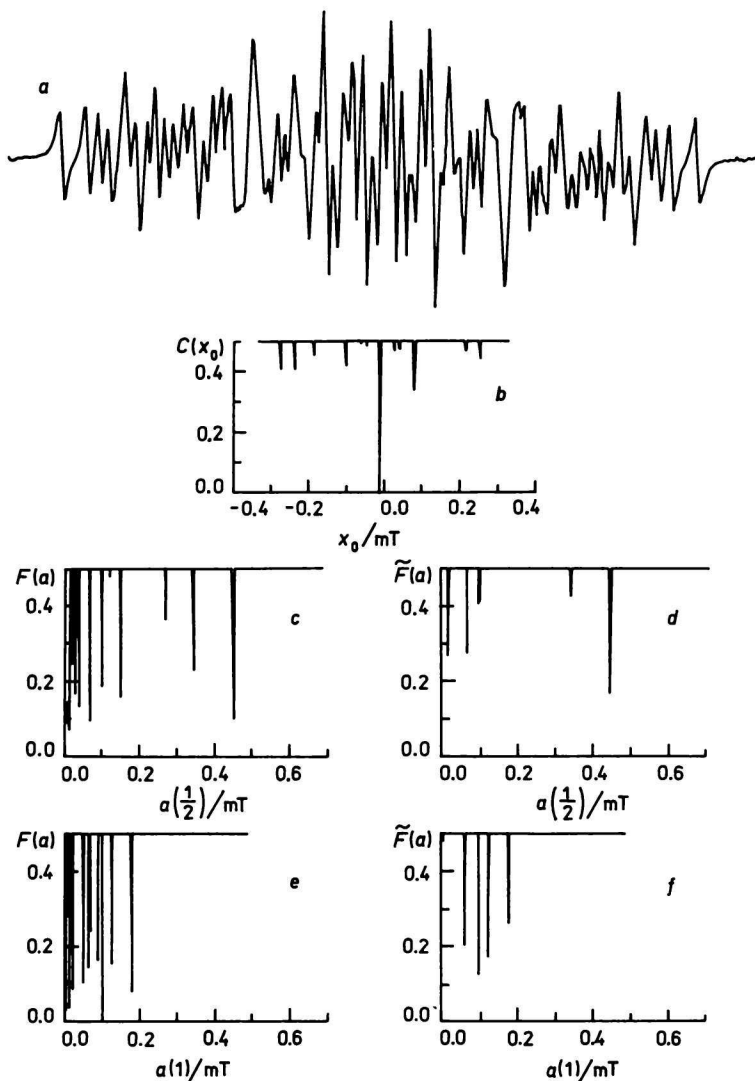

Fig. 1. Experimental EPR spectrum with results of centre search and analyses.
a) Ia spectrum [3]; *b*) centre search; *c*) doublet analysis; *d*) smoothed *c*; *e*) triplet analysis; *f*) smoothed *e*.

respect to the centre of the record. Estimated noise-level in the spectrum evaluated from this centre search was 12 %. In the lower half of Fig. 1 the results of doublet and triplet analyses and of smoothing those analyses are shown. From the doublet analysis the hydrogen splitting constant 0.451 mT is evident. It can, moreover, be seen that it is the biggest splitting constant involved. The
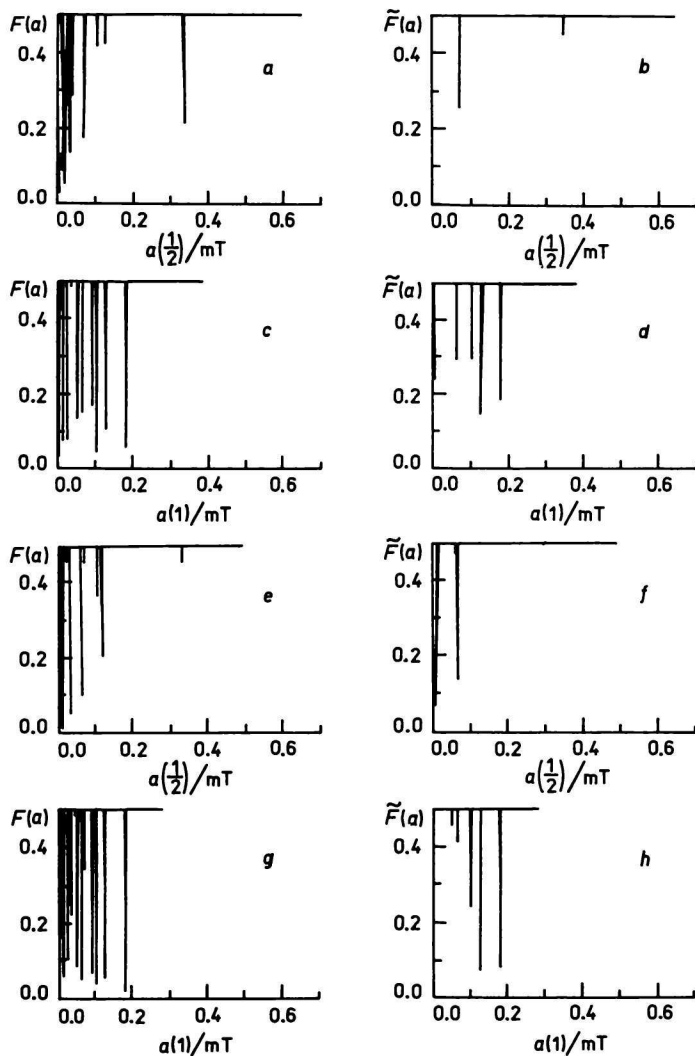

Fig. 2. Analyses of contracted spectra.
a—d) Analyses for $Ia/0.451(H)$ spectrum; *e—h*) analyses for $Ia/0.451(H)/0.346(H)$ spectrum. *a, e* — Doublet analyses, *c, g* — triplet analyses, *b, d, f, h* — smoothed *a, c, e, g*, respectively.

next step in the spectrum analysis is therefore the contraction of the spectrum by this constant and analysis of the resulting $Ia/0.451$(H) spectrum. The results of these analyses are shown in the upper half of Fig. 2. From the doublet analysis it can be concluded that the second biggest splitting constant involved is 0.346 mT, even if some doubt about this may arise from the fact that the corresponding minimum almost disappears after smoothing. However, trying the next contraction using this constant gives fair results, which eliminates the doubt. The results of analysis of the resulting $Ia/0.451$(H)/0.346(H) spectrum are shown in the lower half of Fig. 2. Inspection of all triplet and smoothed triplet analyses in Figs. 1 and 2 leads to the conclusion that there are three
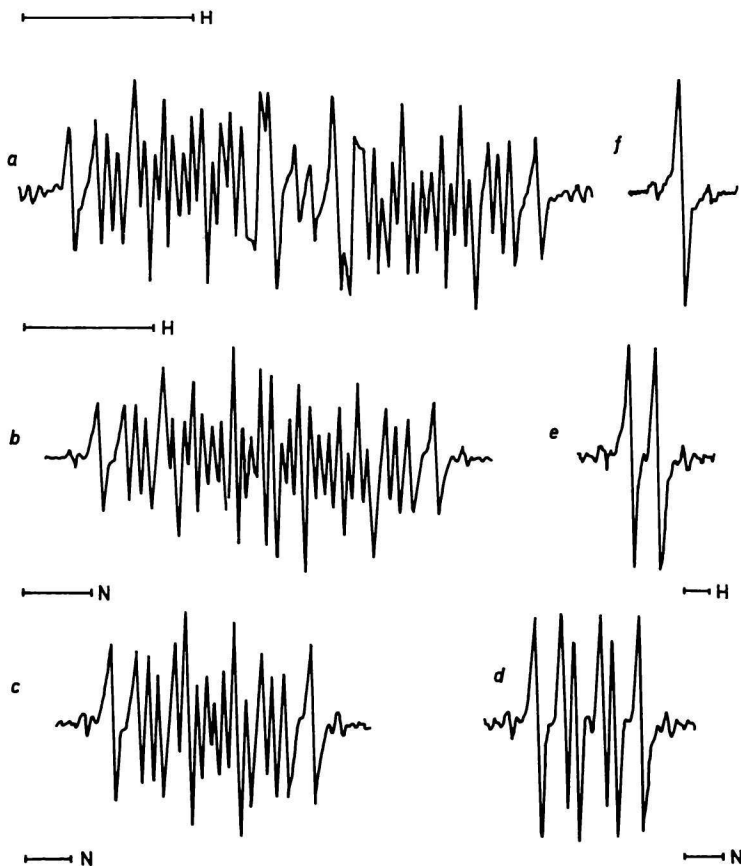

Fig. 3. EPR spectra resulting from the gradual contraction with weighted symmetrization. *a)* $Ia/0.451$(H); *b)* $Ia/0.451$(H)/0.346(H); *c)* $b/0.182$(N); *d)* $c/0.127$(N); *e)* $d/0.103$(N); *f)* $e/0.070$(H). Under every spectrum (except *f*) there is the splitting constant used for its contraction to obtain the next spectrum. Over *a* is the splitting constant used for its production from experimental spectrum *Ia*.

evident nitrogen splitting constants, particularly 0.103 mT, 0.127—0.128 mT, and 0.181—0.182 mT (1 μT differences in last two values are the result of different analysis printouts; the fourth strong minimum appearing in Figs. 1f and 2d appears at 0.064 mT, which is precisely the half of the middle constant value, and this qualifies that minimum as a possible ghost). Inspection of all doublet and smoothed doublet analyses then leads one to the conclusion that along with the two above reported hydrogen splitting constants there is a third one with a value 0.070 mT. Inspection of the outer lines in the spectrum record gives a peak-to-peak linewidth of 0.013 mT. Trying, at this stage of spectrum analysis, a shortcut by using spectrum simulation with the values mentioned, the best fit of all with the 0.182(N)0.127(N)0.103(N)0.451(H)0.346(H)0.070(H)L0.013 spectrum is obtained. This simulated spectrum fits well the *Ia* experimental spectrum even in minute details, with a normalized mean square difference of 0.045. The resulting splitting constant values cope well with the values reported by *Staško* [3]. However, the process of gradual spectrum contraction as described above, using for contraction at every step the greatest determined splitting constant value, can, even without the shortcut mentioned, proceed up to a single-line spectrum. Spectra resulting from this process are exhibited in Fig. 3. Computer-estimated mean noise levels in those spectra were 11 %, 10 %, 13 %, 15 %, 17 %, and 22 %, respectively. Contraction up to a single-line spectrum confirms the correctness of the splitting constants used.

The small difference between 0.103 mT and 0.127 mT splitting constants, comprising only 1.85 multiple of the linewidth, in the environment of the next closest 0.070 mT and 0.181 mT splitting constants with neighbourhood differences amounting to 2.5 and 4.2 multiples of the linewidth, was evidently the source of the above-mentioned difficulties with earlier hfs evaluation. From the triplet analyses in Figs. 1 and 2 the difference between 0.103 mT and 0.127 mT splitting constants and their values and independent appearance is clearly evident. Direct determination of those constants by the process described thus presents no difficulties.

It should be mentioned that during the process of spectrum analysis described no information other than that provided by the EPR spectrum alone was necessary (the terms hydrogen and nitrogen were in fact used above as short for the general but long expression "atom with spin 1/2" and "atom with spin 1"). With a priori knowledge of the number and spin of splitting atoms and some idea of the range of possible splitting constant values, such as that provided by quantum chemistry calculations, a shortcut by the right spectrum simulation would be possible directly from the results presented in Fig. 1 only.

For comparison with the above-mentioned time requirements for the problem solution it may be noted that the most time-consuming steps in the approach described proved to be connected with the computer, particularly the job

preparation and waiting for results. With a computer (including drawing device) immediately available and preprepared forms for jobs, the time requirements for the described case can be estimated at few hours only, even with the described knowledge of results evaluation only and without high skill in EPR spectra analysis.

Conclusion

The above results confirm that the methods used substantially facilitate the solution of EPR spectra hyperfine structure. For the spectra with complexity comparable to that used they even make it possible to solve the hyperfine structure without information about the molecular structure or about the number and spin of splitting atoms, at least insofar as only spins of 1/2 and 1 are involved. The solution can moreover be straightforward, without a surplus of dead ends. The close vicinity of values of some splitting constants, which gives rise to difficulties in the solution of hfs by other methods commonly used, presents no problems for the above-used methods.

References

1. Dračka, O., *J. Magn. Reson. 65*, 187 (1985).
2. Dračka, O., *J. Comput. Phys.,* in press.
3. Staško, A., Berkeš, D., Biskupič, S., Pelikán, P., and Polakovič, J., *Chem. Papers 43*, 177 (1989).
4. Staško, A., private communication.
5. Černohlávek, I., unpublished program CNV, Institute of Computer Science, J. E. Purkyně University, Brno, 1988.

Translated by O. Dračka