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The Fourier expansion of $\psi(x)$ is then

$$F(x)=(1-\tfrac{1}{2}\epsilon)+(4\epsilon/\pi^2)\sum_{m=0}^{\infty}\frac{\cos[(2m+1)\pi x/\epsilon]}{(2m+1)^2}. \quad \text{(A4)}$$

After two termwise differentiations,

$$F''(x)=-(4/\epsilon)\sum_{m=0}^{\infty}\cos[(2m+1)\pi x/\epsilon]. \quad \text{(A5)}$$

Integrating termwise,

$$F''(x)F(x)dx=-2. \quad \text{(A6)}$$

Thus, for this example, Eq. (A1) gives

$$\delta\bar{T}_{12}=\hbar^2/m, \quad \text{(A7)}$$

which agrees with Eq. (18), obtained by the method of convolutions.

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Application of Ligand Field Theory to the Electronic Spectra of Gaseous $CuCl_2$, $NiCl_2$, and $CoCl_2$

Jon T. Hougen,* George E. Leroi,† and Thomas C. James‡

Mallinckrodt Chemical Laboratories, Harvard University, Cambridge, Massachusetts

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The absorption spectra of $CuCl_2$, $NiCl_2$, and $CoCl_2$ in the gas phase at 1000°C have been obtained under low resolution in the visible, near-infrared, and near-ultraviolet regions. The observed absorptions have extinction coefficients of the order of 100 liter/mole·cm, suggesting that they correspond to "forbidden" intraconfigurational $d^n \leftarrow d^n$ transitions analogous to those found in solutions and crystals containing these metal ions. The observed spectra are rather well described by the two ligand field parameters appropriate to a molecule of symmetry $D_{\infty h}$.

INTRODUCTION

THE success of ligand field theory in describing the positions of the low-lying energy levels for a great number of compounds and complexes of the rare earth and transition metal elements is well known.[1,2] This theory is concerned with calculating the energies of the states arising from metal ion configurations of the form [closed shells] f^n and [closed shells] d^n, when these configurations are perturbed by the electrostatic ("stark") field of the surrounding anions. The principal contribution to the nonzero intensities of transitions among these ligand field energy levels for molecules with a center of symmetry arises from the coupling of vibrational motions with electronic motions, i.e., from vibronic interactions. Our understanding of such vibronic interactions is not yet complete, a fact attributable in part to the lack of experimental knowledge concerning the vibrational structure of ligand field transitions. Ligand field transitions of complexes in solution are broadened to an extent which makes the resolution of overlapping vibrational bands difficult. On the other hand, in solids, where rather sharp absorption and fluorescence lines are observed, the analysis of the spectrum is complicated by the necessity of treating the coupling of the lattice modes with the electronic motions of the metal ion. These remarks indicate the desirability of studying gaseous systems, where one can hope eventually to observe the detailed vibrational structure, and where the complications which arise in solid spectra are largely eliminated. Recently, several gaseous metal hexafluorides have been studied.[3–6] These compounds, however, possess 15 vibrational degrees of freedom, which makes a vibronic analysis of the spectrum difficult.

The present authors have turned their attention to the first-row transition metal dihalides in the hope that these simpler systems might eventually lend themselves to a complete vibronic analysis. The isolated gaseous molecules, possessing only four vibrational degrees of freedom, appear to be ideal d electron systems for a study of the coupling of electronic and vibrational motions. In this work we have assigned the observed absorptions of the dichlorides of copper, nickel, and cobalt to electronic transitions between levels of the $3d^9$, $3d^8$, and $3d^7$ metal ion configurations as perturbed by an axial ligand field. Assignments were made using

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[*] Present address: Division of Pure Physics, National Research Council, Ottawa, Canada.

[†] Present address: Department of Chemistry, University of California, Berkeley, California.

[‡] Present address: Department of Chemistry, Northwestern University, Evanston, Illinois.

[1] W. Moffitt and C. J. Ballhausen, Ann. Rev. Phys. Chem. **7**, 107 (1956).

[2] D. S. McClure, Solid State Phys. **9**, 399 (1959).

[3] W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, Mol. Phys. **2**, 109 (1959).

[4] G. L. Goodman, Ph.D. dissertation, Harvard University, Cambridge, Massachusetts, 1959.

[5] G. L. Goodman and M. Fred, J. Chem. Phys. **30**, 849 (1959).

[6] J. C. Eisenstein and M. H. L. Pryce, Proc. Roy. Soc. (London) **A255**, 181 (1960).

low-resolution spectra. The vibrational structure brought out by higher resolution is purposely ignored in this report.

EXPERIMENTAL

The low-resolution absorption spectra of gaseous $CuCl_2$, $NiCl_2$, and $CoCl_2$ were obtained between 3500 cm^{-1} and 38 000 cm^{-1} with a modified Perkin-Elmer model 98 monochromator using either a quartz or a sodium chloride prism. The samples, which had been prepared as described below, were heated to the desired temperatures in a Kanthal-wound resistance furnace which was placed in the optical path of the monochromator. Different light sources were employed for each region of the spectrum: a high-pressure xenon arc for the ultraviolet, a tungsten ribbon filament lamp for the visible, and a Nernst glower for the infrared. Absorption in the region 14 000 cm^{-1} to 40 000 cm^{-1} was also photographed using a Bausch & Lomb medium dispersion quartz prism spectrograph. Optical densities, i.e., $\log I_0/I$, were computed point by point from a background spectrum (I_0) and from a spectrum of the sample cell (I), both taken on the single beam Perkin-Elmer instrument. The extinction coefficients determined from these optical densities, which are shown in Figs. 1–3, have been corrected for the absorption and scattering of the cell windows. The uncertainty associated with the cell window corrections and the uncertainty in the moisture content of the samples during weighing suggest that our absolute extinction coefficients may be in error by as much as a factor of two. Nevertheless, the coarse features of the spectrum are easily discernible.

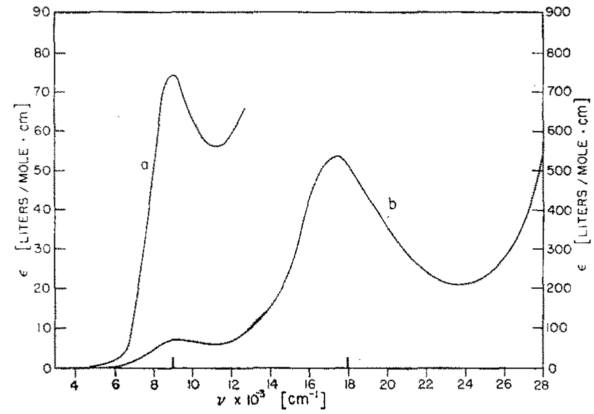

FIG. 1. The absorption spectrum of $CuCl_2(g)$. (a) left-hand scale; (b) right-hand scale.

Reagent-grade anhydrous cupric chloride (Fisher) was dried by heating in the presence of chlorine. Weighed samples of $CuCl_2$ were placed in Vycor cylinders 20 cm long and 4.5 cm in diam, to which quartz windows were fused. The sample was again heated under Cl_2, the cells evacuated, and several mm of chlorine gas readmitted before the cell was sealed off.

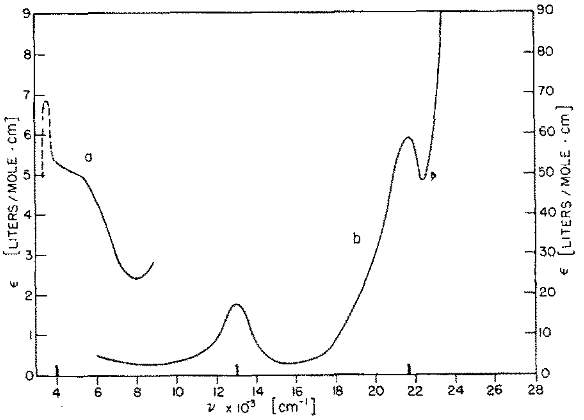

FIG. 2. The absorption spectrum of $NiCl_2(g)$. (a) left-hand scale; (b) right-hand scale.

Sufficient chlorine[7–9] was added to each sample cell to suppress decomposition of the $CuCl_2$ according to the equation

$$CuCl_2 \rightleftharpoons CuCl + \tfrac{1}{2}Cl_2 \qquad (1)$$

at the temperatures used to vaporize the sample. The spectrum of $CuCl_2$ is presented in Fig. 1. Anhydrous $NiCl_2$ and $CoCl_2$ were prepared by heating $NiCl_2 \cdot 6H_2O$ (Mallinckrodt) and $CoCl_2 \cdot 6H_2O$ (Baker) in a stream of hydrogen chloride gas. Weighed samples were placed in the Vycor cells described above, the samples reheated in the presence of HCl, and the cells evacuated and sealed off while the sample was still hot.

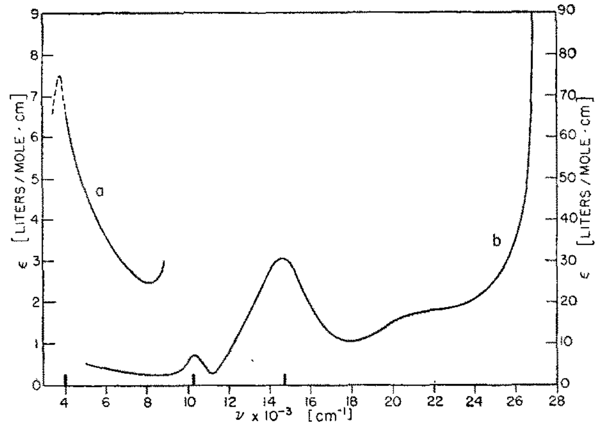

FIG. 3. The absorption spectrum of $CoCl_2(g)$. (a) left-hand scale; (b) right-hand scale.

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[7] L. Brewer, in *The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics*, edited by L. L. Quill (McGraw-Hill Book Company, Inc., New York, 1950), p. 235.

[8] The spectrum through a cell containing 3 mg of $CuCl_2$, but no Cl_2, showed bands in the region of 23 000 cm^{-1} which were not present in the spectra of sample cells containing Cl_2. Since CuCl is known to have band systems throughout the visible (see footnote 9), the authors took the presence or absence of these new bands as an empirical indication of the presence or absence of CuCl.

[9] G. Herzberg, *Molecular Spectra and Molecular Structure* I: *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., p. 525.

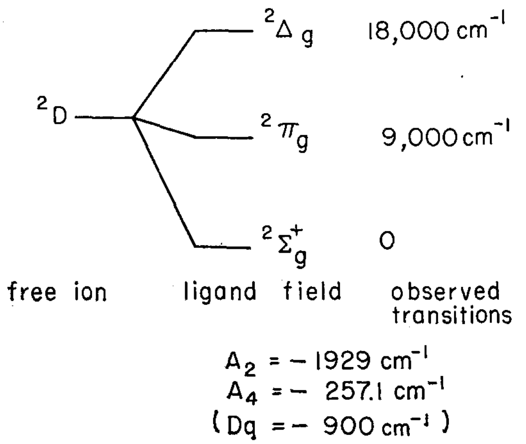

FIG. 4. Energy levels of $CuCl_2$ ($3d^9$).

The spectra of $NiCl_2$ and $CoCl_2$ are presented in Figs. 2 and 3. Vaporization of all three materials took place at temperatures between 700 and 1100°C.

Photographs of the charge transfer spectra in the ultraviolet have been obtained. $CuCl_2$ and $NiCl_2$ absorb strongly from 2800 to 3600 A; $CoCl_2$ absorbs strongly between 2600 and 3200 A. These results agree with earlier photographic observations[10] on $NiCl_2$ and $CoCl_2$.

The spectra were recorded at temperatures above that at which all of the sample present was vaporized. Under these conditions, where the vapor is not in equilibrium with the solid phase, one may infer from the results of Porter and co-workers,[11] who studied the composition of these vapors using mass spectrometric techniques, that for the temperature range employed in our experiments, any observed absorption may safely be ascribed to monomeric molecules. This was also justified empirically by the observation that the spectra of sufficiently hot samples were insensitive to further temperature increases exceeding 150°C.

SPECTRAL ASSIGNMENTS

The molecular symmetry of the gaseous molecules $CuCl_2$, $NiCl_2$, and $CoCl_2$ has not been experimentally established, but their similarity to the group II dihalides suggests that it is $D_{\infty h}$.[12] Furthermore, estimates of the contributions to the bending force constant from interactions of the unfilled d shell with the ligand field suggest that these are insufficient to lead to a bent molecule in either the ground or excited states. Therefore the molecules studied in this work will be considered to be linear symmetric triatomic molecules.

The ligand field theory formalism for molecules of symmetry $D_{\infty h}$ has been utilized elsewhere.[13,14] Nevertheless its development will be sketched here again. We shall first carry through a simple *crystal field* treatment, i.e., a treatment in which only $3d$ electronic wave functions are considered. The generalization to a molecular orbital, *ligand field* treatment is presented in the discussion section. Let the origin of a coordinate system lie at the metal ion M, and let one M—Cl bond define the direction of the polar axis. Let θ be the polar angle and ϕ be the azimuthal angle. Then the Hamiltonian for n d electrons in the field of the M^{+n+2} ion and the two negative ligands can be written[15]

$$H=H_{\text{free ion}}+H_{\text{crystal field}} \qquad (2)$$

$$=\sum_{i=1}^{n}[T_i+V(r_i)]+\sum_{i>j=1}^{n}e^2/r_{ij}$$

$$+2\sum_{i=1}^{n}[\bar{A}_0(r_i)Y_{00}+\bar{A}_2(r_i)Y_{20}(\theta_i)+\bar{A}_4(r_i)Y_{40}(\theta_i)], \qquad (3)$$

where T_i is the kinetic energy, $V(r_i)$ the free-ion potential energy, and $\mathbf{r}_i$ the coordinates of the "i"th electron. The first sum represents the interaction of the n electrons with the central field of the metal ion M^{+n+2}; the second sum represents the interelectronic coulomb repulsions. These two terms together comprise the Hamiltonian for the n d electrons in the free metal ion M^{+2}. The potential of an electron in the electrostatic field of the two symmetrically placed Cl^- ions can be expanded as a power series in the spherical harmonics $Y_{lm}(\theta, \phi)$, with expansion coefficients which are functions of r. The third sum represents this crystal field potential. For molecules with symmetry $D_{\infty h}$, only spherical harmonics of even l, with $m=0$ can occur in the expansion. Because matrix elements between d electron wave functions vanish for spherical harmonics with $l \geq 5$, the expansion has been truncated at $l=4$.

One Electron Formalism. $3d^1$ and $3d^9$

A free ion containing one $3d$ electron outside of closed shells has one fivefold orbitally degenerate Russell-Saunders term: ^2D. The axial crystal field partially removes this fivefold degeneracy and splits the ^2D term into states characterized by the irreducible representations of the point group $D_{\infty h}$. The $3d$ orbital wave functions, labeled by the irreducible representation of $D_{\infty h}$ to which they belong, are

$$\sigma_g^+=r^{-1}R_{3d}(r)\,Y_{20}(\theta)$$

$$\pi_g=r^{-1}R_{3d}(r)\,Y_{2\pm1}(\theta, \phi)$$

$$\delta_g=r^{-1}R_{3d}(r)\,Y_{2\pm2}(\theta, \phi). \qquad (4)$$

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[10] E. Miescher, Helv. Phys. Acta **11**, 463 (1938).

[11] R. C. Schoonmaker, A. H. Friedman, and R. F. Porter, J. Chem. Phys. **31**, 1586 (1959) and references cited therein.

[12] P. A. Akishin and V. P. Spiridonov, Kristallografiya **2**, 475 (1957); Chem. Abstracts **51**, 17297i (1957).

[13] R. E. Robertson and H. M. McConnell, J. Phys. Chem. **64**, 70 (1960).

[14] R. A. Berg and O. Sinanoglu, J. Chem. Phys. **32**, 1082 (1960).

[15] In this Hamiltonian spin orbit coupling has been neglected (as well as all interactions involving still smaller amounts of energy). The effects of spin orbit interaction are not apparent in the broad absorption bands observed under low resolution in this work. See discussion section.

The complete Hamiltonian (3) is diagonal in this representation and yields energy levels given (except for a constant factor) by

$$E_\sigma = 4A_2 + 12A_4$$
$$E_\pi = 2A_2 - 8A_4$$
$$E_\delta = -4A_2 + 2A_4, \tag{5}$$

where,

$$A_2 = [(5/4\pi)^{\frac{1}{2}}/7]\int_0^\infty \bar{A}_2(r) R_{3d}{}^2(r)\,dr$$

and

$$A_4 = [(9/4\pi)^{\frac{1}{2}}/21]\int_0^\infty \bar{A}_4(r) R_{3d}{}^2(r)\,dr \tag{6}$$

are the two crystal field parameters needed to describe the splitting.

The sign and relative importance of these two parameters can be estimated from a point charge model. We find that for a $3d^1$ configuration A_2 and A_4 are positive, corresponding to a repulsive potential between the chloride ions and the electron. For a $3d^9$ configuration treated by the hole formalism, A_2 and A_4 are negative, corresponding to an attractive potential between the chloride ions and the hole. In addition, if we set $R_{3d}(r) = \delta(r, r_0)$ and place the two point charges at $\pm a$ on the polar axis, then the ratio A_2/A_4 is given by $3a^2/r_0^2$. Taking the ratio of the effective radius of the $3d$ shell r_0 to the M—Cl distance a to be $\frac{1}{2}$, we conclude that $|A_2|$ is perhaps an order of magnitude larger than $|A_4|$.

The spectrum of $CuCl_2$ exhibits two transitions located at 9000 and 18 000 cm^{-1}, as shown by the markers on Fig. 1. There are six possible ways of assigning the three labels $^2\Sigma_g{}^+$, $^2\Pi_g$, and $^2\Delta_g$ to three energy levels, but only one of these yields negative A_2 and A_4 with $A_2/A_4 > 1$. The spectrum of $CuCl_2$ can thus be uniquely assigned, leading to the empirically determined parameters

$$A_2 = -1929\ \text{cm}^{-1}$$
$$A_4 = -257.1\ \text{cm}^{-1} \tag{7}$$

and to the energy level diagram presented in Fig. 4.

Many-Electron Formalism

If there is more than one $3d$ electron or more than one $3d$ hole, then the electronic spins can couple to give Russell-Saunders terms of different multiplicity. Since the Hamiltonian given in Eq. (3) does not contain spin dependent terms and cannot mix terms of different multiplicity, we observe that its energy matrix in a Russell-Saunders basis immediately factors into blocks characterized by the total spin angular momentum S. To the extent that S is a good quantum number, only transitions to states with the same multiplicity as the ground state will be observed in the absorption spectrum. Because the complexes of chloride ions with the first-row transition metal ions fall into the "weak field" case, the ground states of $NiCl_2$ and $CoCl_2$ would be expected to have the same multiplicity as the ground states of the free Ni^{++} ion (two d holes; $S=1$) and the free Co^{++} ion (three d holes; $S=\frac{3}{2}$), respectively.

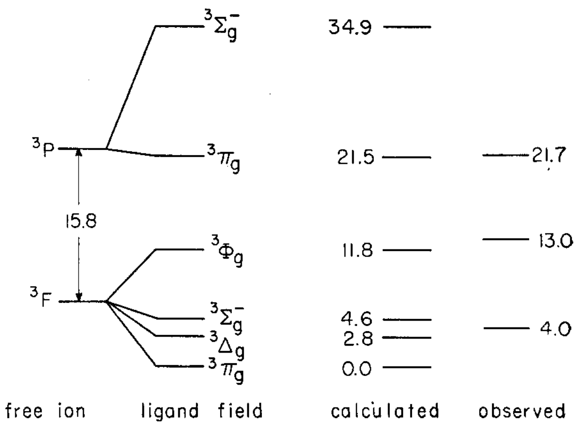

FIG. 5. Energy levels of $NiCl_2$ ($3d^8$) in thousands of cm^{-1}. (For value of 15.8, see C. E. Moore, Natl. Bur. Standards Circ. No. **467**, Vol. II.)

In addition to a coupling of the spins, the several $3d$ electrons or $3d$ holes will experience a mutual coulombic repulsion within the molecule. Because of this two additional parameters F_2 and F_4 are necessary to specify the energy level diagram for systems containing more than one d electron outside of closed shells.[16] However, for compounds and complexes of ligands such as the chloride ion, which lie towards the "ionic" or "weak field" portion of the spectrochemical series, electronic repulsion energies within the molecule can be approximated by the free ion electronic repulsion energies. These latter are responsible for the observed Russell-Saunders term separations in the free ion spectrum. The Russell-Saunders terms for the $3d^8$ configuration of the Ni^{++} ion are: $^1S, D, G$ and $^3P, F$. Those for the $3d^7$ configuration of the Co^{++} ion are: $^2P, D, D, F, G, H$, and $^4P, F$.

The triplet energy levels of $NiCl_2$ and the quartet energy levels of $CoCl_2$ were calculated by noting that in the Russell-Saunders basis, the free ion portion of the Hamiltonian is diagonal and possesses matrix elements equal to the free ion energy levels.[17] The effect of the crystal field portion of the Hamiltonian in splitting these free ion energy levels into states characterized by the projection of the electronic angular momentum along the internuclear axis and in mixing states of the same symmetry arising from the two different free ion terms was completely specified by using for the parameters A_2 and A_4, *the values determined from the assignment of the $CuCl_2$ spectrum.* The

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[16] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935), Chap. 7.

[17] C. Moore, Natl. Bur. Standards (U. S.) Circ. No. **467**, Vol. II (1952).

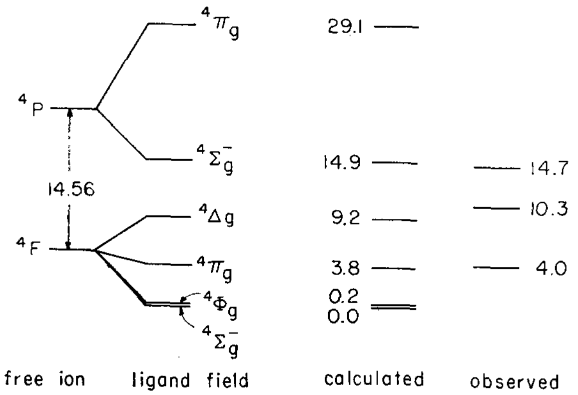

FIG. 6. Energy levels of $CoCl_2$ ($3d^7$) in thousands of cm^{-1}. (For value of 14.56, see C. E. Moore, Natl. Bur. Standards Circ. No. **467**, Vol. II.)

observed transitions indicated by the markers on Figs. 2 and 3 are compared in Figs. 5 and 6 with the energy levels calculated in this manner. The very low-lying infrared transitions could not be observed because the quartz windows were opaque below 3500 cm^{-1}; the very high-lying transitions could not be seen because they were buried in the strong charge transfer spectrum lying in the near ultraviolet.

To substantiate the correctness of the choice of a triplet ground state for $NiCl_2$, the lowest singlet state of $NiCl_2$ was calculated. This state would approximate the $^1\Sigma_g{}^+$ state $(\sigma_g{}^+)^2$. The observed[18] singlet terms of the $3d^8$ configuration of the Ni^{++} ion are the ^1D at 13 036 cm^{-1} and the ^1G at 22 115 cm^{-1} above the center of gravity of the ^3F ground state. The unobserved ^1S term was placed at 28 200 cm^{-1} by analogy to the term values in the $3d^2$ isoelectronic series.[16] These energies together with the crystal field parameters determined from the $CuCl_2$ assignment place the lowest singlet state some 4700 cm^{-1} above the $^3\Pi_g$ ground state of $NiCl_2$. A semi-quantitative argument against a doublet ground state for $CoCl_2$ can be presented as follows: The lowest doublet term[19] in the free Co^{++} ion spectrum, the ^2G term, lies 16 510 cm^{-1} above the center of gravity of the ^4F ground state. If the state of this ^2G term with $M_L=1$ were the pure $(\sigma_g{}^+)^2(\pi_g)^1$ state, the state with the lowest possible crystal field energy, then it would be depressed by the crystal field approximately 22 200 cm^{-1} to a position some 5700 cm^{-1} below the free ion ^4F level. Since the lowest quartet state of the $CoCl_2$ molecule, a $^4\Sigma_g{}^-$ state, has been depressed only 5560 cm^{-1} below the free ion ^4F term value, this $^2\Pi_g$ state would appear to be the ground state of the molecule. However, the $^2G{:}M_L=1$ state contains only 4.3% of the $(\sigma_g{}^+)^2(\pi_g)^1$ state. Since the next two lowest doublet terms lie 3100 and 5700 cm^{-1} above the $^2G{:}M_L=1$ state, the energy of the lowest $^2\Pi_g$ state will be significantly higher than the figure given above, probably some thousands of wave numbers above the lowest $^4\Sigma_g{}^-$ state.

DISCUSSION

The arguments presented in the previous section can be given in a more general fashion. The orbital wave functions of a $3d^1$ configuration transform according to the irreducible representations $\sigma_g{}^+$, π_g, and δ_g of the point group $D_{\infty h}$. However, in a molecule of symmetry $D_{\infty h}$ with the metal ion at the center of symmetry the actual lowest lying orbitals of the above symmetry will not be derived strictly from free metal ion $3d$ orbitals, but will contain admixtures of many other orbitals having the same transformation properties. It is here that the distinction between ligand field theory and crystal field theory is drawn. In crystal field theory one considers molecular orbitals derived solely from metal ion $3d$ orbitals, which are of the form given in (4). These five *crystal field* orbitals, taken by themselves, span a representation of the full rotational group. In ligand field theory the $\sigma_g{}^+$, π_g, and δ_g orbitals each acquire different admixtures of other orbitals of their own symmetry. Consequently, the five *ligand field* orbitals no longer span a representation of the full rotation group. The $\sigma_g{}^+$, π_g, and δ_g orbitals no longer have the same radial charge distribution, for example. Nevertheless, there will still be only two ligand field parameters: $E_1=E_\delta-E_\pi$ and $E_2=E_\pi-E_\sigma$ describing the separations of the three orbitals in the one electron case. We shall consider E_1 and E_2 to be the fundamental ligand field parameters. These are determined empirically from the $CuCl_2$ spectrum to be: $E_1=E_2=9000$ cm^{-1}. A_2 and A_4 may simply be considered as secondary parameters defined by forming appropriate differences among Eqs. (5).

The treatment of the coupling of electronic spins in the many electron case is not changed in passing from crystal field to ligand field theory. The treatment of Coulombic repulsions is drastically altered. Since the orbitals no longer all have a $3d$ radial dependence in ligand field theory, the Coulombic repulsion can no longer be described by only two parameters. To avoid a large increase in the number of parameters, we again express the hope that the Coulombic repulsions in these "ionic" molecules will be well approximated by those in the free metal ion. The effect of the ligand field portion of the Hamiltonian can now be specified completely by using the E_1 and E_2 determined empirically from the $CuCl_2$ spectrum, since all matrix elements among the states under consideration can be expressed as linear combinations of the molecular orbital energy differences $E_\delta-E_\pi$, $E_\pi-E_\sigma$, and the free ion Russell-Saunders splittings. These conceptual changes do not alter the results of the calculations. They simply show that a great deal of covalent bonding can be absorbed in the empirical ligand field parameters E_1 and E_2 (or A_2 and A_4).

The parameters A_2 and A_4 were determined in the

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[18] A. G. Shenstone, J. Opt. Soc. Am. **44**, 749 (1954).

[19] A. G. Shenstone, Can. J. Phys. **38**, 677 (1960).

previous section by assigning the observed absorptions to transitions in a linear molecule. Two plausible assignments of the absorptions to transitions in a bent molecule are illustrated in Fig. 7. In this diagram the parameters A_2 and A_4 determined from the spectral assignment for a linear molecule of $CuCl_2$ were used to calculate the energies for a molecule in which the Cl–Cu–Cl angle ranges from 180° to 90°. It is apparent that if the transitions indicated by arrows, corresponding to Cl–Cu–Cl angles of 136° and 90°, respectively, were assigned to the observed absorptions, A_2 and A_4 would be increased or decreased by some factor without changing their ratio. Clearly, if the ratio of A_2 to A_4 is also varied, many sets of values for the angle and ligand field parameters will provide a description of the observed spectrum of $CuCl_2$. Some of these sets of values would undoubtedly also give reasonably good descriptions of the $NiCl_2$ and $CoCl_2$ spectra. Thus, this work cannot be construed as evidence of the linearity of these three molecules, although certainly a linear model satisfactorily fits the observed energies.

The neglect of spin orbit coupling introduces qualitatively different errors in the one electron and in the many electron cases. The ligand field transitions of $CuCl_2$ can only occur between levels of spin $\frac{1}{2}$, since there is only one hole. Hence, the only first-order consequence of introducing spin orbit coupling is to split the $^2\Pi$ and the $^2\Delta$ states and to mix the $^2\Pi_{1/2}$ with the $^2\Sigma_{1/2}$ and the $^2\Pi_{3/2}$ with the $^2\Delta_{3/2}$. For the free Cu^{++} ion the spin orbit coupling constant ζ_{3d} is[20] about 830 cm^{-1}. Since the separations of the $^2\Sigma_g{}^+$, $^2\Pi_g$, and $^2\Delta_g$ states are 10 times this large, the component of electronic orbital angular momentum along the internuclear axis is a rather good quantum number. Because the spin orbit coupling constant is often lower in complexes than in the free ion, an upper bound for the splitting can be set;

$$^2\Pi_{1/2}-{}^2\Pi_{3/2}\leq 830\ cm^{-1}$$

$$^2\Delta_{3/2}-{}^2\Delta_{5/2}\leq 1660\ cm^{-1}. \qquad (8)$$

Such splittings are comparable with the observed low-resolution half-widths, and their neglect does not affect the spectral assignments.

The spin orbit interaction in $NiCl_2$ and $CoCl_2$ can, in addition to splitting the spin multiplets, destroy the good quantum number S by mixing states of different multiplicity. The free ion one electron spin orbit constant for Ni^{++} is 644 cm^{-1} and will therefore be rather ineffective in mixing singlet character into the $NiCl_2$ triplet ground state because the lowest singlet state lies 4700 cm^{-1} above the ground state. The one electron spin orbit constant for Co^{++} is 528 cm^{-1}, which might also be expected to be ineffective in mixing doublet character into the quartet ground state. Transitions from the high multiplicity ground state to many of the lower multiplicity states lie in the visible and near infrared. These transitions, however, are spin forbidden, and would be very weak unless the separation between levels of different multiplicity were comparable to the spin orbit coupling constant. In that case, the two levels would be intermixed and transitions from the ground state would occur to both. Under low resolution, however, the spectrum would still appear to have only a single broad absorption in this region, which would be assigned solely to the transition within the system of higher multiplicity. For these reasons only levels of the ground state multiplicity have been considered in the spectral assignments.

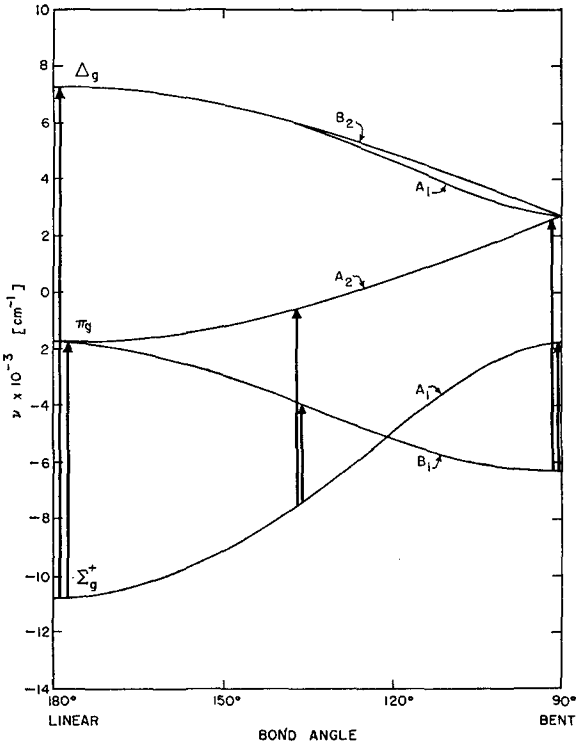

FIG. 7. The ligand field splittings for $CuCl_2$ as a function of bond angle.

The possibility of assigning the $CuCl_2$ spectrum in any of six different ways has been mentioned in the preceding section. One of these six assignments was chosen as the correct one because it led to A_2 and A_4 parameters with the sign and approximate ratio predicted by the point charge model. We shall now qualitatively examine the relative energies of metal ion $3d$ orbitals in MX_2 molecules, to determine if other plausible assignments can be made. The electron density at any point in space of a system containing one electron in a $3d$ orbital is given by

$$|r^{-1}R_{3d}(r)\Theta_{2m}(\theta)\Phi_m(\phi)|^2. \qquad (9)$$

Only the directional properties of these orbitals as a function of θ are of interest here, and these are il-

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[20] The three one electron spin orbit coupling constants ζ_{3d} have been taken from the convenient Table VIII of footnote 2. They can, of course, also be obtained from the term values given in footnote 17.

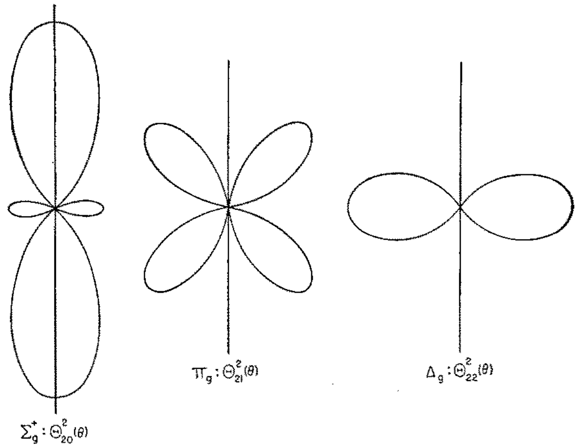

FIG. 8. Variation with polar angle θ of the electron density of the orbitals arising from metal ion $3d^1$ wave functions.

lustrated by a plot against θ of the function (9) averaged over r and ϕ. Thus in Fig. 8

$$\Theta_{2m}^2(\theta)=\int_{r=0}^{\infty}\int_{\phi=0}^{2\pi}R_{3d}^2(r)\Theta_{2m}^2(\theta)\,|\Phi_m(\phi)|^2drd\phi \qquad (10)$$

is plotted against θ. Here the vertical axis is the axis of the molecule and the orbitals can be qualitatively visualized as volumes of revolution about this axis. Clearly the σ_g^+ orbital brings the electron closest to the chloride ions, the π_g orbital brings it less close, while the δ_g orbital allows the electron to remain farthest from the negative ligands. These qualitative considerations lead to the order of levels already chosen.

In addition, it can be rigorously shown for any nonvanishing distribution of negative charge along an axis through the central metal ion, that the energy for electrons of the metal ion $3d\sigma$ orbital is greater than that of the $3d\pi$ orbital, which is greater than that of the $3d\delta$ orbital, i.e.,

$$\int V(\mathbf{r})\,|\sigma_g^+(\mathbf{r})|^2d\tau>\int V(\mathbf{r})\,|\pi_g(\mathbf{r})|^2d\tau >\int V(\mathbf{r})\,|\delta_g(\mathbf{r})|^2d\tau, \qquad (11)$$

where $V(\mathbf{r})$ is the potential due to the negative charge along the axis. As long as there is a σ bond between the M and X atoms in MX_2, or any other bond in which most of the displaced charge density lies on or near the internuclear axis of the bonded atoms, then the order of the orbitals will be that given above. If, on the other hand, the displaced charge is distributed along a ring whose axis is coincident with the internuclear axis, then by varying the radius of the ring and its distance from the metal ion, either the π_g or the δ_g orbital can be raised in energy to a point above the σ_g^+ orbital (see footnote 13). Since such a ring-like charge distribution in the copper-chlorine bond is unlikely, the authors feel quite confident that the assignment of the $CuCl_2$ spectrum is the correct one. This assignment, of course, depends upon the energy for holes rather than for electrons of the $3d\sigma$, $3d\pi$, and $3d\delta$ orgitals. For this case, the inequalities given in (11) must be reversed.

The assignments of $NiCl_2$ and $CoCl_2$ are less certain. For these compounds there are five possible transitions, of which but three have been seen. Since the only test for the correctness of an assignment is an examination of the agreement of observed and calculated energies, there are several plausible ways of assigning these spectra. The fact that the parameters determined from the $CuCl_2$ spectrum do describe the other two spectra simply *suggests* that the assignment given is the correct one.

It is possible by means of crystal field formalism to make a naive comparison between dihalide molecules MX_2 and the hexahalo complex ions MX_6^{-4}. For this comparison we assume that the crystal field potential due to each individual chloride ion in both systems is the same, and that, if the Cu—Cl bond in question is taken as the polar axis, the potential can be expanded in the power series

$$V(\mathbf{r})=\bar{A}_0Y_{00}+\bar{A}_1Y_{10}+\bar{A}_2Y_{20}+\bar{A}_3Y_{30}+\bar{A}_4Y_{40}+\cdots, \qquad (12)$$

where the A_i are functions of r and the Y_{l0} are functions of θ. The present work has determined the average over the radial wave functions of $\bar{A}_2(r)$ and $\bar{A}_4(r)$; the parameters A_2 and A_4 are constants times these averages. Studies on octahedral complexes, because of the higher symmetry involved, determine the average over the radial wave functions only of $\bar{A}_4(r)$; Dq is a constant times this average. Since the expansion (12) is the same for each chloride ion, Dq and A_4 obey the relation

$$Dq=(\tfrac{7}{2})A_4. \qquad (13)$$

The value of A_4 determined in this work leads to a Dq of -900 cm^{-1} for the three hexachloro complexes: MCl_6^{-4}. The observed[2] Dq for the complex $CuCl_6^{-4}$, for example, is -650 cm^{-1}. In any case, the A_4 parameter determined in this work is not unreasonably different from that expected on the basis of octahedral complex studies.

All of the absorptions described above are forbidden for a molecule fixed in a linear, symmetrical configuration, since they violate the Laporte rule for electric dipole radiation, $g\leftrightarrow g$. In addition, many of them violate the selection rule on electronic orbital angular momentum $\Delta\Lambda=\pm1, 0$. The absorptions occur for the most part because these electronic selection rules are relaxed through vibronic interactions. The metal dichlorides have four vibrations; a symmetric stretch, an antisymmetric stretch, and a doubly degenerate bend. Stretching the molecule symmetrically does not lower the symmetry of the molecule; this vibration cannot couple with the electronic motions to make any of the observed transitions allowed. Stretching the molecule antisymmetrically destroys the center of symmetry, but does not destroy the good quantum number Λ; this vibration can interact with the electronic motions to make allowed any transitions $g \leftrightarrow g$, which violate the Laporte rule, providing the selection rule $\Delta\Lambda = \pm 1, 0$ is still obeyed. Bending the molecule destroys the center of symmetry and the good quantum number Λ; this vibration can interact with the electronic motions to make any of the observed transitions allowed. It is not clear, however, in precisely what manner the antisymmetric stretch and the bend are cooperating to give these transitions finite intensities.

Several points not mentioned in the preceding text mar the impression of the apparently good agreement between the observed and calculated spectra. Because the intensities of some transitions are considerably less than those of others in the same spectrum, there is danger that portions of the vibrational and multiplet structure of given transitions may be mistaken for separate electronic band systems and vice versa. Second, since the absorptions are extremely wide, their centers, which were the experimentally determined quantities, may differ from the band system origins, which were to be the calculated quantities, by several thousand wave numbers. And finally, while the A_2 and A_4 parameters might be expected to change monotonically across the periodic table, one does not expect the dichlorides of three adjacent metals to have identical crystal field parameters. It is important to note that these criticisms are *within* the framework of the simple ligand field model.

CONCLUSIONS

The triatomic molecules $CuCl_2$, $NiCl_2$, and $CoCl_2$ can be considered to be *d* electron systems, i.e., to contain 3*d* electrons, more or less localized on the central metal ion. The ligand field formalism appropriate to such *d* electron systems describes the observed spectra rather well by means of a single set of two ligand field parameters. Alternatively, a set of crystal field parameters can be calculated, one of which can be converted to a Dq of -900 cm^{-1}, which is in agreement with observations on octahedral complexes. The ratio of the two crystal field parameters is consistent with a simple point charge model. These molecules, or the corresponding fluorides, may well be favorable cases in which to attempt a detailed vibronic spectral analysis. Such a detailed investigation will presumably not alter the general interpretation presented here, nor significantly change the parameters, but it will unambiguously determine the labels of the states between which the observed transitions take place, and should provide some insight into the vibronic couplings involved.

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