

Electron Spin Resonance of 1,4Naphthosemiquinone Ion

John E. Wertz and Juana L. Vivo

Citation: [The Journal of Chemical Physics](#) **24**, 479 (1956); doi: 10.1063/1.1742514

View online: <http://dx.doi.org/10.1063/1.1742514>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/24/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Elastic scattering of low-energy electrons by 1,4-dioxane](#)

J. Chem. Phys. **140**, 184303 (2014); 10.1063/1.4874646

[Summary of the performances of the superconducting electron cyclotron resonance ion source at 14 GHz](#)

Rev. Sci. Instrum. **69**, 4082 (1998); 10.1063/1.1149254

[Observation of Néel structure walls on the surface of 1.4 \$\mu\$ mthick magnetic films using spinpolarized scanning electron microscopy](#)

Appl. Phys. Lett. **49**, 980 (1986); 10.1063/1.97502

[Transferredelectron photoemission to 1.4 \$\mu\$ m](#)

Appl. Phys. Lett. **29**, 87 (1976); 10.1063/1.88977

[Electronic Zeeman Measurements on 1,4Dibromonaphthalene](#)

J. Chem. Phys. **48**, 637 (1968); 10.1063/1.1668694



at "bond order" 0.33 corresponding to the XCl_3 coordinations of these crystals.

Very recently freezing point depression measurements² yielded the number of ions produced when CdCl_2 , ZnCl_2 , etc. are dissolved at low concentration in molten NaNO_3 both with and without added chlorides such as KCl and CaCl_2 . It was proved that CdCl_2 and ZnCl_2 associate with Cl^- to form complex anions which contain at least four chlorines. Equilibrium constants calculated from these data were consistent with presence of Cd^{2+} , CdCl_2 , and CdCl_4^{2-} , but no agreement was found on the assumption of CdCl^+ , and CdCl_3^- . Therefore, it was concluded that CdCl_3^- is an unimportant species while CdCl_4^{2-} is quite important.

Electrical conductivity, surface tension, and viscosity measurements³ have recently suggested the occurrence of complexes such as CdCl_3^- and PbCl_3^- in salt melts. The substitution of CdCl_4^{2-} ions for CdCl_3^- ions is just as feasible in the interpretation of these results as of the Raman spectra above. PbCl_3^- , however, is distinguished from CdCl_3^- and ZnCl_3^- by the lone $6s^2$ electrons of Pb^{2+} , which makes a nonplanar PbCl_3^- , with the electron pair occupying one corner of a distorted tetrahedral configuration, more plausible than PbCl_4^{2-} .

The increase in force constants from Cd to Hg chloride complexes that remained unexplained¹ may be readily understood if it is realized that the "covalent bond character" of the $\text{X}-\text{Cl}$ binding ($\text{X}=\text{Zn}, \text{Cd}, \text{or Hg}$), or, rather, the degree of mutual polarization of cation and anion, clearly is at a minimum in the cadmium compounds: Zn^{2+} , because of its smaller size, is more strongly polarizing, and Hg^{2+} is more polarizable than Cd^{2+} .

¹ W. Bues, Z. anorg. u. allgem. Chem. **279**, 104-114 (1955).

² E. R. Van Artsdalen, J. Phys. Chem. (to be published); Paper presented at Ion Pair Symposium, American Chemical Society Meeting, Minneapolis, 1955.

³ Harrap, Boardman, Palmer, and Heymann, Trans. Faraday Soc. **51**, 259, 268, and 277 (1955).

Electron Spin Resonance of 1,4-Naphthosemiquinone Ion*

JOHN E. WERTZ AND JUANA L. VIVO

School of Chemistry, University of Minnesota, Minneapolis, Minnesota
(Received November 14, 1955)

A PREVIOUS communication¹ pointed out that one observes the expected number $(2nI+1)$ of hyperfine splitting components in the electron spin resonance (ESR) spectrum of the semiquinone ions derived from 1,4-benzoquinone and its chlorine-substituted derivatives. Here n represents the number of ring protons, and $I (= \frac{1}{2})$ is their nuclear spin. The magnetic moment of the chlorine nucleus is too small to give observable splitting. For the semiquinones from phenylquinone, 2,5 and 2,6-diphenylquinone one observes, respectively, four, three, and three components, indicating that the interaction of the unpaired electron with the protons of the substituting phenyl groups is far smaller than for those of the principal ring. We attribute this to the noncoplanar orientation of the substituting rings with the principal one.

In the naphthoquinones one is assured of coplanarity of the quinoid ring and the adjacent one, and hence one might hope for an extra ESR multiplicity. This is indeed observed for 1,4-naphthosemiquinone ion in basic alcohol solution, as shown in Fig. 1. Ignoring the protons in the 5, 6, 7, and 8 positions, one would expect three components from the hyperfine interaction of the unpaired electron with the protons in the 2 and 3 positions. One does indeed observe three groups of lines spaced 3 gauss apart. Considering that the other protons might interact much more weakly with the electron, their effect would be further to split the hyperfine levels arising from protons 2 and 3. If the protons 5 to 8 interact equally with the unpaired electron, one would expect that each level would give rise to a quintet from this ultra-hyperfine interaction. This expectation corresponds with observation, these components being separated by 0.3 gauss. This system

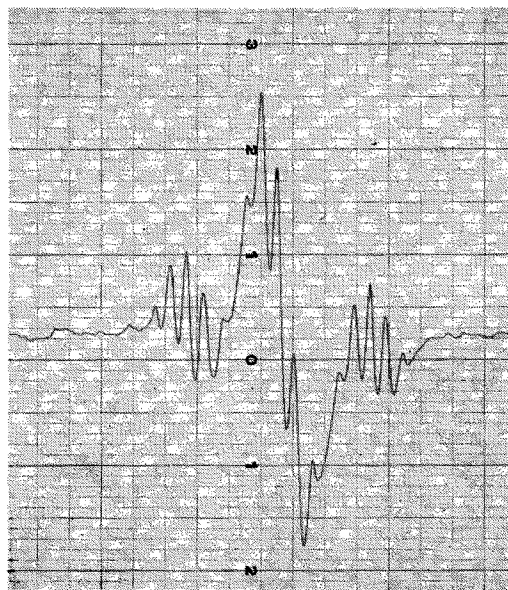


FIG. 1. The ESR absorption derivative curve for the 1,4-naphthosemiquinone ion.

is thus ideal for evaluating the relative densities of the wave function of the unpaired electron at the protons in the two rings.

The 2,3-dimethylseminaphthoquinone ion by analogy would be expected to give seven components from the six equivalent methyl protons, and each of these should be a quintet. Seven groups are indeed observed. For the resolution at which we worked, there was an accidental coincidence of the outermost ultrahyperfine components of adjacent quintets. Since the two outermost groups are very weak, we counted the number of lines for the five inner groups and observed the expected twenty-one individual lines. These are separated by 0.57 ± 0.04 gauss.

The 2-methyl-1,4-naphthosemiquinone ion gives five groups of lines with twenty-four discernible components. The line assignment for this and numerous other naphthosemiquinone radicals is under study.

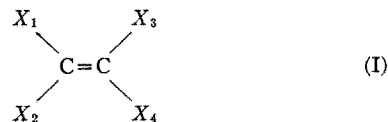
* This research was made possible by grants-in-aid from the Graduate School of the University for the purchase of equipment, and was supported in part by the U. S. Air Force under Contract AF 18 (600)-479, monitored by the Office of Scientific Research, Air Research and Development Command.

¹ John E. Wertz and Juana L. Vivo, J. Chem. Phys. **23**, 2441 (1955).

Nuclear Spin Coupling Constants in Halogenated Olefins

H. M. McCONNELL, C. A. REILLY, AND A. D. McLEAN*
Shell Development Company, Emeryville, California
(Received December 5, 1955)

WE give here a preliminary report of the results of a study of nuclear spin-spin couplings in a number of liquid halogenated olefins. Spectra were obtained with a Varian Associates V-4300 High Resolution NMR Spectrometer operated at 40 Mc/sec with magnetic fields of 9396 and 9983 gauss, respectively, for the H^1 and F^{19} resonances. The olefins can be represented by the general formula,



where the various X_i in (I) are listed in Table I for each compound.

TABLE I. Nuclear spin coupling constants in the halogenated olefins $CX_1X_2=CX_3X_4$.

X_1	X_2	X_3	X_4	J_{12}	J_{13}	J_{23}	J_{14}	J_{24}	J_{34}
H	F	Cl	Cl	81
H	H	F	F	~ 4	~ 1	34	34	~ 1	37
H	H	F	Cl	~ 3	8	40
F	F	F	Cl	41	< 3	13
F	F	F	Cl	78	58	115
F	F	F	Br	75	57	124
F	F	F	CN	27	35	118
F	F	F	H	87	33	119	12	< 3	72
F	F	F	CF ₃	57	39	116	8	22	13
F	F	Cl	CF ₃	*	12	21	...
Cl	F	Cl	CF ₃	20	...

* The $=CF_2F^{19}$ resonance is complex and has not been completely analyzed.

Tabulated coupling constants, J_{ij} (cy/sec), refer to couplings between magnetic nuclei of atoms (or groups) X_i and X_j in (I). J_{ij} is defined so that $hJ_{ij}I_i \cdot I_j$ is the energy (ergs) of the $i-j$ spin-spin interaction. I_i and I_j are the corresponding spin momentum vectors in units of \hbar .

The NMR spectra of (I) were analyzed using general theoretical methods described previously.¹ Except for $CH_2=CF_2$, $CH_2=CFCl$, and the perfluoro methyl compounds, simple first-order perturbation theory in the spin-spin interaction accounts for all the observed multiplets and their relative intensities. In the perfluoro methyl compounds hindered rotation of the CF_3 groups is thought to account for extra signals seen in the F^{19} resonances of these groups. Many of the assignments (Table I) of coupling constants to specific pairs of nuclei in structure (I) may be incorrect because in most cases there is no unambiguous way of assigning some particular multiplet splitting to a particular pair of nuclei. Our assignments are based on (a) comparisons of coupling constants and chemical shifts (not given here) found in compounds (I), and (b) theoretical arguments regarding various interactions which can contribute to nuclear couplings.²

Nuclear couplings within a single group (e.g., $=CF_2$) sometimes differ markedly in different compounds (e.g., 27–87 cy/sec). One outstanding regularity in Table I is the *trans* $F^{19}-F^{19}$ coupling which is 118 ± 6 cy/sec for five different compounds.

A more detailed account of this work will be given later.

* Present address: Department of Physics, University of Chicago, Chicago 37, Illinois.

¹ McConnell, McLean, and Reilly, J. Chem. Phys. **23**, 1152 (1955).

² H. M. McConnell, J. Chem. Phys. **23**, 760 (1955) and to be published.

Selective Scattering of Light by Pigment-Containing Plant Cells*

PAUL LATIMER AND EUGENE RABINOWITCH
Photosynthesis Research Project, Department of Botany,
University of Illinois, Urbana, Illinois
(Received December 6, 1955)

WE have observed a strong spectral selectivity in the scattering of light by pigmented algal cells. Sharp scattering maxima appear on the long wavelength side of absorption bands, and less pronounced minima seem to occur on their short wavelength side.

The cell suspension was illuminated with a parallel beam of light from a Bausch and Lomb grating monochromator (3.3 mμ band half-width). The intensity of light scattered at approximately 90° (more precisely, 75°–105°) to the incident beam was measured with a photomultiplier tube and was compared with that of the incident light by replacing the cell suspension with a magnesium oxide surface. The scattered light collected by the measuring device was of the order of 0.3% of the incident light. The amount of scattering per cell did not vary with the cell concentration.

Corrections were made for attenuation of the incident and scattered beams in the suspension¹ but not for absorption of

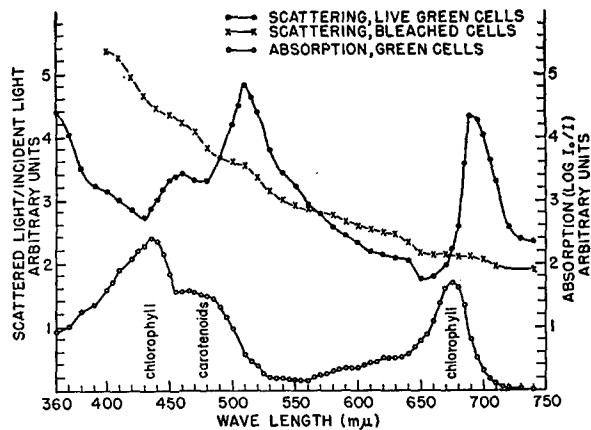


FIG. 1. Scattering and absorption of light by the green alga chlorella. The intensity of light scattered at 90° to the incident beam is shown as a function of wavelength. Absorption was determined with an integrating sphere.

scattered light by pigment within the scattering cell itself, since this would require a detailed knowledge of the geometry and optical properties of the cell. The asymmetry of the scattering curve in relation to the absorption curve clearly shows, however, that the scattering maxima are not produced primarily by selective absorption of nonselectively scattered light.

In spectral regions away from the fluorescence band of the cells, colored glass filters were used to prevent fluorescence from entering the detector with the scattered light. Close to and in the fluorescence band, the sum of the scattered light and fluorescence was measured and a correction was made for fluorescence. Scattered light and fluorescence were distinguished by their different degrees of polarization with polaroid plates, and by their different spectral composition (except in a part of the fluorescence band) with colored glass filters.

The light scattering by the cells is due: (1) to colorless structures, which scatter with a relatively uniform wavelength dependence (not unlike the scattering by bleached cells, shown in Fig. 1), and (2) to highly pigmented chloroplasts (or grana), the index of refraction of which changes sharply with wavelength, as described approximately by the classical dispersion formula. The second component accounts for the maxima and minima of the scattering curve of green cells. A similar spectral selectivity has been reported recently by Goedheer,² and by Menke and Menke,³ for the double refraction of higher plant chloroplasts. Proton scattering by atomic nuclei shows the same type of selectivity for proton energies in the neighborhood of the resonance levels of the target nucleus.⁴

Further study of the phenomenon of selective scattering by live cells, first described in this note, may supply information about the packing and arrangement of pigment molecules in biological systems, and may even reveal the presence of pigments which are not easily found by other techniques. As an example, it is seen in the figure that the selective scattering produced by the carotenoids in Chlorella is much more conspicuous than their contribution to the absorption spectrum. The latter is so effectively obscured by chlorophyll absorption that it has even been asserted that carotenoids do not exist as such in the living cell.⁵

We wish to thank Professor James Franck, Professor Robert Emerson, and Mr. Thomas Bannister for their helpful suggestions and Mrs. Ruth V. Chalmers for growing the algal cells.

* This work was carried out with the assistance of the Office of Naval Research.

¹ Brice, Nutting, and Halwer, J. Am. Chem. Soc. **75**, 824 (1953).

² J. C. Goedheer, Biochim. Biophys. Acta (Amsterdam) **16**, 471 (1955).

³ W. Menke and G. Menke, Z. Naturforsch. **10 b**, 416 (1955).

⁴ Bender, Shoemaker, Kaufman, and Bouricius, Phys. Rev. **76**, 273 (1949).

⁵ V. N. Lubimenko, Rev. gen. botan. **39**, 547 (1927).