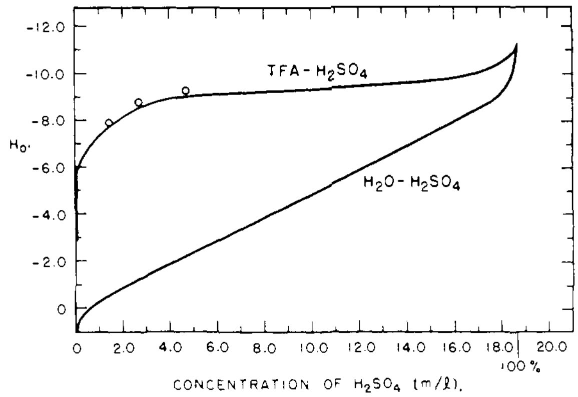

Fig. 1.—The $H_0$ function for sulfuric acid solutions in water and trifluoroacetic acid. O, D and K points from ref. 4, see text.

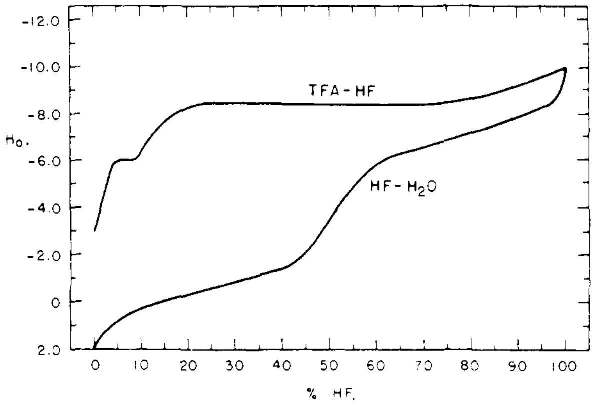

Fig. 2.—The $H_0$ function for hydrogen fluoride solutions in water and trifluoroacetic acid.

the 2,4-dichloro-6-nitroaniline indicator which has been reported by Kilpatrick and Hyman[3] and reconfirmed in this study. The values of $H_0$, the function for some sulfuric–trifluoroacetic acid mixtures suggested by Kilpatrick and Hyman using hexamethylbenzene as an indicator, are also in poor agreement with the values shown in Fig. 1.

Similar lack of agreement between indicators has been noted by other workers, especially, Bates and Schwarzenbach,[8] and Paul and Long[7] have discussed this to some extent. In the case of the hexamethylbenzene, it is perhaps not unreasonable to observe that the rearrangement needed in order to place a proton on the organic molecule makes this reaction somewhat different from the addition of a proton to the nitrogen in an amine group. Great care must be exercised in extrapolating pure proton transfer measurements given by $H_0$ values using Hammett indicators to problems where the important reaction is not entirely proton transfer.

The hydrogen fluoride–trifluoroacetic acid system also shows no surprises if compared with the hydrogen fluoride–water system. Since these solutions were prepared by weight, the data in Table II and Fig. 2 are given on a weight per cent. basis. The rise in acid strength with the first addition of HF is somewhat steeper than in the water case. This may be associated with the lower dielectric constant of the trifluoroacetic acid and, therefore, the greater increase in such constant on the addition of HF.

**Acknowledgments.**—Much of the special equipment has been fabricated by J. R. Pickhardt. The authors would like to acknowledge gratefully the continued interest in this program of Drs. M. Kilpatrick and J. J. Katz and the stimulating discussions resulting.

LEMONT, ILLINOIS

(8) R. S. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **38**, 699 (1955).

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE UNIVERSITY]

# Paramagnetic Resonance Spectra of Adsorbed Manganese(II), Copper(II) and Oxovanadium(IV)[1]

BY ROGER J. FABER[2] AND MAX T. ROGERS

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Paramagnetic resonance spectra were obtained for Mn(II), Cu(II) and oxovanadium(IV) adsorbed on cation- and anion-exchange resins, activated charcoal, zeolite and silica gel. Essentially ionic bonding was found for the Mn(II) samples except when adsorbed on an anion exchanger, where a large amount of covalent bonding was indicated. The electrostatic field symmetry was largely cubic with a small component of lower symmetry. The spectrum of Cu(II) was sensitive to the nature of the active group in the adsorbent, and values of $g_{||}$, $g_{\perp}$ and $A$ were measured for most adsorbents. Increasing covalent character is to be expected in bonds between adsorbent and adsorbed ion in going from sulfonic acid-type exchangers through carboxylic acid-type to the amine-type; $g$-values, hyperfine structure intervals and line widths all changed in a manner consistent with this hypothesis. Values of $g_{||}$, $g_{\perp}$, $A$ and $B$ were obtained for oxovanadium(IV); $g$-values were nearly isotropic and close to the free electron value. The hyperfine structure was very anisotropic and the intervals decreased in going from sulfonic acid-type to amine-type adsorbents; this behavior is consistent with the theoretical prediction that the intervals should decrease with increase in covalent bonding.

## Introduction

The large amount of data on the paramagnetic resonance spectra of transition metal ions in crystals of known structure makes it possible to draw conclusions concerning the bonding and the environment of transition ions in unknown surroundings on the basis of their paramagnetic resonance spectra.

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[1] Taken from a thesis submitted by Roger J. Faber to the School of Advanced Graduate Studies of Michigan State University in partial fulfillment of the requirements for the Ph.D. degree. Presented in part before the Physical and Inorganic Division of the 139th National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

[2] Union Carbide Corp. Fellow for 1956–1957.

Abragam and Pryce[3] have accounted for the $g$-factors and hyperfine structure intervals when essentially ionic bonding occurs between the paramagnetic ion and its neighbors. Stevens and Owen[4] have proposed a theory for the case of covalent bonding. By extending the theory of Abragam and Pryce, Van Wieringen[5] found a direct relationship between the magnitude of the hyperfine structure interval in Mn(II) and the percentage ionic character in the bonds between this ion and its neighbors. McGarvey[6] applied the covalent bonding theory of Stevens and Owen to the case of tetragonal symmetry in Cu(II) chelates.

Because the characteristic parameters of the paramagnetic resonance spectra depend upon the nature of the electron distribution and upon the local electrostatic field symmetry about the paramagnetic ion, the spectra of transition ions adsorbed on various adsorbents should shed some light on the questions of the nature of the bonding between adsorbate and adsorbent and on the local environment of the adsorbate.

## Experimental

**The Spectrometer.**—The paramagnetic resonance spectrometer employed in this research was of conventional design, employing a transmission cavity which resonated at 9,240 mc. The microwave power was generated by a type 2K25 reflex klystron and detected by a type 1N23E silicon diode crystal. The electromagnet was constructed in this Laboratory and was capable of variation between zero and 10,000 gauss. A voltage-regulated power supply and selenium rectifier network supplied the uniform direct current for the magnet. The magnetic field was modulated at 100 c.p.s. by means of an audio amplifier which supplied current to a pair of coils mounted coaxially on the poles of the magnet.

Spectra were obtained by slowly varying the magnetic field at a constant rate and plotting the first derivative of the absorption signal on a recording potentiometer. The spectra were calibrated with respect to field strength by means of a proton resonance spectrometer and a 1,000 c.p.s. crystal oscillator. Whenever the proton resonance frequency became equal to an harmonic of the crystal oscillator, a pip was placed on the recorder trace. This procedure resulted in field markers at 235-gauss intervals along the spectrum. The actual field strengths to which these markers corresponded were determined by calibrating the resonance frequency of the sample cavity by means of a small crystal of diphenylpicrylhydrazyl mounted at the sample position.

**Preparation of the Samples.**—The adsorbent materials were dried at 110° for 4 hr., and approximately 3-gram samples were weighed accurately into separate flasks. Various known quantities of standardized tenth molar solutions of the paramagnetic salts were added, and the flasks were stoppered. The solutions were allowed to equilibrate with the adsorbents at room temperature with occasional shakings of the flasks. The adsorbent was then removed on a paper filter and washed several times with distilled water. The filtrate and washings were collected and analyzed for the cation they contained. The quantity of paramagnetic cation adsorbed was calculated as the difference between the amount present in the filtrate and the amount added originally. The adsorbents used in these experiments were: the sulfonic acid-type cation exchangers Dowex-50 and Amberlite IR-100; Amberlite IRC-50H, a carboxylic acid-type cation exchanger; powdered commercial zeolite; activated sugar charcoal (activated in air at 400°); silica gel, Davison Chemical Co., 60–200 mesh, and Amberlite IR-4B, an amine-type anion exchanger. The paramagnetic ions investigated were Mn(II), Cu(II) and oxovanadium(IV).

**Analysis.**—Manganese was determined by potentiometric titration with permanganate as described by Lingane and Karplus.[7] Copper was determined by the iodometric method.[8] The determination of vanadium by permanganate titration was not very precise, probably because of interference from organic material leached out of the resins. Because the line width of the oxovanadium(IV) spectrum was constant throughout the range of concentrations produced in these experiments, however, no attempt was made to overcome this analytical difficulty.

## Interpretation of Spectra and Experimental Results

**Manganese.**—In electrostatic fields of cubic symmetry the Mn(II) spectrum shows a nuclear hyperfine structure of six lines. In fields of lower symmetry a fine structure appears: each of the six lines is split into five because of the sixfold orbital degeneracy associated with the total spin angular momentum quantum number $S = 5/2$. Van Wieringen[5] has shown that in cubic fields the hyperfine structure interval, in gauss, is approximately numerically equal to the percentage ionic character in the bonds between the ion and its neighbors.

Figure 1 shows a series of spectra obtained from samples of Dowex-50 containing amounts of Mn(II) varying from 0.367 to 0.010 mmole/g. As the concentration decreases the decreasing line width produces better resolution of the hyperfine structure pattern. In the more dilute samples a partial resolution of a slight fine structure is also evident. Similar spectra were obtained with Mn(II) adsorbed on the other cation exchangers, although the spectra obtained from Mn(II) adsorbed on zeolite showed only very slight resolution of the hyperfine structure pattern even in the most dilute samples. Ignoring the fine structure, all the spectra obtained from Mn(II) on the cation exchangers Dowex-50, Amberlite IR-100, zeolite, charcoal and silica gel conformed to the equation

$$H(m) = h\nu/g\beta - A'm - [I(I + 1) - m^2]g\beta A'^2/2h\nu \quad (1)$$

Here $H(m)$ is the field position of the hyperfine structure line corresponding to a given value $m$ of the nuclear spin quantum number, $\nu$ is the frequency of the microwave radiation and $I$ is the total nuclear spin. The experimental values of $g$, the magnetogyric ratio, and $A'$, the hyperfine structure interval, were 2.00 and 96 ± 3 gauss, respectively, for all the samples investigated. Owing to the smearing of the fine structure pattern in powder samples, it was not possible to measure the value of the fine structure interaction constant $D$.

A sample containing 0.031 g. of Mn(II) per gram of Amberlite IR-100 and showing a strong, well-resolved hyperfine structure pattern was dehydrated at 175° for 18 hr. At the end of this time the free radical resonance normally present in the resin was greatly enhanced, probably because of partial charring of the resin, and the Mn(II) resonance pattern was greatly weakened. Exposure of the dehydrated sample of the air resulted in the restoration of the original Mn(II) spectrum but with no diminution of the free radical resonance.

The spectra obtained from samples containing Mn(II) adsorbed on the anion exchanger, Amberlite IR-4B, consisted of a single, unresolved, broad band. The separation between the positive and negative extremes of the derivative plot varied from 236 gauss in the most concentrated sample (0.387 mmole/g.) to 277 gauss in the least concentrated sample (0.014 mmole/g.). The lack of resolution of the hyperfine structure may be attributed to smearing by an anisotropic fine structure, but the narrowness of the resulting single band indicates a reduced hyperfine structure interval. $A'$ probably lies between 50 and 60 gauss.

**Copper.**—Spectra were obtained from samples containing varying amounts of Cu(II) adsorbed on Dowex-50, Amberlite IR-100, Amberlite IRC-50H, charcoal, zeolite and Amberlite IR-4B. All of the spectra conformed to the equation derived by Sands[9] for Cu(II) with random orientation of tetragonal symmetry axes, based upon the usual Hamiltonian expression

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[3] A. Abragam and M. H. L. Pryce, *Proc Roy. Soc.* (*London*), **A206**, 164 (1951).

[4] (a) K. W. H. Stevens, *ibid.*, **A219**, 542 (1953); (b) J. Owen, *ibid.*, **A227**, 183 (1955); (c) *Disc. Faraday Soc.*, **19**, 127 (1955).

[5] J. S. Van Wieringen, *ibid.*, **19**, 118 (1955).

[6] B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

[7] J. J. Lingane and R. Karplus, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 191 (1946).

[8] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1948, pp 247-249.

[9] R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

$$
\begin{aligned}
H = \beta[g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + D[S_z^2 - {} \\
1/3\, S(S+1)] + AS_zI_z + B(S_xI_x + S_yI_y) + {} \\
Q[I_z^2 - 1/3\, I(I+1)] - \gamma\beta_N \mathbf{H}\cdot\mathbf{I} \quad (2)
\end{aligned}
$$

In the presence of nuclear hyperfine structure the equation of Sands predicts four extremes in the derivative plot centered at $g_{\perp}$ and four others centered at $g_{\|}$. The separation $A'$ of the extremes centered at $g_{\|}$ and the separation $B'$ of the peaks centered at $g_{\perp}$ are related to the absolute values of the hyperfine structure interaction constants, $A$ and $B$, of equation 2 by the equations

$$A' = [A]/g_{\|}\beta \qquad (3)$$

$$B' = [B]/g_{\perp}\beta \qquad (4)$$

Figure 2 shows a typical series of spectra obtained from Cu(II) adsorbed on Dowex-50 for various concentrations of Cu(II). The four peaks centered at $g_{\|}$ on the left-hand side of the spectrum are visible only at the higher concentrations where the signal strength is adequate. Even the reduced line width at the lowest concentration is insufficient to resolve the four peaks centered at $g_{\perp}$ (on the right-hand side of the spectrum). Spectra with the same general characteristics were obtained with Cu(II) adsorbed on Amberlite IR-100, charcoal, zeolite and Amberlite IR-4B. Concentrations achieved with Cu(II) adsorbed on Amberlite IRC-50H were not great enough to permit the observation of the peaks at $g_{\|}$; hence only $g_{\perp}$ was measured for this adsorbent. Spectra of an ammoniated Cu(II) complex adsorbed on Amberlite IR-100, Dowex-50, charcoal[10] and zeolite were also obtained. These ammoniated samples were prepared from the hydrated samples mentioned above by thoroughly moistening them with a 4 $M$ ammonium hydroxide solution and then drying them at 110° in a stream of ammonia gas. Cu(II) was also adsorbed by Amberlite IR-4B from solutions of the tetrammine cation, and tetrabromo-, tetrachloro- and tetratartrato copper(II) anions. These spectra had the same general features as those in Fig. 2.

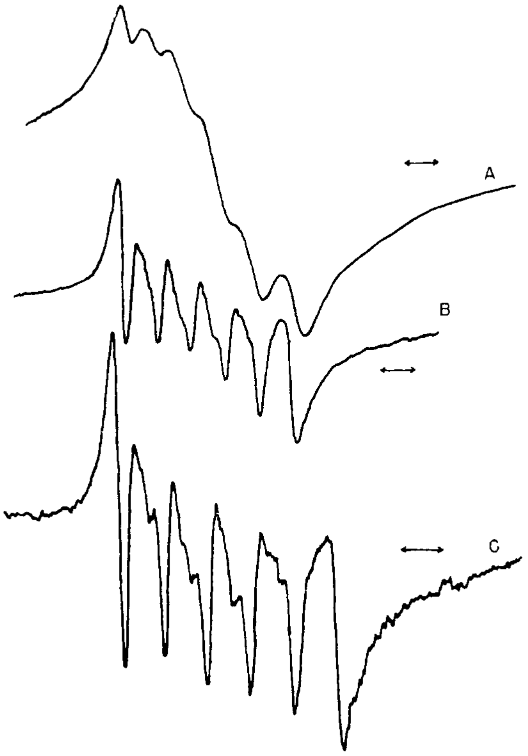

Fig. 1.—Spectra of Mn(II) adsorbed on Dowex-50. The concentration of Mn(II) is: (A) 0.367 mmole/g., (B) 0.061 mmole/g.; (C) 0.023 mmole/g. The arrows in these and the following spectra represent a displacement of 100 gauss along the $x$-axis.

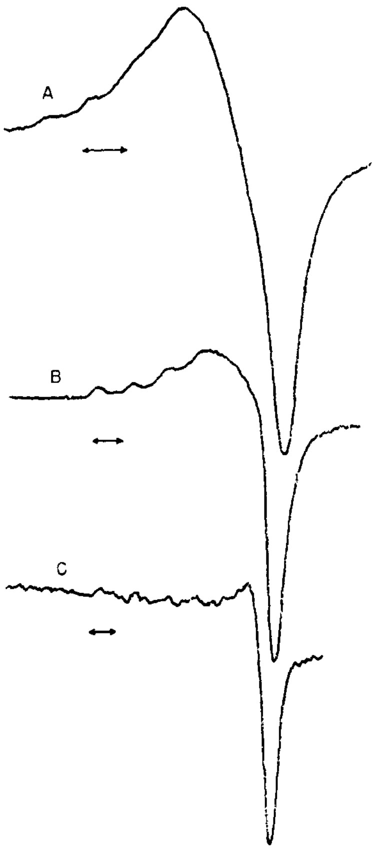

Fig. 2.—Spectra of Cu(II) adsorbed on Dowex-50. The concentration of Cu(II) is: (A) 0.474 mmole/g.; (B) 0.174 mmole/g.; (C) 0.031 mmole/g.

Table I contains the measured values of the field positions of the four peaks centered at $g_{\|}$ (designated by $H(3/2)$, $H(1/2)$, $H(-1/2)$, $H(-3/2)$, respectively) and also the extrapolated mean field position of the peaks centered at $g_{\perp}$, designated by $H_{\perp}$. The apparent field position $H_{\perp}$ varied as the concentration decreased, because of the decreasing contribution of dipolar broadening to the line width. In an attempt to minimize the disturbing effect of finite line width on the measured value of $g_{\perp}$, $H_{\perp}$ was plotted as a function of concentration in Fig. 3 and extrapolation was made to zero concentration.

TABLE I

LINE POSITIONS IN COPPER(II) SPECTRA (IN GAUSS)

| Adsorbent | $\overline{H}_{\perp}$ | $H(3/2)$ | $H(1/2)$ | $H(-1/2)$ | $H(-3/2)$ |
|---|---|---|---|---|---|
| | | Hydrated samples | | | |
| IR-100 | 3147 | 2592 | 2704 | 2808 | .. |
| Dowex-50 | 3147 | 2583 | 2692 | 2818 | .. |
| Zeolite | 3168 | 2606 | 2735 | .. | .. |
| Charcoal | 3162 | 2614 | 2796 | 2928 | 3053 |
| IRC-50H | 3169 | .. | .. | .. | .. |
| IR-4B | 3170 | 2748 | 2923 | 3102 | 3278 |
| | | Ammoniated samples | | | |
| IR-100 | 3188 | 2712 | 2891 | 3082 | 3268 |
| Dowex-50 | 3188 | 2711 | 2878 | 3055 | .. |
| Zeolite | 3188 | 2701 | 2877 | 3050 | .. |
| Charcoal | 3188 | 2702 | 2863 | 3053 | .. |

This extrapolated value, $\overline{H}_{\perp}$, was used to calculate $g_{\perp}$ for the hydrated Cu(II) samples and to provide a first approximation to $g_{\perp}$ for the ammoniated samples. The zero slope

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[10] It was necessary to subtract the absorption due to the free radicals present in the charcoal from the total absorption in this sample in order to obtain the absorption line shape of the Cu(II) resonance, since these two overlapping resonances were approximately equal in magnitude.

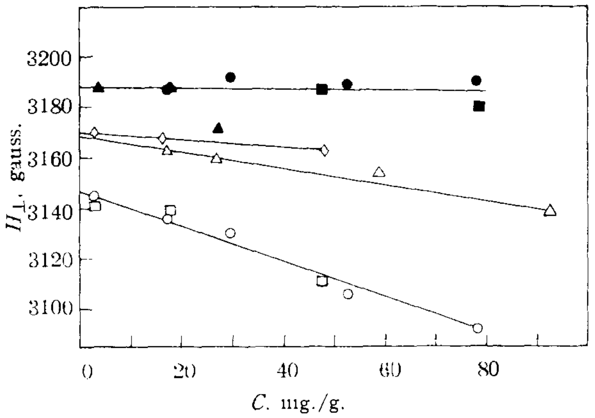

Fig. 3.—Relationship between $H_\perp$ and concentration for the Cu(II) spectra. Amberlite IR-100 hydrated ○, and ammoniated ●; Dowex-50 hydrated □, and ammoniated ■; zeolite hydrated △, and ammoniated ▲; and Amberlite IR-4B ◇.

of the lines for the ammoniated samples is probably due to a secondary effect, as described in the Discussion section which follows. Consequently, an estimated value of $g_\perp$ = 2.055 is probably more nearly correct for these samples. From the positions, $H_{||}(m)$, of the peaks centered at $g_{||}$, it was possible to calculate $g_{||}$ and the nuclear hyperfine structure interval $A'$, by the relationship found by Sands[9]

$$H_{||}(m) = \bar{H}_{||} - mA' \quad (5)$$

where

$$\bar{H}_{||} = h\nu/\beta g_{||} \quad (6)$$

The $g$-values and hyperfine structure constants obtained in this manner are collected in Table II.

TABLE II

COMPUTED PARAMETERS FOR COPPER(II) SPECTRA

| Adsorbent | $g_\perp$ | $g_{\|}$ | $A'$, gauss | $A$, cm.$^{-1}$ |
|---|---|---|---|---|
| | Hydrated samples | | | |
| IR-100 | 2.096 | 2.39 | 110 | 0.0122 |
| Dowex-50 | 2.099 | 2.40 | 115 | .0128 |
| Zeolite | 2.083 | 2.35 | 130 | .0142 |
| Charcoal | 2.086 | 2.32 | 140 | .0152 |
| IRC-50H | 2.080 | .. | .. | .... |
| IR-4B | 2.079 | 2.19 | 180 | .0184 |
| | Ammoniated samples | | | |
| IR-100 | 2.068 | 2.21 | 188 | 0.0194 |
| Dowex-50 | 2.078 | 2.22 | 172 | .0178 |
| Zeolite | 2.072 | 2.22 | 175 | .0182 |
| Charcoal | 2.07 | 2.22 | 177 | .0184 |
| IRC-50H | Not stable | | | |
| IR-4B | 2.079 | 2.19 | 180 | .0184 |

**Vanadium.**—Spectra were obtained from samples of oxovanadium(IV) adsorbed on Dowex-50, Amberlites IR-100 and IR-4B and activated charcoal. The spectra in Figs. 4 and 5 consisted of thirteen to fourteen lines, the eight strongest forming a group with an interval of about 70–80 gauss. The other, weaker lines were part of another group of eight, partially obscured by the first group and with a much larger hyperfine structure interval.

Since the unpaired electron in the oxovanadium(IV) complex experiences a strong, axially symmetrical field due to the presence of the oxygen, the Hamiltonian expression is the same as for Cu(II) in tetragonal symmetry, and the equation of Sands for random orientation of the symmetry axes may be extended to this case. The values for the $g$-factors and hyperfine structure intervals, computed in the same manner as for the Cu(II) spectra, are collected in Table III.

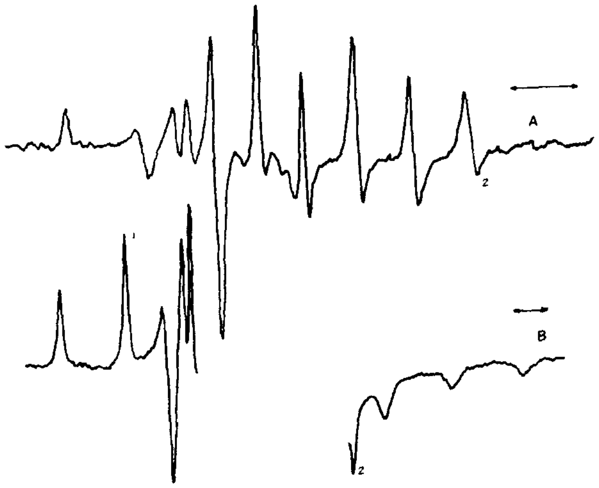

Fig. 4.—Spectra of oxovanadium(IV) adsorbed on Dowex-50. Curve A shows the intense central part of the spectrum; curve B shows the weak outer portion. The vertical scale in B has been enlarged and the horizontal scale reduced with respect to curve A, and most of the central portion has been omitted. The numbers 1 and 2 show relative positions of identical peaks in the two curves.

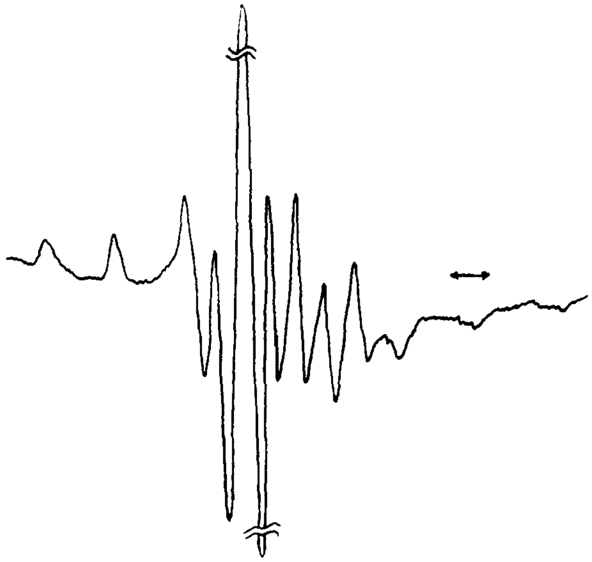

Fig. 5.—The spectrum of oxovanadium(IV) adsorbed on Amberlite IR-4B.

## Discussion of Results

**Manganese.**—The observed value of 96 gauss for the hyperfine structure interval of all samples containing Mn(II) adsorbed by cation exchangers is the same, within experimental error, as the values found for Mn(II) in ionic crystals and in aqueous solution.[5,11–13] When adsorption occurs, probably at most one of the six water molecules coördinated to the aqueous ion is replaced by a bond to the adsorbent. The hyperfine structure interval is evidently not very sensitive to small changes in the amount of covalent character of only one of these bonds.

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(11) J. E. Guessie and D. Williams, *Phys. Rev.*, **99**, 612 (1955).

(12) M. Tinkham, R. Weinstein and A. F. Kip, *ibid.*, **84**, 848 (1951).

(13) B. M. Kozyrev, *Disc. Faraday Soc.*, **19**, 135 (1955).

TABLE III

COMPUTED PARAMETERS FOR OXOVANADIUM(IV) SPECTRA

| Adsorbent | $g\perp$ | $g\|$ | $B'$, gauss | $B$, cm.$^{-1}$ | $A'$, gauss | $A$, cm.$^{-1}$ |
|---|---|---|---|---|---|---|
| IR-100 | 1.983 | 1.93 | 81 | 0.00750 | 200 | 0.0180 |
| Dowex-50 | 1.979 | 1.88 | 80 | .00740 | 210 | .0184 |
| Charcoal | 1.983 | .. | 76 | .00704 | 190 | ... |
| IR-4B | 1.989 | 1.93 | 66 | .00612 | 175 | .0158 |

The effect of adsorption upon the electrostatic field symmetry, however, is quite apparent in the spectra obtained from the cation exchangers. The presence of a weak fine structure in the spectra of Mn(II) on cation exchangers indicates a small departure from cubic symmetry produced by the presence of the negatively charged active group of the adsorbent. The symmetry thus produced is probably tetragonal. The contribution of the remaining water of hydration to the predominantly cubic local field symmetry is shown by the results of dehydrating the sample of Mn(II) on Amberlite IR-100. Removal of some or all of the coördinated water molecules resulted in a decrease of resolution which indicates an increased departure from cubic symmetry. This procedure was reversible, however, for the complete spectrum was restored simply by allowing the sample to recover water of hydration from the atmosphere.

The Mn(II) spectra obtained from powdered zeolite showed only a hint of resolution into six components. This lack of resolution even in dilute samples indicates a local electrostatic field of lower symmetry than was present in the other cation exchangers.

Because of the low concentration in the most dilute sample containing Mn(II) on Amberlite IR-4B, it seems unlikely that either spin-lattice or exchange interactions would be appreciable. Consequently, the narrow width of 277 gauss in this sample probably results from a hyperfine structure interval of about 50 or 60 gauss. This approximate value for $A'$ indicates, following the proposal of Van Wieringen,[5] about 40 or 50% covalent bonding between the Mn(II) and the resin. That the effect of covalent bonding between the ion and the resin should be observed in these spectra seems reasonable when one considers the results of Nachod[14] with Cu(II) adsorbed on an anion-exchange resin. He postulates the formation of bonds between the ion and two or more nitrogen atoms which are part of the active groups of the resin. If the adsorbed Mn(II) is in a similar environment, the bonds to the resin might have a high degree of covalent character and their influence on the spectrum might be considerable.

**Copper.**—From the Cu(II) spectra it was possible to obtain values for the spectral parameters $g_{\|}$, $g_{\perp}$ and $|A|$ of equation 2. The line width in all the samples was too great to allow the determination of $|B|$.

The various Cu(II) samples may be classified into four groups on the basis of the measured parameters as follows.

(1) The Amberlite IR-100 and the Dowex-50 samples possessed the highest $g$-factors and the smallest hyperfine structure intervals of all the samples. The active group in both adsorbents is a sulfonic acid. Since this is a strong acid, the bond between the Cu(II) and the adsorbents is probably largely ionic.

(2) Somewhat smaller $g$-factors and larger hyperfine structure intervals were shown by the charcoal, zeolite and Amberlite IRC-50H samples. Only $g_{\perp}$ was measurable for the latter. The active group in this resin is a carboxylic acid; in the zeolite it is a silicate group; in the charcoal the active group is probably similar to a carboxylic acid.

(3) Still smaller $g$-factors and larger hyperfine structure intervals were found in the spectra from the samples containing ammoniated Cu(II). No differences between the various adsorbents were evident.

(4) All the samples involving Amberlite IR-4B as the adsorbent had identical $g$-factors and hyperfine structure intervals within the limits of experimental error. The value of $g_{\|}$ obtained from these spectra was the same as that obtained from the spectra of group 3 (above), but $g_{\perp}$ was larger.

On the basis of this classification a few generalizations may be made. The progression of the $g$-values follows the molecular orbital theory prediction[2-4] that covalent bonding should reduce the magnitude of the $g$-factor. In the hydrated samples the spectrum is sensitive to changes in covalent character of the bond between the ion and the adsorbent. In the ammoniated samples this effect is not evident, partly because the greater line width in these samples leads to more uncertainty in the measured quantities.

The molecular orbital theory also predicts that because the unpaired electron is shared with the ligands, a decrease in hyperfine structure interaction with the central nucleus should occur with increasing covalent bonding. Since no change in electron configuration is required by this theory of covalent bonding, the configurational interaction postulate of Abragam and Pyrce[3] is applicable. According to this postulate, the hyperfine interaction constants $A$ and $B$ are given by the equations

$$A = [(g_{\|} - 2) + 3/7\,(g_{\perp} - 2) - 4/7 - \kappa]P \quad (7)$$

$$B = [(g_{\perp} - 2) - 3/14\,(g_{\perp} - 2) + 2/7 - \kappa]P \quad (8)$$

In these equations the term $\kappa$ represents an isotropic contribution to the hyperfine structure. This contribution arises from s orbitals and is proportional to the unpaired electron density at the copper nucleus. Calculation of $\kappa$ for the various samples produced the results collected in Table IV. In the calculations the constant $P$ was assigned a value of 0.032 cm.$^{-1}$, which is an average computed from published results for the spectrum of cupric ion in various crystals, and the sign of $A$ was taken to be negative.

The values for $\kappa$ in Table IV may be compared with the values 0.25 computed by Abragam and Pryce for the copper(II) Tutton salts,[3] and 0.26 calculated by Sands[9] for cupric ions in glass. The results of Ingram and Bennett for copper(II) phthalocyanine[15] lead to a value for $\kappa$ of 0.23. The

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[14] F. C. Nachod (ed.), "Ion Exchange: Theory and Application," Academic Press, Inc., New York, N. Y., 1949, p. 214.

[15] D. J. E. Ingram and J. E. Bennett, *Disc. Faraday Soc.*, **19**, 140 (1955).

TABLE IV

HYPERFINE STRUCTURE CONSTANTS AND CONFIGURATIONAL INTERACTION CONSTANTS FOR THE COPPER(II) SAMPLES

| Adsorbent | $A$, cm.$^{-1}$ | $\kappa$ |
|---|---|---|
| | Hydrated samples | |
| IR-100 | −0.0122 | 0.24 |
| Dowex-50 | .0128 | .27 |
| Zeolite | .0142 | .26 |
| Charcoal | .0152 | .26 |
| IR-4B | .0184 | .23 |
| | Ammoniated samples | |
| IR-100 | 0.0194 | 0.27 |
| Dowex-50 | .0178 | .23 |
| Zeolite | .0182 | .25 |
| Charcoal | .0184 | .24 |
| IR-4B | .0184 | .23 |

hyperfine structure interval of copper(II) acetylacetonate in dioxane[6] indicates a value for $\kappa$ of 0.22.

A slight indication of a trend is discernible in these results. In compounds in which the cupric ion is predominantly surrounded by water dipoles, $\kappa$ is found in the range 0.25 to 0.27, whereas in the more covalent complexes, $\kappa$ is found in the range 0.22 to 0.25. Specifically with regard to the results with the cation exchangers, $\kappa$ is lower in the ammoniated samples than in the corresponding hydrated samples, except for the samples involving Amberlite IR-100. Because these small differences are about of the same magnitude as the uncertainty in $\kappa$, these observations merely suggest that differences in covalent bonding are reflected by differences in the magnitude of $\kappa$. More precise $g$-values, such as might be obtained at lower temperature, might be required to establish this surmise.

The covalent bonding theory of Stevens and Owen cannot be applied quantitatively to the results of this investigation without approximate values for the orbital energy level separations, $\Delta_3$ and $\Delta_4$, which are responsible for the visible absorption spectrum of Cu(II). The theory states that for the case where both $\sigma$ and $\pi$ bonding occur

$$g_{||} = 2.00 - a^2b^2 8\lambda'/\Delta_3 \tag{9}$$

$$g_{\perp} = 2.00 - a^2(1 + b^2)\,\lambda'/\Delta_4 \tag{10}$$

In these equations, the parameters $a^2$ and $b^2$ both lie between zero and one. When no covalent $\sigma$ bonding occurs, $a^2 = 1$; when no covalent $\pi$ bonding occurs, $b^2 = 1$. For the purpose of testing the predictions of the molecular orbital theory, the quantities $\Delta_3$ and $\Delta_4$ for hydrated and for ammoniated Cu(II) on zeolite may be approximated by 12,000 and 14,000 cm.$^{-1}$, respectively, for the hydrated ion and 13,000 and 15,000 cm.$^{-1}$, respectively, for the ammoniated samples, as indicated by optical reflectance spectra. Using these approximations and assigning $\lambda'$ a value of −825 cm.$^{-1}$, one obtains $a^2 = 0.74$, $b^2 = 0.84$ for the hydrated samples, and $a^2 = 0.57$, $b^2 = 0.74$ for the ammoniated samples.

Because of the numerous approximations involved in the calculations, these results are not quantitatively significant. Qualitatively however, the results are quite reasonable, for they state that covalent bonding does indeed occur appreciably in the ammoniated complex and that the contribution of covalent $\sigma$-bonding is more important than that of covalent $\pi$-bonding.

Another indication of the presence of covalent bonding is a hyperfine structure due to interaction with nuclei in the ligands. A large interaction of this sort in a chloro derivative of tetraphenylporphyrin was found by Ingram, *et al.*[16] Ingram and Bennett[15] have proposed that an unresolved hyperfine structure interaction with nitrogen nuclei may account for the line width in copper(II) phthalocyanine. If such an interaction is present, they suggest, a constant line width with increasing dilution should be observed. The plots of $H_\perp$ *versus* concentration for the various Cu(II) samples in Fig. 3 are similar to plots of line width *versus* concentration, since the difference between $H_\perp$ and $\bar{H}_\perp$ is proportional to the line width. It will be noted that the slopes of these plots for the ammoniated samples and for the samples involving Amberlite IR-4B are virtually zero, whereas a considerable change in $H_\perp$ with concentration was observed for the hydrated samples. Hence, it seems probable that an unresolved hyperfine structure is responsible for the greater line widths observed in the ammoniated Cu(II) spectra and the spectra obtained from the IR-4B samples. This hyperfine structure would be produced by covalent bonding between the Cu(II) and the surrounding nitrogen nuclei.

No hyperfine structure was observed centered upon the upper end, $H_\perp$, of the Cu(II) powder spectra. Consequently, no measurement of the quantity $B'$ in equation 4 could be made. In the hydrated samples, where the line width at maximum dilution is presumably due to spin-lattice interaction, the lack of resolution indicates that $B'$ is less than one-third of the observed line width. Since these are powder spectra, no true value for the line width can be obtained. Instead, the separation between the points of maximum positive and negative slope about $H_\perp$ in the spectrum of Cu(II) on Dowex-50 must be taken. This approximation gives a line width of 75 gauss. Consequently, $B'$ is less than 25 gauss, and $B$ is less than 0.0026 cm.$^{-1}$. This result is comparable to Sands'[9] observed value of 0.0024 cm.$^{-1}$. Calculation of $B$ by means of equation 8 leads to the result $B = 0.0030$ cm.$^{-1}$, in fairly good agreement with the approximate upper limit set by the line width.

The situation is somewhat more complicated in the samples of Cu(II) on IR-4B and in the ammoniated Cu(II) samples, since the line width may be due to unresolved hyperfine structure involving interaction with nitrogen nuclei. A calculation using equation 8 and based on the average observed $g$-factors and hyperfine structure intervals leads to $B = 0.0032$ cm.$^{-1}$ for the IR-4B, and $B = 0.0019$ cm.$^{-1}$ for the ammoniated samples. These quantities are both too small to account for the considerably greater width of the line centered at $H_\perp$ in these samples. This fact also suggests that an unresolved hyperfine structure is the principal contribution to the line width.

Sussman and Nachod[14] reported preliminary and somewhat inconclusive results on the adsorption of Cu(II) by an anion-exchange resin. Cu(II) was

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(16) D. J. E. Ingram, J. E. Bennett, P. George and J. M. Goldstein, THIS JOURNAL, **78**, 3545 (1956).

removed from a copper(II) sulfate solution upon passage through a bed of a salt of an anion-exchange resin and also was removed from ammoniacal copper(II) sulfate solution upon passage through a bed of alkali-regenerated anion-exchange resin. The suggested over-all stoichiometry is

$$Cu^{++} + 2(RNH)Cl = (Cu(RN)_2)Cl_2 + 2H^+ \quad (11)$$

for the first reaction, and

$$Cu(NH_3)_4{}^{++} + 4RN = (Cu(RN)_4)^{++} + 4NH_3 \quad (12)$$

for the second reaction. In these equations, RN represents the alkali-regenerated anion exchanger base. These authors claimed to have found experimental evidence for the diamine in equation 11 but were uncertain whether the tetrammine or diammine was found in the reaction represented by equation 12.

The paramagnetic resonance absorption spectra of the IR-4B samples prepared from copper(II) sulfate solution and from ammoniacal copper(II) sulfate solution were indistinguishable. Hence, it seems probable that the Cu(II) complexes formed in the two reactions represented by equations 11 and 12 are the same. Furthermore, since the observed spectra indicate tetragonal symmetry, with $g$-factors and hyperfine structure constants very nearly equal to those of the ammoniated Cu(II) spectra on cation exchangers, the tetrammine structure of equation 12 seems to be a more probable product in both reactions.

The spectra of the samples prepared from the tetrachloro- and tetrabromocuprate(II) anions and Amberlite IR-4B are also indistinguishable from the spectrum of Cu(II) on IR-4B. The copper was probably adsorbed not in the form of a complex anion but rather as the same complex as that formed from aqueous solution of cupric ion. No color change was observed when a solution of tetratartratocuprate(II) anion was placed in contact with the resin, and no Cu(II) spectrum appeared in the subsequently dried sample of resin. Apparently the tartrate complex was too stable to release free Cu(II) ions to the resin.

Kozyrev[13] reported that the spectrum of Cu(II) in supercooled organic solvents at 90°K. consisted of an "exchange peak" at $g = 2.091$ and also four hyperfine-structure peaks separated by an interval of 130 gauss and centered at $s = 2.369$. It now seems probable that this spectrum was actually a random powder spectrum of the sort observed in this investigation, produced by the reduction of the random molecular motions at low temperature. Interpreted in this manner, Kozyrev's results lead to $g_{\parallel} = 2.369$, $g_{\perp} = 2.091$, and $|A| = 0.0146$ cm.$^{-1}$ which are in good agreement with the values obtained by Sands[9] and those obtained in this investigation.

**Vanadium.**—No theoretical investigation of the paramagnetic resonance absorption of vanadium(IV) has appeared to date. Two analogous systems have been treated, however. Bleaney[17] considered the case of titanium(III), which is isoelectronic with vanadium(IV), in a trigonal field. Polder's[18] treatment of Cu(II) in a tetragonal field considers the electron configuration to be equivalent to a single positive electron in the d orbitals, that is, an electron "hole." Neither of these analogous systems is completely equivalent to the case of vanadium(IV), however, for Bleaney's treatment is based on trigonal symmetry, and Polder's treatment results in an inversion of the orbital energy levels. Both theories predict $g$-values approaching 2.00 when the energy separation between orbital levels becomes very large, that is, when the symmetry of the axial field departs strongly from cubic symmetry. Since the vanadium in the samples used in this investigation was in the form of oxovanadium (IV), the presence of oxygen would produce a strongly non-cubic, axially-symmetrical field. The electrostatic field symmetry accounts, then, both for the proximity of the $g$-factors to the free-spin value, 2.00, and for the very weak spin-lattice interaction as shown by the narrow line width.

All of the spectra of oxovanadium(IV) on various adsorbents conform to the equation developed by Sands[9] for random orientation of symmetry axes. The striking differences in appearance between these spectra and those obtained from the Cu(II) samples arise from the fact that the $g$-values of the oxovanadium(IV) spectra are nearly isotropic; the major contribution to the anisotropy comes from a highly anisotropic hyperfine structure. For a given value of the nuclear magnetic quantum number, $m$, the absorption line shape has sharp boundaries, $B_{\parallel}$ and $B_{\perp}$, which occur at field strengths given by the equations

$$B_{\parallel} = H_{\parallel} - mA'_{\parallel} \quad (13)$$

$$B_{\perp} = H_{\perp} - mA'_{\perp} \quad (14)$$

These sharp boundaries produce the peaks in the first derivative plots of the oxovanadium(IV) spectra. Since the $g$-factor is nearly isotropic, the upper boundary corresponds sometimes to the parallel orientation and sometimes to the perpendicular orientation of the symmetry axis.

For the oxovanadium(IV) spectra the separation, in gauss, between the upper and lower boundaries of the broad absorption line corresponding to a given orientation of the nuclear spin, varies with $m$. The separation is greater for the extreme values of $m$ than for intermediate values and is a minimum for some intermediate value. The apparent intensity or sharpness of the peaks which mark the upper and lower boundaries is dependent upon the separation between the boundaries, being greatest for the lines whose boundaries are closest together.

The spectrum of vanadyl ion on Amberlite IR-4B, Fig. 5, provides a striking example of this effect. One line in this spectrum is much more pronounced than the others; in fact, the maximum and minimum values of the slope lie outside the scope of the figure. This line corresponds to the transition for $m = 1/2$, where the separation between upper and lower boundaries is probably of approximately the same magnitude as the line width.

From the $g$-factors and hyperfine structure constants collected in Table III, a trend similar to the one observed in the Cu(II) samples may be discerned. The $g$-factors remain constant, probably within the limits of experimental error. This fact indicates that the strongly non-cubic electrostatic

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(17) B. Bleaney, *Proc. Phys. Soc.*, **A63**, 407 (1950).

(18) D. Polder, *Physica*, **9**, 709 (1942).

field produced by the oxygen of the oxovanadium(IV) radical overshadows any minor changes in spin-orbit interaction produced by the adsorbent. The hyperfine structure intervals, however, do vary from one adsorbent to another. The interval is largest in the two sulfonic acid-type cation exchangers, slightly smaller on charcoal, and much smaller when bonding to nitrogens on the anion exchanger occurs.

The magnitude of the hyperfine structure interaction (about 0.018 cm.$^{-1}$ for $|A|$) indicates that the promoted s-electron hypothesis of Abragam and Pryce[3] may also be required for oxovanadium(IV). The decrease of the splitting with increase of covalent character in the bonding suggests a shift of the magnetic electron toward the ligand. The molecular orbital theory developed by Stevens and Owen[4] predicts such an effect.

It would also be interesting to know the signs of $A$ and $B$ for oxovanadium(IV) in order to permit comparison with possible theory. Only the absolute values of the hyperfine structure constants are obtained by measuring the splittings, however. Consequently, recourse must be made to indirect arguments. In certain cases, at least, the signs may be inferred from an examination of the variation of the absolute values of $A$ and $B$ as the amount of covalent bonding is varied. For example, inspection of equations 7 and 8 for the hyperfine structure constants of Cu(II) reveals that increase of covalent bonding corresponds to larger values of $\kappa$ and the more negative values of $A$ and $B$. This means that the absolute value of the splitting constant will increase if the sign is negative and decrease if the sign is positive. Table II illustrates the application of this fact to the Cu(II) samples examined in this research. The absolute value of $A$, which according to equation 7 has a negative sign, increased as the amount of covalent bonding increased.

The observation by Pake and Sands[19] of an eight-line spectrum for oxovanadium(IV) in aqueous solution confirms the presence of an isotropic contribution to the hyperfine structure. Further, because of both Cu(II) and V(IV) having $3d^9$ ground states it is reasonable to suppose that $A$ and $B$ for oxovanadium(IV) are given by equations of the same general form as equations 7 and 8 and therefore $A$ and $B$ would both become more negative as the configuration interaction constant $\kappa$ increases.

We have observed that the absolute values of both $A$ and $B$ increase as the covalent bonding increases. Hence, we may conclude that both $A$ and $B$ are negative.

The thirteen line spectrum observed by Kozyrev[13] for oxovanadium(IV) salts in non-aqueous solutions at 90°K. is undoubtedly a random pattern of the sort observed in this investigation. The reduction of molecular motion at the low temperature would produce a random orientation of the symmetry axes such as occurred in the powder spectra reported here. Interpretation of Kozyrev's results in this manner leads to $g_{\parallel} = 1.92$; $g_{\perp} = 1.960$; $A = 0.0178$ cm.$^{-1}$; $B = 0.0070$ cm.$^{-1}$; which are in good agreement with the results of this investigation.

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(19) G. E. Pake and R. H. Sands, *Bull. Amer. Phys. Soc.*, **29**, No. 8, 18 (1954).

EAST LANSING, MICHIGAN

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[CONTRIBUTION FROM THE CATHOLIC UNIVERSITY OF AMERICA]

# Absorption Spectra of Some Active Species[1]

BY FRANCIS OWEN RICE AND RONALD B. INGALLS

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We have measured the absorption spectrum of the blue solid obtained in the thermal decomposition of $HN_3$ as well as those of $S_2$, RS (where R represents various organic radicals and $(NH_2NH)_n$. Films were deposited in a plane aluminized quartz surface kept at liquid nitrogen temperatures and the percentage of absorbed monochromatic light over the range 20,000 to 3000 Å. was measured. The measurements are only semi-quantitative because we were not successful in preventing considerable scattering of the light by the film.

Recent work in this Laboratory has shown that it is possible to decompose various compounds in a flowing system at low pressures and freeze out active species on a liquid nitrogen cooled surface. In this way colored deposits were obtained which are stable indefinitely at liquid nitrogen temperatures, are usually paramagnetic, and always undergo on warming (at temperatures below −100°) a transition to stable colorless compounds. It seemed desirable to obtain the absorption spectra of the colored materials in the visible, near ultraviolet and near infrared. In this paper we shall describe the results of a spectroscopic study of the blue deposit (possibly a polymer of NH) formed by the decomposition of hydrazoic acid,[2] the purple deposit ($S_2$) formed from sulfur vapor,[3] the yellow and red deposits[4] formed by the decomposition of symmetrical organic disulfides (probably RS) and the yellow deposit formed by the thermal decomposition of hydrazine[5] (possibly the hydrazyl radical, $NH_2NH$ or tetrazane, $NH_2NHNHNH_2$).

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(1) This work was supported in part by Contract AT-(40-1)-1305.

(2) F. O. Rice and M. J. Freamo, THIS JOURNAL, **73**, 5529 (1951); **75**, 548 (1953).

(3) F. O. Rice and C. Sparrow, *ibid.*, **75**, 848 (1953).

(4) J. Michaelson, Ph.D. Dissertation, Catholic University of America, 1955.

(5) F. O. Rice and F. Scherber, THIS JOURNAL, **77**, 291 (1955).