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Experimental and Crystal Field Study of the Absorption Spectrum at 2000 to 8000 Å. of Manganous Perchlorate in Aqueous Perchloric Acid[1]

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Visible and near ultraviolet absorption spectra and molar extinction coefficients (molar absorptivities) have been determined at 8 to 55° for water solutions of manganous perchlorate together with perchloric acid at acidities where hydrolysis of the manganous ion is negligible. The absorption spectrum of the manganous species in these solutions is similar in many respects to the spectra reported for water solutions of manganous chloride and manganous sulfate. The spectrum of manganous perchlorate solutions, however, contains several shoulders indicating the presence of several hidden peaks; some of these shoulders suggest the existence of neighboring twin peaks that appear as a single peak under the prevailing conditions. A very low peak has been found in a very deep valley; this peak has been assigned to a doubly forbidden transition. The wave lengths of the principal absorption peaks have been accounted for quantitatively in terms of the crystal field theory. This has been done with single values for the Racah parameters, B and C, and the crystal field parameter, Dq. The values of these parameters have been obtained by means of calculations based on the Tanabe and Sugano matrices of interaction for the energy levels arising from d-electron configurations in a field of cubic symmetry with no additional approximations. The values of B and C obtained in this way are significantly lower than the corresponding values for the free gaseous ion.

Introduction

Visible and near ultraviolet absorption spectra of metallic ions in crystals and in liquid solutions have recently become of especial interest because of the success of the crystal or ligand field theory in explaining the spectra when the ions contain one or more d-electrons.[3] In particular it has been found that the wave lengths of the absorption maxima can be accounted for surprisingly well in terms of the crystal field parameter, Dq, by fitting the energy levels corresponding to the absorption maxima to Orgel diagrams[4] of the energy levels of the ion as a function of Dq. The energy values of the diagrams have been calculated prior to our work by employing values of the Racah parameters[5] B and C which have been obtained from the energy levels of the free gaseous ion for which $Dq = 0$.

In this paper we have fitted the energy levels of the Mn^{+2} ion in aqueous solution to the theory by simultaneously adjusting all three parameters, B, C and Dq. This procedure is meaningful in this case because of the large number of peaks in the absorption spectrum of $Mn^{+2}\cdot aq$ and the corresponding large number of energy levels. Our calculations have been based on the appropriate matrices of interaction set up by Tanabe and Sugano[6] for energy levels arising from d^n configurations in a crystal field of cubic symmetry.

Measurements of the absorption spectrum of Mn^{+2} in aqueous perchloric acid, presumably of the fully hydrated Mn^{+2}, namely, $Mn^{+2}\cdot aq$, are of value also for the determination of the absorption spectra of the different species of the ion in combination with other ligands in water. The fully hydrated ion is, of course, always present in water and corrections for the light absorbed by it are necessarily based on its absorption spectrum and are not always negligible.

The perchlorate ion was chosen for our study because this anion is less likely than other common anions to form complexes with metallic cations in water. Also the perchlorate anion of itself absorbs light to a very small extent between 2000 and 8000 Å.

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(1) This is publication No. 69 of the M.I.T. Solar Energy Conversion Project.

(2) The part of the work performed by G. F. K. was supported in part by the Office of Naval Research.

(3) For a review of crystal field theory and for numerous references pertaining to this theory, see W. Moffit and C. J. Ballhausen, "Annual Review of Physical Chemistry," Vol. VII, 1956.

(4) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004, 1824 (1955).

(5) (a) G. Racah, *Phys. Rev.*, **62**, 438 (1942); (b) **63**, 367 (1942); (c) **76**, 1352 (1949).

(6) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954).

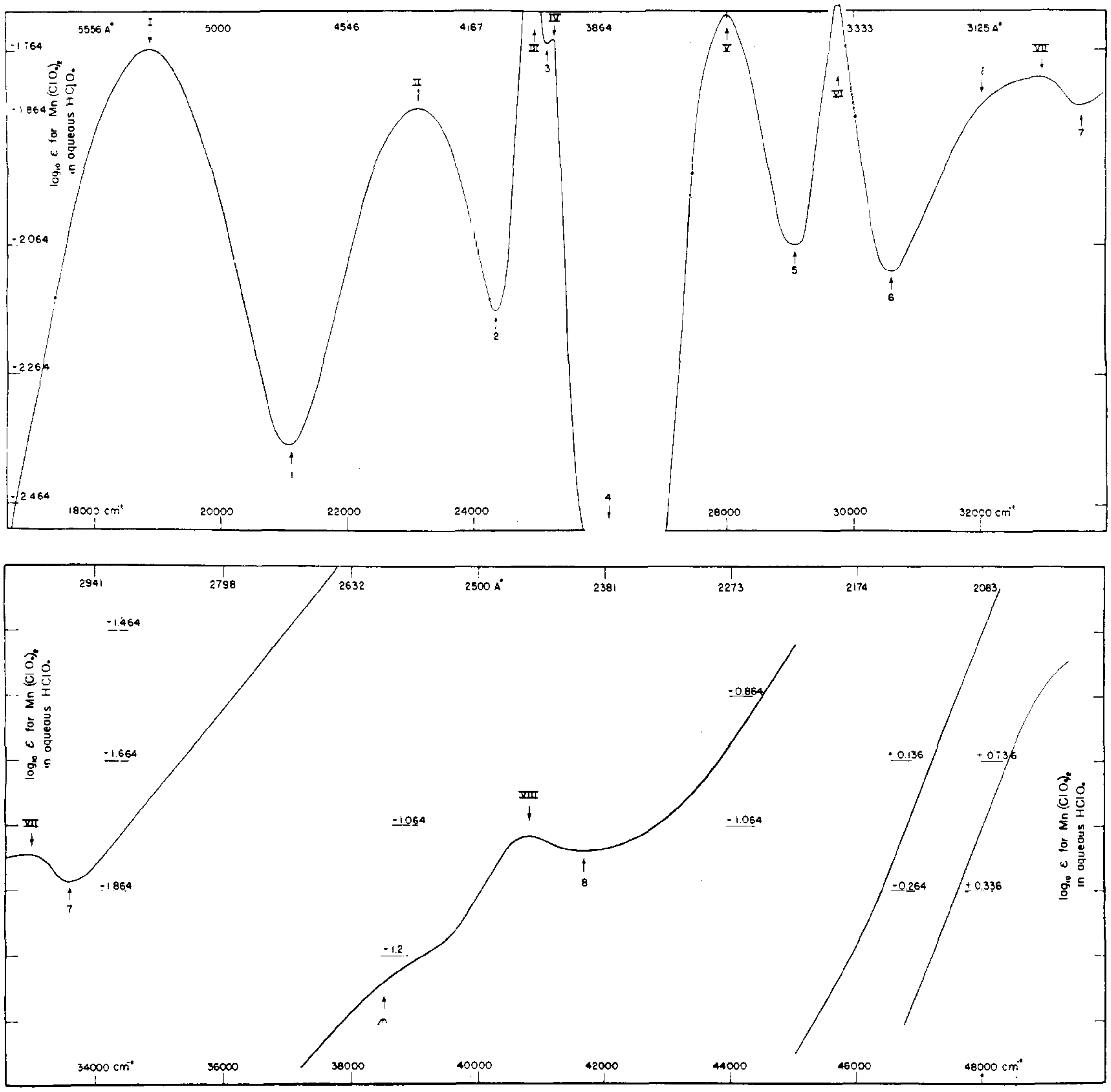

Fig. 1.—Visible and near ultraviolet absorption spectrum of manganous perchlorate in aqueous perchloric acid. Values of ϵ are for the molar extinction coefficient (molar absorptivity) expressed in liter/g. atom Mn-cm.; these are average values at 8 to 55° for the two solutions of the compositions given in Table I since the absorbances A of these solutions exhibited no trend with change in temperature over this range of temperature.

Materials and Preparations.—Conductivity water was employed for the preparation of the solutions. Impurities were kept at less than a few tenths of one per cent. Especial care was taken to avoid traces of iron, nitrates, chlorides and suspended material. None of the solutions exhibited the Tyndall effect. Acidities were adjusted with stock solutions of J. T. Baker analyzed reagent grade perchloric acid, Lot 4222.

Manganous perchlorate solutions were prepared as follows: About 120 g. of $MnCl_2 \cdot 4H_2O$ Merck reagent, Lot 7382 was added slowly in small portions to about 105 ml. of hot 12 N perchloric acid contained in a porcelain casserole. Additions were made only after complete dissolution of the previously added solid. The solution was then heated gently to a thick sirup. The sirup was cooled before it was diluted with water to a volume of about 200 ml. This digestion and subsequent dilution were repeated until the test for chloride was negative on a portion of the solution. Care was taken to prevent oxidation of the manganese during these operations; this could not be accomplished when an attempt was made to remove all the chloride by strongly heating the initial sirup.

Analyses.—Manganese concentrations were determined[7] by oxidation to permanganate by the use of excess sodium bismuthate while keeping the concentration of manganese in all forms at less than 0.5 mg. Mn per ml. and the amount of $NaBiO_3$ at 0.05 g. or more per mg. Mn. The excess bismuthate was removed by filtration through asbestos. The solid was washed with 0.06 N HNO_3. The filtrate and wash water were run directly into a solution of excess ferrous sulfate. The excess ferrous sulfate was determined by titration with a

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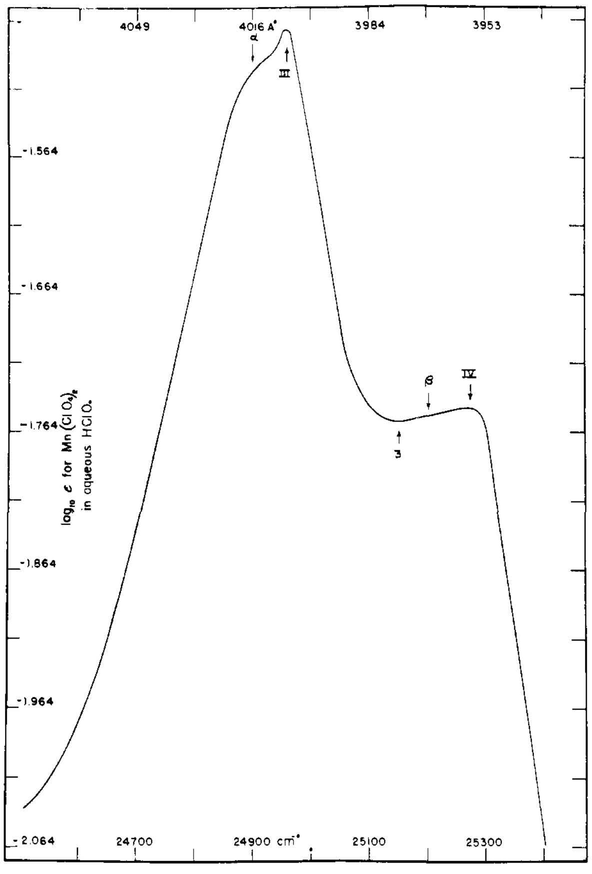
[7] L. F. Hamilton and S. G. Simpson, "Quantitative Chemical Analysis," The Macmillan Co., New York, N. Y., 1952, pp. 464–466.



solution of potassium permanganate which had been standardized against sodium oxalate.

Acid concentrations were determined[8] after removal of the manganous ions as the oxalate by addition of a slight excess of a saturated solution of sodium oxalate. The filtrate was titrated with a standardized solution of sodium hydroxide using the phenophthalein end-point.

Optical densities, absorbance values and molar extinction coefficients (molar absorptivities) were obtained in the manner described elsewhere.[9]

Compositions of the solutions whose optical densities were measured and pertinent information are given in Table I.

TABLE I

COMPOSITIONS AND SPECIFIC GRAVITIES OF THE AQUEOUS SOLUTIONS OF MANGANOUS PERCHLORATE, $Mn(ClO_4)_2$, TOGETHER WITH PERCHLORIC ACID, $HClO_4$

Also given are the temperatures of the optical density measurements, O.D.M. Concentrations are in moles per liter at 25°. Specific gravities are in grams per ml. also at 25°.

Soln.	Salt	$HClO_4$	Sp. grav.	Temp. O.D.M.
1	1.873	0.784	1.095	25°, 55°
2	2.693	0.341	1.122	8°, 25°, 54°

Results and Their Evaluation.—The light absorption spectrum obtained for manganous perchlorate in aqueous perchloric acid is presented in the different parts of Fig. 1. Values of interest pertaining to the spectrum are given in Table II. Measurements of this kind have not been previously reported on aqueous solutions of manganous perchlorate. Similar absorption spectra have been obtained, however, for manganous sulfate and chloride in aqueous sulfuric and hydrochloric acids, respectively.[10]

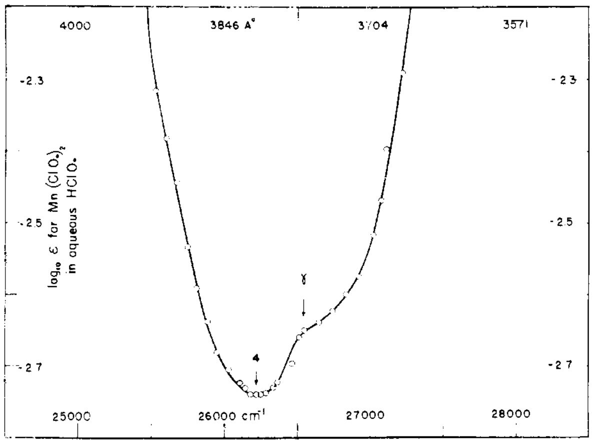


TABLE II

VALUES PERTAINING TO THE ABSORPTION SPECTRUM SHOWN IN FIG. 1 OF THE MANGANOUS PERCHLORATE IN SOLUTIONS 1 AND 2 OF THE COMPOSITIONS GIVEN IN TABLE I

Extinction coefficients ϵ and absorbance values A are in terms of logarithms to the base 10, concentrations are in moles per liter and light paths l are in cm. The values of ϵ are for 25°; they are also about the average values for the range 8 to 55°. No trend was observed in the values of ϵ at any wave length with change in temperature. Relative values of A as a function of wave length were reproduced within ±0.005.

Point of interest	λ, Å.	1/λ, cm.⁻¹	log ε	ε	A	
Maxima						
I	5300	18870	−1.738	0.0183	0.494	10
II	4325	23120	−1.818	.0152	0.410	10
III	4006	24960	−1.421	.0379	1.022	10
IV	3956	25275	−1.714	.0193	0.519	10
V	3574	27980	−1.670	.0214	.576	10
VI	3361	29750	−1.664	.0217	.585	10
VII	3034	32960	−1.839	.0145	.391	10
VIII	2450	40810	−1.106	.0783	.211	1
Shoulders						
α	4016	24900	−1.454	0.0352	0.947	10
β	3968	25200	−1.752	.0177	.477	10
γ	3768	26540	−2.652	.0022	.060	10
δ	3125	32000	−1.848	.0142	.382	10
n	2591	38600	−1.370	.0427	.119	1
Minima						
1	4744	21080	−2.418	0.0038	0.103	10
2	4110	24330	−2.159	.0069	.187	10
3	3976	25150	−1.735	.0184	.496	10
4	3815	26215	−2.740	.0018	.0485	10
5	3441	29060	−2.054	.0088	.238	10
6	3270	30580	−2.145	.0072	.193	10
7	2976	33600	−1.860	.0138	.372	10
8	2400	41670	−1.131	.0739	.199	1

We have employed the crystal field theory in its best empirical form to evaluate our best single

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(8) M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

(9) L. J. Heidt and J. Berestecki, *ibid.*, **77**, 2049 (1955).

(10) (a) References to these spectra have been cited by C. K. Jørgensen especially in his report to the Xth. Solvay Council, Brussels, May, 1956; (b) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1504, 1954; (c) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

values of the Racah parameters *B* and *C* and of the crystal field parameter, *Dq*, which account for the positions of the absorption peaks of the manganous ions in our solutions. This has been done by determining the best single values of *B* and *C* which account for the observed energy levels of free gaseous Mn^{+2}, then employing these values as a first approximation to evaluate by means of the appropriate energy matrices of Tanabe and Sugano[6] the best single values of *B*, *C* and *Dq* which fit our results for Mn^{+2} in water. No attempt has been made by us to interpret our values of the Racah parameters *B* and *C* and of the crystal field parameter *Dq* in terms of a really fundamental theory.

The best single values of *B* and *C* for the free gaseous manganous ion (Mn III, spectroscopic notation and Mn^{+2}, chemical notation) were obtained in the following way. This ion has 5 unpaired d-electrons so the multiplicity is $1 + 2(5/2) = 6$ for the ground state or level.[11] The ground state has no spacial degeneracy so its symbol is ^6S. The energy levels of states near the ground state of the free gaseous ion[11] are listed in Table III together with the values of their energies based on a value of zero for the ground state. Also given are Racah's values[5] for these energy levels in terms of *B* and *C*. The parameters *B* and *C* represent the electrostatic interactions between the *d*-electrons; they are defined by Racah as $B = F_2 - 5F_4$ and $C = 35F_4$ where the *F*'s are the Slater integrals.[11] These definitions for *B* and *C* are more convenient to use than the more familiar Slater integrals because the coefficients of these parameters are integers in the expressions for the energy levels arising from d^n configurations. In addition, the matrices of Tanabe and Sugano are set up in terms of these parameters.

TABLE III

ELECTRONIC ENERGY LEVELS[11] OF FREE GASEOUS Mn^{+2} NEAR THE GROUND ^6S STATE

Numerical values are given in cm.$^{-1}$ for the energies divided by *hc*. $B = 786$ cm.$^{-1}$ and $C = 3790$ cm.$^{-1}$ from the experimental values[12] of the energies of the states ^4G and ^4D based on a value of zero for the ground state ^6S. These values of *B* and *C* were employed to calculate the energies of the other states.

State	Energy in terms of Racah parameters	Calcd.	$1/\lambda$
^6S	0	0.0	0.0
^4G	$10B + 5C$	26800	26800
^4P	$7B + 7C$	32000	29200
^4D	$17B + 5C$	32300	32300
^4F	$22B + 7C$	43800	43600
^2I	$11B + 8C$	39000	. . .

The numerical values obtained for *B* and *C* are 786 and 3790 cm.$^{-1}$, respectively, from the wave lengths corresponding to the transitions ^4G to ^6S and ^4D to ^6S in the emission spectrum of Mn^{+2}(g). When these values of *B* and *C* are employed to calculate the energies of the ^4F and ^4P states, the calculated energy of the ^4F state is seen from Table III to be in good agreement with the observed value but the calculated energy of the ^4P state is too low by about 3000 cm.$^{-1}$; a similar situation, however, will later be seen to exist in the case of the ion in water.

The best single values of *B*, *C* and *Dq* for Mn^{+2} in water were obtained by recognizing that the ion in water is surrounded by water molecules which perturb the energy levels of the free ion. In the case of the ground ^6S level of the ion, the water molecules interact only weakly with this level since the level has no orbital degeneracy. This weak interaction is found[13] to arise from a complex combination of the spin orbit and crystal field interactions which removes some of the spin degeneracy of the ^6S level and thereby produces new levels differing from the original ^6S level by only a few cm.$^{-1}$. This very small difference would not show up in our absorption spectrum.

In the case of the quartet excited states of Mn^{+2}, however, the octahedron of water molecules immediately surrounding the ion splits these states to a much greater extent than it splits the ^6S state. The perturbation giving rise to the splitting of the quartet levels can be thought of as an additional term in the potential of a hamiltonian of cubic symmetry such as the term: (constant)$(x^4 + y^4 + z^4)$ for each electron.[3]

The constant of this expression is essentially the constant *Dq* of the crystal field theory and the graph that one obtains by plotting the energies of the different energy levels as a function of *Dq* is the so-called Orgel diagram.[4]

The symbols for the new excited quartet energy levels arising from the field are listed in Table IV. These symbols like the analogous ones for the free ion specify the multiplicity and symmetry of the various states. The symbol T means that the level has a threefold spacial degeneracy in addition to its spin degeneracy. The symbol E means a twofold spacial degeneracy and the symbol A means that the level is spacially non-degenerate. The remaining subscripts tell more of the symmetry properties of the levels[3] and help to identify the levels which can interact with each other in the presence of the field. The three levels marked T_{1g} interact with each other. The three levels marked T_{2g} interact with each other as do the two E_g levels but the

TABLE IV

ELECTRONIC ENERGY LEVELS OF Mn^{+2} IN A CRYSTALLINE FIELD OF CUBIC SYMMETRY

The ground level is the ^6S state which is affected negligibly by this field.

Level of Mn^{+2}(g)	Level of ion in field[3]	Energy[4,6]
^4G	$^4T_{1g}$	$< {}^4T_{2g}$
	$^4T_{2g}$	$< {}^4G$
	^4E_g	$\simeq {}^4G$
	$^4A_{1g}$	$\simeq {}^4G$
^4P	$^4T_{1g}$	$> {}^4P$
^4D	$^4T_{2g}$	$< {}^4D$
	^4E_g	$\simeq {}^4D$
^4F	$^4A_{2g}$	$\simeq {}^4F$
	$^4T_{1g}$	$> {}^4F$
	$^4T_{2g}$	$> {}^4T_{1g}$

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(11) See E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge University Press, Cambridge, England, 1951.

(12) C. E. Moore, N. B. S. Circular No. 467, "Atomic Energy Levels," Vol. II, U. S. Government Printing Office, Washington, D. C., 1952.

(13) B. Bleaney and K. W. H. Stevens, *Rep. Prog. Phys.*, **16**, 108 (1953), London: Physical Society.

levels $^4A_{1g}$ and $^4A_{2g}$ do not interact with any of the other levels.

Values of the energies E of the new levels were obtained by calculating the interaction between levels of the same symmetry in the presence of the octahedral field. This was done by setting up the matrix of interaction between these levels and finding the roots of the secular determinant. Thus for the three levels of $^4T_{1g}$ symmetry there is a three by three matrix of interaction. This matrix has been set up by Tanabe and Sugano[8]; its determinant is given in Table V. There is also a 3 × 3 matrix for the three $^4T_{2g}$ levels, a 2 × 2 matrix for the two ^4E_g levels, a 1 × 1 matrix for the one $^4A_{1g}$ level and a 1 × 1 matrix for the $^4A_{2g}$ level. All of these matrices are given in the article by Tanabe and Sugano. The levels ^6S, $^4A_{1g}$, $^4A_{2g}$ and ^4E_g do not depend on Dq so absorption peaks corresponding to transitions from the ground state ^6S to any of these levels would be expected to be sharp.

TABLE V

DETERMINANT OF THE TANABE AND SUGANO 3 × 3 MATRIX OF INTERACTION FOR THE THREE ENERGY LEVELS OF T_{1g} SYMMETRY WHICH ARE DERIVED FROM THE ^4G, ^4P AND ^4F LEVELS OF $Mn^{+2}(g)$ BY A CRYSTAL FIELD OF CUBIC SYMMETRY

The corresponding matrix of interaction does not have in it the energy E. B and C are the Racah parameters. Dq is the parameter arising entirely from the crystal field. The ^6S level has been chosen as the zero of energy. The value of E for the three $^4T_{1g}$ energy levels are the three values of E which satisfy this equation.

$$\begin{vmatrix} -10Dq + 10B + 6C - E & -3\sqrt{2}B & C \\ -3\sqrt{2}B & 19B + 7C - E & -3\sqrt{2}B \\ C & -3\sqrt{2}B & 10Dq + 10B + 6C - E \end{vmatrix} = 0$$

The sharp peak at 24960 (25275) cm.$^{-1}$ (neglecting fine structure) of Mn^{+2} in water has served us as it has served Orgel[4] as a basis for identifying the transitions from the ground state ^6S to the states ^4E_g and $^4A_{1g}$ derived from the state ^4G; also the sharp peak at 29750 cm.$^{-1}$ identifies the transition from the state ^6S to the state ^4E_g derived from the state ^4D. The other well-defined peaks are at 18870, 23120 and 27980 cm.$^{-1}$; they are assumed to correspond to the transitions from the ground ^6S to the level $^4T_{1g}$ derived from ^4G, from ^6S to $^4T_{2g}$ derived from ^4G and from ^6S to $^4T_{2g}$ derived from the level ^4D, respectively.

The values of the parameters B, C and Dq given by the above assignments were determined by choosing C as the unit of energy because the values of E are then a function of only the two parameters B/C and $10Dq/C$. Next a range of values of B/C was chosen near the value for the free gaseous ion and the corresponding values of E/C were calculated for each of the energy levels as a function of $10Dq/C$. The values of E/C for each of the three energy levels of $^4T_{1g}$ symmetry were found for each selected value of $10Dq/C$ by evaluating the determinant of the appropriate matrix and finding the three values of E/C for which the determinant vanishes. A similar process was carried out for the states of other symmetry.

We now divided the experimentally observed energy levels by various values of C and for each of these values of C we found the best values of B/C and $10Dq/C$ that fitted all five of the stated observed levels and finally selected the best possible values of C, B/C and $10Dq/C$ in the least squares sense. This lengthy calculation was carried out on an I.B.M. 704 computer.[14]

The best values for B, C and Dq found in this way accounted for the five energy levels within 3%. The comparison is in Table VI where, *e.g.*, $^4T_{1g}(^4G)$ identifies the $^4T_{1g}$ level derived from the ^4G level of the free gaseous ion.

TABLE VI

ELECTRONIC ENERGY LEVELS OF Mn^{+2} IN AQUEOUS PERCHLORIC ACID

In parentheses is given the state of free gaseous Mn^{+2} from which the state in the field of cubic symmetry is derived. Numerical values for the energies are in cm.$^{-1}$ above the ground ^6S state. Calculated values have been obtained by means of the appropriate Tanabe and Sugano matrices of interaction.

State	Calcd.	1/λ of abs. peak
$^4T_{1g}(^4G)$	19400	18870
$^4T_{2g}(^4G)$	22800	23120
$^4E_g, {}^4A_{1g}(^4G)$	25200	24960 25275
$^4T_{2g}(^4D)$	28200	27980
$^4E_g(^4D)$	29900	29750

The best values obtained by us for the parameters B, C and Dq based on the five energy levels cited in Table VI were now used to predict the energies of the remaining levels of the Orgel diagram. The predicted and experimental values of E for the two remaining principal peaks of all forms of the Mn^{+2} in solutions 1 and 2 are listed in Table VII. The agreement between the predicted and experimental values of E for the $^4A_{2g}$ level arising from the ^4F level of the free ion is excellent.

TABLE VII

PREDICTED ENERGY LEVELS OF Mn^{+2} IN AQUEOUS PERCHLORIC ACID

Numerical values for the energies are in cm.$^{-1}$ above the ground ^6S state.

State	Calcd.	1/λ of abs. peak
$^4T_{1g}(^4P)$	35000	32960
$^4A_{2g}(^4F)$	40700	40820
$^4T_{1g}(^4F)$	41900	...
$^4T_{2g}(^4F)$	46000	...

The predicted and experimental values of E for the remaining level $^4T_{1g}$ (^4P) agree within 10%; this is not as close as we would have been led to expect by the good agreement between the calculated and experimental values for the other levels. Inspection of Table III shows, however, that the values of B and C determined from the experimental values of E for the states ^4G and ^4D of the free gaseous ion predicted a value of the energy of the state ^4P for this ion which is too high by about 3000 cm.$^{-1}$ whereas they predicted precisely the position of the ^4F level. If about the same discrepancy between the calculated and experimental values of E for states derived from the ^4P

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(14) The computations were carried out at the M.I.T. Computation Center, Cambridge, Mass.

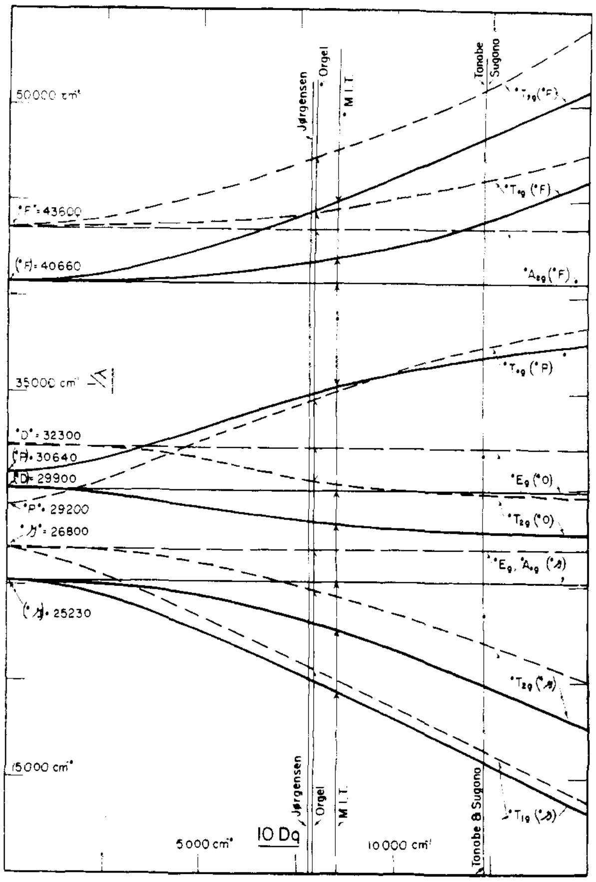

Fig. 2.—Orgel diagram of the energies *vs.* Dq for the energy levels of Mn^{+2} in a crystal field of cubic symmetry. The dotted lines reproduce Orgel's values which were obtained as explained in the text. The solid lines reproduce our values which are all based on single values of the Racah parameters B and C. The values of Orgel's lines at $Dq = 0$ are at the values of the stated energy levels for free gaseous Mn^{+2}; these levels are marked with an asterisk. In order to fit his lines at a single value of Dq to the values of $1/\lambda$ at the principal absorption maxima, Orgel found it necessary to move downward all his energy levels. This downward shift amounted to 1800, 2200 and 2600 cm.$^{-1}$ in the case of the levels derived from ^{4}G*, ^{4}P* and ^{4}D*, respectively. Our lines at a single value of Dq fit the experimental values of $1/\lambda$ at these maxima without any adjustment.

level is carried along into the crystal field we can explain the 2000 cm.$^{-1}$ discrepancy between the calculated and observed position of the level $^4T_{1g}$ (^{4}P).

The good agreement between our observed and calculated values of the energy levels of Mn^{+2} in aqueous perchloric acid makes us believe that our assignment of levels as presented in Tables VI and VII is correct. This assignment differs, however, from that of Jørgensen[15] in that he assigns values of 32400 cm.$^{-1}$ to $^4T_{1g}(^4P)$ which is his $^4\Gamma_4(P)$ level, 35400 cm.$^{-1}$ to $^4A_{2g}(^4F)$ which is his $^4\Gamma_2(F)$ level, 36900 cm.$^{-1}$ to $^4T_{1g}(^4F)$ which is his $^4\Gamma_4(F)$ level and 40600 cm.$^{-1}$ to $^4T_{2g}(^4F)$ which is his $^4\Gamma_5(F)$ level compared to our experimental values of 32900 and 40820 cm.$^{-1}$ for the first two levels and to our calculated values of 41900 and 46000 cm.$^{-1}$ for the last two levels, respectively.

Orgel calculated[4] the energies of the levels of Mn^{+2} in a field of cubic symmetry as a function of Dq by employing the values of B and C for the states of the free gaseous ion. He fitted the curves obtained in this way to the energies corresponding to the absorption peaks of the ion in water by shifting as a unit all the curves derived from the same state of the free gaseous ion. This procedure[4] is an approximation since changes in B and C change the relative separations of the energies of the levels as a function of Dq even for levels derived from the same state of the free gaseous ion.

Orgel obtained $10Dq$ by identifying the sharp twin peaks at 24960 and 25275 cm.$^{-1}$ as belonging to the pair of transitions from the ground ^{6}S state to the states ^4E_g and $^4A_{1g}$ derived from the state ^{4}G. He found that these peaks and the peaks at 18870 and 23120 cm.$^{-1}$ could be fitted to the curves for the states ^4E_g, $^4A_{1g}$, $^4T_{1g}$ and $^4T_{2g}$ which are all derived from ^{4}G when he shifted downward by 1800 cm.$^{-1}$ all the levels derived from ^{4}G and assigned a value of 7900 cm.$^{-1}$ to $10Dq$. He then found that the absorption peaks at 27980 and 29750 cm.$^{-1}$ were also fitted by this value of $10Dq$ when all the levels derived from the ^{4}D and ^{4}P states of the free gaseous ion were shifted downward by 2600 and 2200 cm.$^{-1}$, respectively.

The procedure employed by Orgel leaves undetermined the values of B and C corresponding to the energy levels of the ion in water. This procedure, however, gives values for B and C that differ from the values for the free gaseous ion and that also differ for each energy level even when derived from the same state of the free gaseous ion. Essentially the same procedure has been employed by Jørgensen. Our procedure on the other hand gives values of B and C as well as of Dq that do not depend upon the energy level. The values of B, C and Dq obtained by various authors are given in Table VIII.

TABLE VIII

VALUES OF THE RACAH PARAMETERS, B AND C, FOR FREE GASEOUS Mn^{+2} AND OF B, C AND $10Dq$ FOR Mn^{+2} IN WATER

In the case of our work, the values for Mn^{+2} aq. are for Mn^{+2} in all forms in aqueous perchloric acid. The values of B and C were not evaluated by Orgel or by Jorgensen for that which they have designated as $Mn^{+2}\cdot aq$.

	B	C	$10Dq$	Ref.
$Mn^{+2}(g)$	786	3790	0	This work
$Mn^{+2}\cdot aq$	..	..	7900	Orgel[4]
$Mn^{+2}\cdot aq$	..	..	7800	Jørgensen[15]
$Mn^{+2}\cdot aq$	860	3850	12300	Tanabe and Sugano[6]
$Mn^{+2}\cdot aq$	671	3710	8480	This work

The Orgel diagrams for the Mn^{+2} ion as a function of Dq are given in Fig. 2 for the values of B and C employed by Orgel (broken lines) and by us (solid lines). It will be seen that the two sets of lines are significantly different and that his $10Dq$ value of 7900 cm.$^{-1}$ differs significantly from the values of 12300 and 8480 obtained by Tanabe and Sugano and us, respectively. This is due to the significantly different values employed for B and C. Attempts at predicting the values of B, C and

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[15] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 53 (1957).

Dq from fundamentals have not as yet been very successful, but we do feel that in the absence of a fundamental theory it is best to use the empirical theory as accurately as possible in terms of the matrices of Tanabe and Sugano with no additional approximations.

The fine structure observed at the $^4A_{1g}$, ^4E_g twin peaks at 24960 and 25275 cm.$^{-1}$ could be due to a variety of causes such as: (1) a resolving of the accidental degeneracy of these levels due to electrostatic interaction with their environments, (2) spin orbit interaction and (3) a crystal field that is not purely octahedral but has some distortion.

The second possibility is unlikely for the following reason. The two main peaks are separated by about 300 cm.$^{-1}$. The fine structures of the ^4G and ^4D states of the free gaseous ion are about 10 and 50 cm.$^{-1}$, respectively.[11] The spin orbit interaction responsible for this splitting, therefore, is too small to explain the effect.

The third possibility is unlikely since if it were the case, splittings of comparable order of magnitude would be present in some of the other degenerate levels in the crystal field. The same argument could also be used against the second possibility.

The first possibility then appears to be the most likely even though it is a little difficult to predict an order of magnitude for the effect. The degeneracy predicted for the $^4A_{1g}$ and ^4E_g levels is purely accidental and is due essentially to our approximations. A general interaction of cubic symmetry could remove this degeneracy.

Another point worth mentioning is the occurrence of the very low peak in absorption at about 26500 cm.$^{-1}$. This peak is most likely caused by a transition from the ground state to a state of spin 1/2. This spin change of 2 is doubly forbidden[11] and would give rise to the relatively weak absorption which is observed. There is one such state which cuts across the Orgel diagram and has about the proper values of *E* at the value of *Dq* for the other levels in the crystal field. This state is of $^2T_{2g}$ symmetry and is designated as the $^2F_2(d\epsilon^5)$ state by Tanabe and Sugano; it has the ^2I state of the free ion as its parent. Unfortunately the value of *E* for this energy level is the root of a 10×10 secular equation, and we have not as yet calculated the values of *E* for this level as a function of *Dq* from our best values of *B* and *C*.

Transitions between states of different multiplicity are "forbidden,"[11] consequently the probability of transitions from the ground state ^6S to states of fourfold multiplicity is small so the light absorption coefficients, ϵ, would be expected to be small as observed, namely, 0.02. The doubly forbidden transition ^6S to the state $^2T_{2g}$ derived from ^2I would be expected to give rise to an even smaller value of ϵ as is observed, namely, 0.002.

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Further Studies on the Catalytic Decomposition of Hydrogen Peroxide by Triethylenetetramine–Fe(III) Complex and Related Substances

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The rate-determining step in the catalytic decomposition of hydrogen peroxide by $(TETA)Fe(OH)_2^+$ was determined by studying the hydrogen isotope-effect on the reaction rate. A similar study was also made on the enzyme catalase. The complex tris-(2-aminoethyl)-amine–Fe(III) was synthesized and studied for its similar catalytic action. The inhibition of $(TETA)Fe(OH)_2^+$-catalysis by cyanide was quantitatively investigated and correlated with some magnetic susceptibility data.

Introduction

The catalytic decomposition of hydrogen peroxide by triethylenetetramine–Fe(III) complex, $(TETA)Fe(OH)_2^+$, was studied previously.[2] The mechanism of this catalysis may be represented by Fig. 1, in which the ferric ion is polarized in the strong ligand-field of the triethylenetetramine and forms octahedral complexes. In these complexes, four of the octahedral orbitals of Fe(III) are used to form coördination bonds with the tetramine, the two remaining adjacent orbitals may be used to combine with hydroxide ions or hydroperoxide ions or both. The hydroperoxide ion, OOH^-, is potentially capable of acting as a bidentate ligand and forming metal chelates such as compound III in Fig. 1. But as depicted in Fig. 1, the O–O bond in compound III is too short to allow the maximum overlap of the bonding orbitals of Fe(III) and those of the bidentate ligand. Consequently the O–O bond in compound III is under strain and rendered more reactive, because the energy consumed in breaking this O–O bond is partially compensated by the energy gained in forming the two stronger Fe–O bonds. Accordingly it was found[2] that $(TETA)Fe(OH)_2^+$ decomposes hydrogen peroxide with great efficiency; the measured activation energy was only 6.6 kcal./mole. The above mechanism is further supported by the observation that tetraethylenepentamine–Fe(III) complex is practically inert for the decomposition of hydrogen peroxide as compared to $(TETA)Fe(OH)_2^+$.

Kinetic measurements showed that the rate of oxygen liberation in the above catalysis is approximately proportional to the concentration of hydrogen peroxide up to $[H_2O_2] = 0.94$ *M*. This shows that, at least in the concentration range studied,

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(2) J. H. Wang, THIS JOURNAL, **77**, 4715 (1955).