

Errata: Statistical Thermodynamics of Polymer Solutions. I. Theory of the Second Virial Coefficient for a Homogeneous Solute

Edward F. Casassa and Hershel Markovitz

Citation: *The Journal of Chemical Physics* **30**, 852 (1959); doi: 10.1063/1.1730062

View online: <http://dx.doi.org/10.1063/1.1730062>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/30/3?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Theory of the Second Virial Coefficient of Polymer Solution](#)

J. Chem. Phys. **51**, 3457 (1969); 10.1063/1.1672534

[Statistical Thermodynamics of Polymer Solutions. IV. The Second Virial Coefficient for Comblike Branched Molecules](#)

J. Chem. Phys. **41**, 3213 (1964); 10.1063/1.1725699

[Statistical Thermodynamics of Polymer Solutions. III. The Second Virial Coefficient for Branched Star Molecules](#)

J. Chem. Phys. **37**, 2176 (1962); 10.1063/1.1732984

[Statistical Thermodynamics of Polymer Solutions. II. Excluded Volume Effect and Second Virial Coefficient](#)

J. Chem. Phys. **31**, 800 (1959); 10.1063/1.1730466

[Statistical Thermodynamics of Polymer Solutions. I. Theory of the Second Virial Coefficient for a Homogeneous Solute](#)

J. Chem. Phys. **29**, 493 (1958); 10.1063/1.1744530

A promotional banner for AIP Applied Physics Reviews. The background is a blue gradient with a molecular structure of blue spheres and connecting lines. On the left, there is a small image of the journal cover for 'AIP Applied Physics Reviews' showing a 3D grid structure. The main text 'NEW Special Topic Sections' is in large, white, sans-serif font. Below it, in smaller white text, is 'NOW ONLINE' and 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends'. The AIP logo and 'Applied Physics Reviews' text are in the bottom right corner.

NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Errata: Statistical Thermodynamics of Polymer Solutions. I. Theory of the Second Virial Coefficient for a Homogeneous Solute

[J. Chem. Phys. **29**, 493 (1958)]

EDWARD F. CASASSA AND HERSHEL MARKOVITZ

Mellon Institute, Pittsburgh, Pennsylvania

THE following equations,

$$A_2 = \text{const}[1 - \exp(-1.42\psi)]/1.42\psi$$

and

$$F^0(\psi) = [1 - \exp(-1.420\psi)]/1.420\psi,$$

should appear in the abstract and on page 499, respectively, in place of analogous expressions with the exponent positive. Elsewhere relations of this form are given correctly, and the discussion is in no way affected.

In printing, the cuts for Figs. 4 and 5 (pages 500, 501) have been interchanged.

Notes

Infrared Spectrum of $\text{Mg}(\text{OH})_2$

HANS A. BENESI

Shell Development Company, Emeryville, California

(Received October 27, 1958)

WE recently recorded infrared spectra of several samples of finely powdered $\text{Mg}(\text{OH})_2$ ranging from 0.05 to 0.3 mg/cm² in sample thickness. The only prominent feature found in the spectral range 3000 to 5000 cm⁻¹ was a *single*, intense, extremely sharp absorption band at 3698 cm⁻¹. This result was puzzling because Mara and Sutherland¹ had reported that infrared spectra of thin sections of brucite [naturally occurring $\text{Mg}(\text{OH})_2$] contain a total of *sixteen* absorption bands in the OH stretching region. The apparent anomaly was resolved when measurements were made using sample thicknesses that were ten to twenty-fold thicker than those reported above, for the complex spectrum reported by Mara and Sutherland could then easily be recognized. It was now evident that the spectrum of $\text{Mg}(\text{OH})_2$ consists of an extremely intense absorption band, presumably arising from the OH stretching fundamental, superimposed on weak satellite bands.

The 3698 cm⁻¹ band is unusually sharp and intense. With lithium fluoride optics and a spectral slit width of 1.5 cm⁻¹, the probable error of the frequency is ± 2 cm⁻¹, the observed maximum absorptivity is 9.6 cm²/mg, and the band width at half-height is 5 cm⁻¹. On the other hand, the strongest satellite bands have absorptivities in the neighborhood of 0.03 cm²/mg. As has been suggested by others^{2,3} these satellite bands

probably arise from combinations of the stretching fundamental with librational modes of the hydroxyl ion. This suggestion is reinforced by the present findings which show that there is a 300-fold difference in maximum absorptivity between the two types of absorption bands.

¹ R. T. Mara and G. B. B. M. Sutherland, J. Opt. Soc. Am. **43**, 1100 (1953).

² R. M. Hexter and D. A. Dows, J. Chem. Phys. **25**, 504 (1956).

³ W. R. Busing and H. W. Morgan, J. Chem. Phys. **28**, 998 (1958).

Electron Spin Resonance of Nitrobenzene Negative Ion

RAYMOND L. WARD

Radiation Laboratory, University of California,
Livermore, California

(Received November 17, 1958)

THE electron spin resonance of nitrobenzene negative ion, prepared by the reaction of potassium with nitrobenzene in 1,2-dimethoxyethane (DME), has been interpreted by the means of deuterium substitution.

It was reported that the electron spin resonance hyperfine pattern could be calculated with the following spin Hamiltonian¹:

$$\mathcal{H} = g\beta_o \mathbf{H}_o \cdot \mathbf{S} + \sum_o A_o \mathbf{I}_o \cdot \mathbf{S} + \sum_m A_m \mathbf{I}_m \cdot \mathbf{S} + A_p \mathbf{I}_p \cdot \mathbf{S} + A_N \mathbf{I}_N \cdot \mathbf{S}$$

with the appropriate choices of hyperfine coupling constants. A_o , A_m , and A_p are, respectively, the ortho-, meta-, and para-hydrogen hyperfine coupling constants, and A_N is the N¹⁴ coupling constant.

The value for A_N has been determined by N¹⁵ substitution and reported earlier.¹ The value reported was too large due to a field calibration error. The value has been redetermined accurately by a field calibration with an auxiliary proton resonance probe and found to be 11.1 ± 0.1 gauss. The value for the ratio of the ortho- and para-hydrogen coupling constants to the

TABLE I. Coupling constants and length of hyperfine patterns for nitrobenzene negative ion.

	Coupling constant ^a	Length of hyperfine pattern ^a
N ¹⁴ -nitrobenzene negative ion	$A_N = 11.1 \pm 0.1$	33.4 ± 0.4
Orthonitrobenzene- <i>d</i> ₁ , negative ion	$A_o = 3.7 \pm 0.1$	29.2 ± 0.4
Paranitrobenzene- <i>d</i> ₁ , negative ion	$A_p = 3.7 \pm 0.1$	29.8 ± 0.4
Metanitrobenzene- <i>d</i> ₁ , negative ion	$A_m \leq 0.65$	33.0 ± 0.4

^a Measured in gauss.

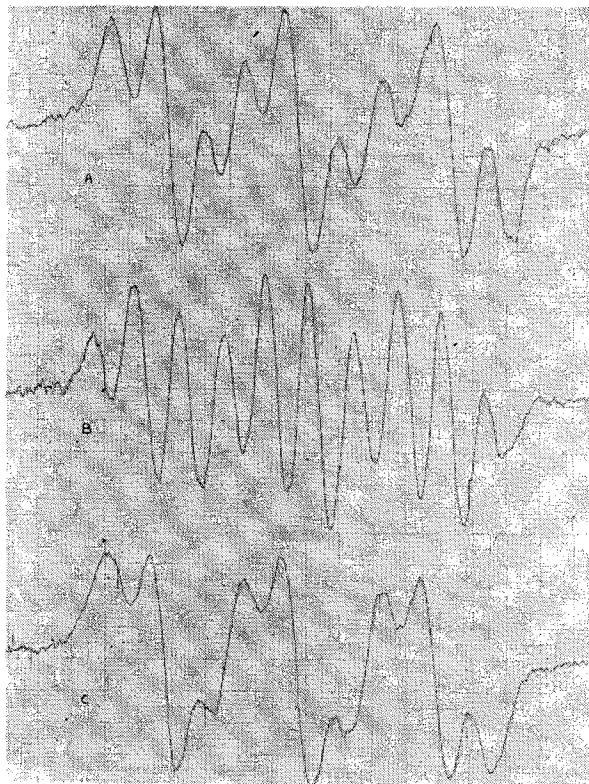


FIG. 1. dX''/dH vs H for (A) *o*-nitrobenzene- d_1 -negative ion, (B) *m*-nitrobenzene- d_1 -negative ion, and (C) *p*-nitrobenzene- d_1 -negative ion prepared with K and 1,2-DME.

nitrogen coupling constant previously reported is in no way affected. This leads to a value of $A_o = A_p = 1/3A_N = 3.7 \pm 0.1$ gauss. The value of A_m chosen to fit the spectrum in reference 1 was $A_m = 0$.

To confirm the aforementioned choices of hydrogen coupling constants, and to set an upper limit on the meta-hydrogen coupling constant, it was necessary to perform deuterium substitution at specific positions in the molecule. Monodeuteronitrobenzenes have been prepared with the following deuterium content: orthonitrobenzene- d_1 , 85.0%; metanitrobenzene- d_1 , 88.1%; paranitrobenzene- d_1 , 84.8%.

The observed hyperfine patterns of the monodeuteronitrobenzene negative ions appear in Fig. 1. In no case was any deuterium splitting observed. It can be readily seen that the hyperfine patterns compare quite favorably with what one would expect with the above choice of coupling constants.

In the case of the meta protons one would expect no change in the normal N^{14} -nitrobenzene negative ion hyperfine pattern upon deuterium substitution. This is because of the small value of A_m (less than the line width), and because the magnetic moment of the deuterium atom is smaller than the magnetic moment of the proton. The observed meta-monodeuteronitrobenzene negative ion hyperfine spectrum is spectrum B of Fig. 1. This spectrum agrees with that of the N^{14} -

nitrobenzene negative ion spectrum previously reported both in number of peaks, intensity ratios, and over-all length.¹ The spectra in Fig. 1 yield values for the ortho- and para-hydrogen coupling constants, and from the line widths it is possible to make an estimate of an upper limit for the meta-hydrogen coupling constant. The values of the coupling constants and the lengths of the hyperfine patterns appear in Table I.

It should be noted that the shorter length of the ortho- and para-monodeuteronitrobenzene negative ion hyperfine patterns is what one would expect from the foregoing discussion. A comparison of the spectra A and C in Fig. 1 yields the important and interesting result that the magnitude of the ortho- and para-hydrogen coupling constants are equal. The slight difference in the resolution of the two spectra is due to a concentration effect.

I wish to thank J. W. Frazer, P. A. Cogswell, and H. X. DiGrazia for the deuterium analysis and B. E. Holder and M. P. Klein for many helpful discussions and encouragement.

¹ R. L. Ward and M. P. Klein, J. Chem. Phys. **28**, 518 (1958). Errata J. Chem. Phys. **29**, 678 (1958).

Note on the Observation of Molecules by Field Emission Microscopy

R. J. HILL AND P. W. M. JACOBS

Department of Chemistry, Imperial College, London, S.W.7, England

(Received June 16, 1958)

FIELD emission microscopy has undoubtedly attracted considerable interest because of the reported resolution of single molecules (see references 1-10 for relevant details). The characteristic quartet shapes obtained by Müller² with copper phthalocyanine seemed at first to support this view, but later Müller,⁵ Haefler,⁶ and Wolf⁷ established that similar patterns could be obtained from many different molecules, not

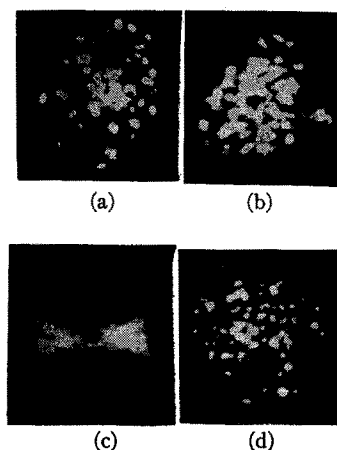


FIG. 1. Field emission microscope patterns observed with the same emitter (a) after normal baking for 15 hr; (b) after baking for 15 hr with the diffusion pump cold for 3 hr; (c) after baking for 3 hr with a liquid nitrogen trap between the oven and pumps to exclude oil vapor; (d) as in (c) but in the presence of toluene vapor.