AN ABSTRACT OF THE THESIS OF

RONALD FRANCIS KONOPKA   for the MASTER OF SCIENCE
                (Name)   (Degree)

in   CHEMISTRY   presented on June 16, 1969
                                          (Date)

Title: SYMMETRY ALLOWED CHARGE-TRANSFER TRANSITIONS

BETWEEN SPIN-ORBIT STATES IN THE GASEOUS DIHALIDES

OF Mn, Co, Ni, AND Cu

Abstract approved: ███████████████████████████
                                Dr. C.W. DeKock

The spin-orbit states of both the ground and several
charge-transfer-excited electronic configurations of
gaseous MnX_2, CoX_2, NiX_2, and CuX_2 are derived. Only one-
electron transitions from the ground electronic state are
considered. The molecules are treated as linear in both
the ground and excited states. In each case, the spin-
orbit states of the excited configurations are components
of zero-order terms with the same multiplicity as the
ground state zero-order term. The symmetry allowed,
electric dipole excited, spin-orbit states are found for
each molecule. Polarization properties of transitions to
these states are also considered. The transitions ex-
pected for each gaseous molecule and the information ob-
tained from symmetry and polarization studies are
discussed.

Symmetry Allowed Charge-Transfer Transitions
Between Spin-Orbit States in the Gaseous
Dihalides of Mn, Co, Ni, and Cu

by

Ronald Francis Konopka

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1970

APPROVED:

Professor of Chemistry
in charge of major

Chairman of Department of Chemistry

Dean of Graduate School

Date thesis is presented   *June 16, 1969*

Typed by Jane Thies for   Ronald Francis Konopka

ACKNOWLEDGEMENT

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SYMMETRY ALLOWED CHARGE-TRANSFER TRANSITIONS BETWEEN SPIN-ORBIT STATES IN THE GASEOUS DIHALIDES OF Mn, Co, Ni, and Cu

I. INTRODUCTION

Since the middle 1950's there has been considerable interest in the study of the physical properties of the gaseous dihalides of the 3d transition metals. These molecules are of interest for several reasons. Three-center molecules composed of only a metal atom and two halogens lend themselves to the possibility of complete molecular orbital calculations. Offenhartz (17) has undertaken complete a priori molecular orbital calculations to determine the effects of electron correlation, ligand polarization, and d-orbital expansion in a gaseous linear 3d transition-metal dihalide. Because these molecules possess at most only four vibrational modes, a complete analysis of vibronic interactions may also prove possible. Vibronic interaction is a coupling of electronic motion with vibrational motion (9, p. 26-34). If sufficiently strong, vibronic interaction may alter the geometry of a molecule in either the ground or excited states. Lohr (14) has considered the effect of vibronic interactions on the geometry of gaseous $CuCl_2$, using extended Hückel type semi-empirical LCAO-MO calculations. Finally, these simple, high-symmetry transition-metal molecules provide a testing ground for theories of

bonding in transition-metal compounds.

Electronic transitions in these molecules break down into three types: primarily metal-metal, primarily halogen-halogen, and primarily metal-halogen (See Figure 1). Charge-transfer transitions are of the latter type, involving an electron transfer from the halogen to the metal during the excitation.

Our interest is in the charge-transfer spectra of the gaseous dihalides of Mn, Fe, Co, Ni, and Cu. These transitions have been observed for $MnCl_2$, $FeCl_2$, $NiCl_2$, and $CuCl_2$ both in the gas phase and isolated in an argon matrix ($CuCl_2$ cannot be isolated in argon due to the reaction $2CuCl_2 \longrightarrow 2CuCl + Cl_2$) (5,7). It was not possible from these studies to assign the transitions; however, the number of observed transitions was consistent with the previously assigned ground state.

Bird and Day (1) have used spin-orbit coupling effects to assign in detail the charge-transfer spectra of anionic tetrahalides of Fe, Co, and Ni in rigid glassy solutions at $77^{\circ}K$. They concluded that spin-orbit coupling at the halogen is sufficiently large to become decisive in any interpretation of the charge-transfer spectra of the bromides and iodides. Furthermore, they observed that the bands which in the chlorides are single became increasingly separated into components of comparable intensities in the heavier halides due to spin-orbit coupling effects of the

halogen. Their work suggests that an analysis of the possible spin-orbit states and the symmetry-allowed transitions between them could be of use in assigning the charge-transfer bands of the gaseous dihalides of Mn, Fe, Co, Ni, and Cu. In addition, this analysis would indicate which of the molecules would provide the most information when spin-orbit coupling effects are included.

II. ELECTRIC DIPOLE TRANSITIONS

The charge-transfer transitions of interest in the gaseous dihalides of Mn, Fe, Co, Ni, and Cu are electric dipole transitions. For such transitions, absorption intensity is proportional to the Einstein coefficient of induced absorption B_{mn}

$$(1) \quad P_{mn} = B_{mn}E(\omega_{mn})$$

where P_{mn} is the probability per unit time of a transition from a state n to state m, and $E(\omega_{mn})$ is the energy density (in units of ergs per cubic centimeter per cycle per second) of the radiation of frequency ω_{mn} interacting with the molecule.

Time-dependent perturbation theory for electric dipole radiation gives the following equation for the Einstein coefficient in terms of the moment of the transition from state n to state m (18, p. 302-305)

$$(2) \quad B_{mn} = \frac{16\pi^4}{3h^2}\left[\left(u_{x\,mn}\right)^2 + \left(u_{y\,mn}\right)^2 + \left(u_{z\,mn}\right)^2\right]$$

$u_{x,y,zmn}$ is a definite integral of the form

$$(2a) \quad \langle \psi_m \mid u_{x,y,z} \mid \psi_n \rangle$$

where ψ_m is the wave function for the excited electronic state of the molecule, $u_{x,y,z}$ is the x, y, or z component

of the electronic electric dipole moment of the molecule, and ψ_n is the ground state wave function. Equation (2) assumes the molecular dimensions are small relative to the wave length of the perturbing radiation, and the excited state and ground state are non-degenerate. If a degeneracy exists in the ground or excited state, then equation (2) becomes

$$(3) \quad B_{mn} = \frac{16 \pi^4}{3 h^2} \frac{1}{d_m} \sum_{i,k,p} \left(U_{p m_i n_k} \right)^2 \quad p = x, y, z$$

where d_m is the degeneracy of the ground state, and the indices i and k indicate summation over all combinations of the sublevels of the excited and ground state (10, p. 382).

A transition is allowed only if at least one of the moments of equation (2a) is non-zero. If any one of the moments in equation (2a) is non-zero, its magnitude gives a measure of the transition intensity in that direction. Such a determination requires a knowledge of the symmetry of the wave functions for the ground and accessible excited states.

The functions ψ in equation (2a) are solutions to the Schrödinger equation

$$(4) \quad H \psi = E \psi$$

where H represents the total energy of the molecule not including the translational kinetic energy. The functions are assumed to have the form

$$(5) \qquad \psi = \psi_e \left(q, Q, \beta \right) \psi_v (Q) \psi_r (\alpha)$$

where ψ_e is the electronic wave function, ψ_v the vibrational wave function, and ψ_r the rotational wave function. ψ_e is a function of all the electron coordinates, q, the nuclear coordinates, Q, and the electron spin coordinates, β. The vibrational wave function ψ_v is a function of all the nuclear coordinates, Q, and the rotational wave function ψ_r is a function of three angles, α, which become two for a linear molecule. This is the usual Born-Oppenheimer approximation.

The integral (2a) becomes

$$(6) \qquad \langle \psi_m | U_{x,y,z} | \psi_n \rangle = \langle \psi_{em} \left(q, Q, \beta_m \right) | U_{x,y,z} | \psi_{en} (q, Q, \beta_n) \rangle$$

$$\cdot \langle \psi_{vm} (Q) | \psi_{vn} (Q) \rangle$$

$$\cdot \langle \psi_{rm} (\alpha) | \psi_{rn} (\alpha) \rangle$$

The following assumptions are made with respect to the various parts of the product on the right-hand side of equation (6):

(a) For the charge-transfer bands under consideration, it is assumed that appropriate excited state vibrational and rotational levels are available for the electronic transition.

(b) The spin-orbit coupling in the gaseous 3d transition-

metal dihalides is assumed to be sufficiently weak so
that the Russell-Saunders coupling scheme holds. The
orbital angular momentum for a given electronic con-
figuration, denoted $\vec{L}$, is the sum of the individual
orbital angular momenta of the electrons. The spin
angular momentum $\vec{S}$ is the sum of the individual spins
of the electrons. For each configuration of elec-
trons several values of $\vec{L}$ and $\vec{S}$ are allowed, consist-
ent with the Pauli exclusion principle. $\vec{L}$ and $\vec{S}$
then couple to give a set of spin-orbit states for
the molecule. The set of spin-orbit states associated
with a given $\vec{L}$ and $\vec{S}$ are states of definite total
angular momentum $\vec{J}$, the magnitude of which may take
on the values $L + S$, $L + S - 1$, $L + S - 2$, ...
$|L - S|$. Each value is associated with a definite
energy state of the electron configuration. For a
more comprehensive discussion see (9, p. 19) and (10,
p. 333-337).

(c) The Russell-Saunders coupling in the gaseous 3d
transition-metal dihalides is assumed to be suffi-
ciently weak so that only those excited states acces-
sible from the ground state in the absence of spin-
orbit coupling need be considered. This restriction
includes preservation of the spin rule ($\triangle S = 0$), so
that β_m must be the same as β_n in equation (6)
for the transition moment integral to be non-zero.

Bird and Day (1) have found this to be a good approximation in an analysis of the charge-transfer spectra of anionic tetrahalides of Fe, Co, and Ni. DeKock and Gruen (5) also found the charge-transfer spectra of the gaseous 3d transition-metal dichlorides consistent with this assumption.

The problem to be solved is the determination on the basis of group theoretical (symmetry) considerations which integrals

$$(7) \quad \langle \psi_{em}(q, Q, \beta_n) | U_{x,y,z} | \psi_{en}(q, Q, \beta_n) \rangle$$

are non-zero, where the functions

$$(7a) \quad \psi_{em}(q, Q, \beta_n)$$

$$(7b) \quad \psi_{en}(q, Q, \beta_n)$$

are the wave functions for the excited spin-orbit charge-transfer state and ground spin-orbit state respectively. The functions (7a,b), which are solutions to the electronic part of equation (4), possess definite transformation (symmetry) properties. If the spin associated with the functions is integral, then the symmetry properties of the functions are characterized by the irreducible representations of the standard molecular point group, since the functions remain single-valued under any operation of this group. If the spin associated with the functions (7a,b) is non-integral, then the functions are double-valued under

some operations of the standard molecular point group. In order to classify the symmetry properties of these functions it is necessary to extend the standard point groups. The symmetry properties of the functions (7a,b) with half-integral spin are characterized by the irreducible representations of these extended (double) point groups. For a more comprehensive discussion see (9, p. 14-17).

For integral (7) to be non-zero, the integrand must be a totally symmetric function, or in other words, must be characterized by the totally symmetric representation of either the standard or extended molecular point group. If the irreducible representation of the excited state (7a) is Γ_m , that of u_x, u_y, or u_z is Γ_U , and that of the ground state (7b) Γ_n , for integral (7) to be non-zero

$$(8) \qquad \Gamma_n \times \Gamma_U \supset \Gamma_m$$

(19, p. 134-136).

III. MOLECULAR MODEL

There is substantial evidence which suggests that the gaseous dihalides of Mn, Fe, Co, Ni, and Cu are linear in the ground state. Leroi et al (13) have observed the infrared absorption spectra of gaseous $MnCl_2$, $CoCl_2$, $FeCl_2$, $NiCl_2$, $CuCl_2$ and $CoBr_2$ at temperatures ranging from $600^{\circ}C$ to $1,000^{\circ}C$ in the region between 220 and $4,000$ cm^{-1}. Only the antisymmetric stretch was observed, lending credence to a linear model. Milligan, Jacox, and McKinley (16) have observed the infrared spectra of gaseous NiF_2 and $NiCl_2$ in an argon matrix at $14^{\circ}K$ in the region between 400 and 4,000 cm^{-1}. The isotopic splitting of the asymmetric stretch was calculated in both cases assuming a linear molecule. The correspondence between calculated and observed values was found to be good. Furthermore, the symmetric stretch frequency of gaseous NiF_2, which would be infrared active if the molecule were bent, was calculated to be 606 cm^{-1} but was not observed experimentally. More recently, Thompson and Carlson (20) have made matrix-isolation studies on gaseous $MnCl_2$, $CoCl_2$, $NiCl_2$, and $NiBr_2$ in argon at $4^{\circ}K$. The infrared absorption spectra were recorded between 40 and 800 cm^{-1}. In each case both the asymmetric stretch and the bending mode were observed. The isotopic splittings of the asymmetric stretching frequency were found to be compatible with a linear geometry. In addition, no absorptions were

observed in the region predicted for the symmetric stretch, again indicative of a linear geometry in the ground electronic state.

DeKock and Gruen (7) have observed the gas phase spectra near $1,000^{\circ}$K of all the stable gaseous 3d transition-metal dichlorides except $MnCl_2$ in the region between 4,000 and 50,000 cm^{-1}. Low intensity bands in the region 4,000 to 22,000 cm^{-1} were interpreted as Laporte forbidden $d^n \longleftarrow d^n$ transitions. The $d^n \longleftarrow d^n$ transitions were reasonably well fitted by two ligand field parameters appropriate for a molecule linear in both the ground and excited states. Calculations have been made by DeKock and Gruen (6) in an attempt to include spin-orbit coupling effects in interpreting the $d^n \longleftarrow d^n$ transitions of gaseous $NiCl_2$, $NiBr_2$, and NiI_2 in the region 4,000 to 20,000 cm^{-1}. The molecules were assumed linear in both ground and excited states. Agreement with observed absorption bands was found to be good. The charge-transfer spectra of $MnCl_2$, $FeCl_2$, $CoCl_2$, and $NiCl_2$ isolated in an argon matrix at 4.2°K have been observed in the region 4,000 to 50,000 cm^{-1} by DeKock and Gruen (5). In each case, the number of observed charge-transfer bands agreed well with the ground state of the molecule predicted earlier (with the exception of $CoCl_2$) by interpreting the $d^n \longleftarrow d^n$ transitions on the basis of a linear model. All excited states were assumed to have a linear geometry.

Some theoretical calculations have been made on the compounds in question. Charkin and Dyatkina (3) have predicted the linearity of the gaseous dihalides of Mn, Fe, Co, Ni, and Cu using the energy of the valence state of the metal atom. Lohr (14) has made extended Hückel calculations on gaseous $CuCl_2$, taking into account spin-orbit coupling and vibronic interactions. Results indicated that gaseous $CuCl_2$ is linear in both the ground state and the excited $^2\widetilde{\Pi}_g$ and $^2\Delta_g$ crystal field states.

Using the third law of thermodynamics and assuming linear geometry, Thompson and Carlson (20) have calculated the entropy of gaseous $NiCl_2$ to be 85.6 eu at 850°K. Recent vapor pressure measurements of $NiCl_2$ by McCreary and Thorn (15) lead to an experimental entropy of 85.4 eu for the gaseous molecule at 850°K. Such close agreement lends excellent support to an assignment of a linear geometry for these molecules. Büchler, Stauffer, and Klemperer (2) have observed that $MnCl_2$ and the difluorides of Mn, Co, Ni, and Cu were not deflected by an inhomogeneous electric field, indicating that the molecules are linear. Observations on the dihalides of Group IIA suggested that a linear structure is favored by large halogens and small metal atoms. Therefore, if the difluorides are linear, the dichlorides, di-bromides, and di-iodides are expected to be linear. Kasai, Whipple, and Weltner (12) have studied the electron spin resonance spectrum of CuF_2 isolated in an argon matrix at

$4^{\circ}K$. The observed ESR spectrum supports a linear molecule with a $^{2}\Sigma_{g}^{+}$ ground state.

Hastie, Huage, and Margrave (8) have recorded the infrared spectra of matrix-isolated CoF_2, NiF_2, and CuF_2 in the region 400 to 4,000 cm^{-1}. From measured isotopic shifts for the asymmetric stretch, and taking the anharmonicity of this mode to be the same as that for diatomic transition-metal fluorides, the molecules have been predicted to be bent with the following bond angles: CoF_2, 165°; NiF_2, $154^{\circ}-167^{\circ}$; CuF_2, $163^{\circ}-170^{\circ}$.

With the exception of the work of Hastie, Huage, and Margrave, currently available data and theoretical calculations support the linear structure for the gaseous dihalides of Mn, Fe, Co, Ni, and Cu in the ground state.

The molecular orbital diagram for a gaseous linear 3d transition-metal dihalide is given in Figure 1. Qualitatively, the bonding, antibonding, and nonbonding molecular orbitals split into two types, those which are primarily metal in character and those which are primarily ligand in character. The $1\sigma_{g}^{+}$, $1\pi_{g}$, $2\sigma_{g}^{+}$, $1\sigma_{u}^{+}$, $2\sigma_{u}^{+}$, and $1\pi_{u}$ are primarily ligand orbitals and the $1\delta_{g}$, $2\pi_{g}^{*}$, $3\sigma_{g}^{+*}$, $4\sigma_{g}^{+**}$, $2\pi_{u}^{*}$, and $3\sigma_{u}^{+*}$ orbitals are primarily metal orbitals. DeKock and Gruen (5) have used this molecular orbital diagram in their interpretation of the charge-transfer bands of $MnCl_2$, $FeCl_2$, $CoCl_2$, and $NiCl_2$ in an argon matrix at $4.2^{\circ}K$, and achieved good agreement with
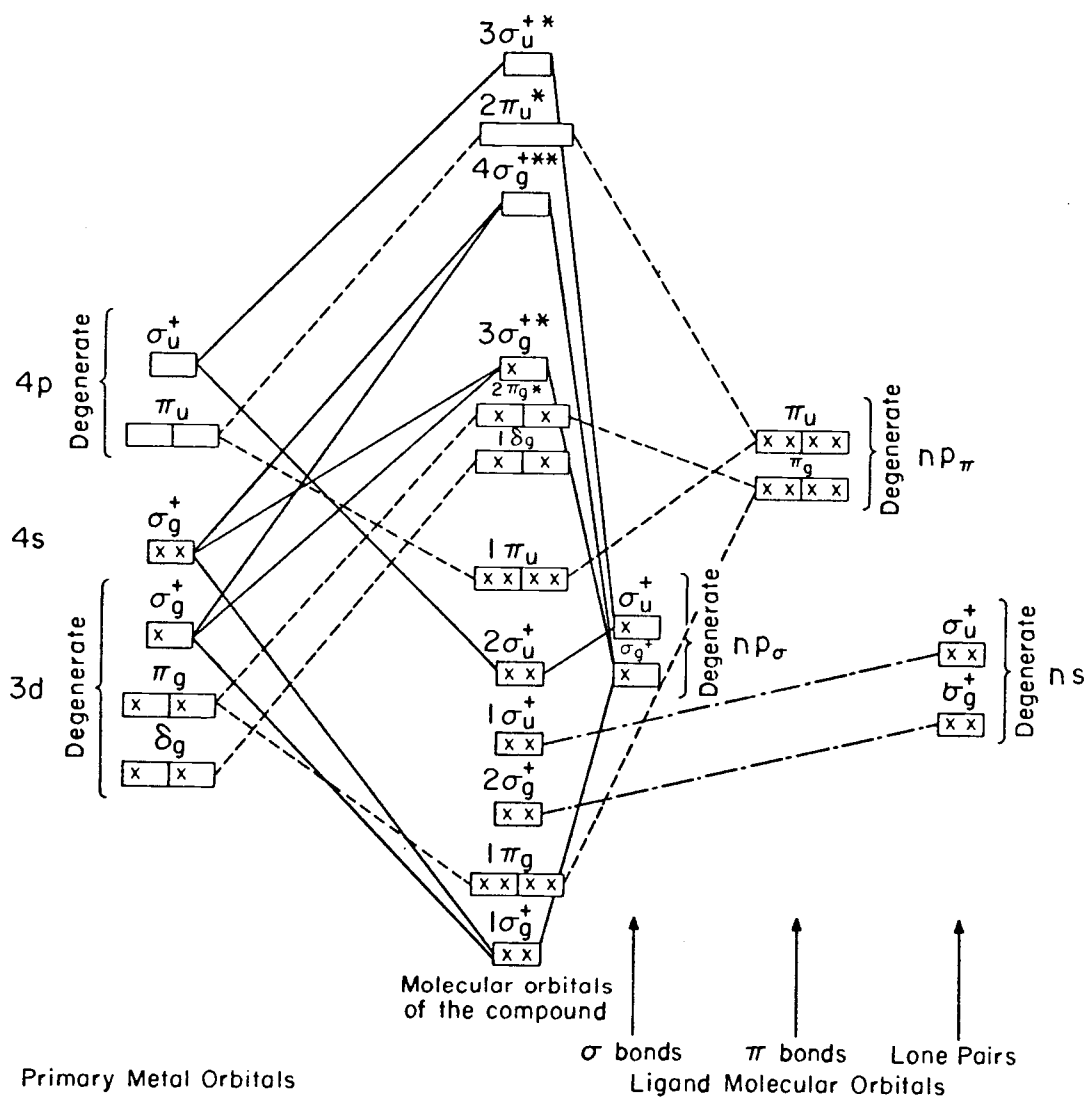
observed spectra.

Figure 1. Molecular orbitals for a linear triatomic transition-metal compound ($D_{\infty h}$) after DeKock and Gruen, J. Chem. Physics 49, 4522 (1968).

IV. TERM MANIFOLDS AND SYMMETRY ALLOWED TRANSITIONS

In deriving the manifold of spin-orbit states for the gaseous dihalides of Mn, Co, Ni, and Cu only excited electronic configurations reached by one-electron transitions from the ground state were considered. The ground state term and terms of accessible excited states for each molecule have been tabulated by DeKock and Gruen (5) for the case of no spin-orbit coupling. Excited state terms have the same multiplicity as the ground state. This is in agreement with preservation of the spin selection rule ($\triangle$ S = 0) mentioned earlier. The gaseous 3d transition-metal dihalides of interest are treated as linear in ground and excited states.

The spin-orbit states associated with a given zero-order term are found by taking the direct product of the spin irreducible representations with the orbital irreducible representation. Each direct product is then decomposed to find the component irreducible representations which are the allowed spin-orbit states for the term. For integral spin, direct products are taken and decomposed within the standard molecular point group; for non-integral spin, the same operations are carried out in the extended point group of the molecule. Tables of spin irreducible representations and direct product decompositions have been prepared by Herzberg (9, p. 569-573).

The $^6\Phi_u$ term of the first excited configuration of MnX_2 serves as an example of the procedure for finding the spin-orbit states. The spin irreducible representations are

$$(9a) \quad S = 5/2 \supset E_{1/2g} + E_{3/2g} + E_{5/2g}$$

The direct products and the irreducible representations they contain are

$$(9b) \quad E_{1/2g} \times \Phi_u \supset E_{5/2u} + E_{7/2u}$$

$$(9c) \quad E_{3/2g} \times \Phi_u \supset E_{3/2u} + E_{9/2u}$$

$$(9d) \quad E_{5/2g} \times \Phi_u \supset E_{1/2u} + E_{11/2u}$$

For non-zero spin-orbit coupling the $^6\Phi_u$ state splits into the terms on the right-hand side of (9b,c,d).

Tables I, II, III, and IV contain the electronic configurations, zero-order terms, and spin-orbit terms for gaseous MnX_2, CoX_2, NiX_2, and CuX_2, respectively. Spin-orbit states labeled with an asterisk are the symmetry allowed excited states found with the aid of equation (8). Tables V, VI, VII, and VIII contain the decompositions of the direct products of the irreducible representations of the dipole moment components with that of the ground state.

The gaseous dihalides of Fe have not been included in

this study because the ground spin-orbit term was not available. DeKock and Gruen (5) have found the number of observed charge-transfer bands of matrix-isolated $FeCl_2$ at 37,500; 39,800; 41,600; 44,100; and 47,600 cm^{-1} consistent with a $^5\Delta_g$ ground state. In the dibromide and di-iodide, the $^5\Delta_g$ zero-order term may split into a maximum of six distinct spin-orbit components, any one of which may be the ground state. Furthermore, each excited electronic configuration of gaseous $FeCl_2$ gives rise to a number of zero-order terms, many of which would split into several spin-orbit states in the dibromide and di-iodide. Because of the large number of choices for the ground state, the large number of spin-orbit excited states, and the closeness of the charge-transfer bands in the gaseous dichloride, any serious attempt to assign transitions in the FeX_2 system using spin-orbit coupling effects at the halogen must be postponed until the ground state spin-orbit term is known.

V. DISCUSSION

The high-temperature absorption spectra of the gaseous
dihalides of Mn, Co, Ni, and Cu would be difficult to inter-
pret. Several spin-orbit states and their vibrational
levels would be populated, giving broad absorption bands
with complicated vibrational structure. In addition,
possible overlapping of bands would complicate assignments.
Matrix-isolation of these dihalides would simplify the ob-
served spectra considerably, since only the ground elec-
tronic and vibrational states would be appreciably populated.

There are three different one-electron charge-transfer
transitions of interest in the gaseous dihalides of Mn, Co,
Ni, and Cu

$$(10a) \quad 1\pi_u \longrightarrow 1\delta_g$$

$$(10b) \quad 1\pi_u \longrightarrow 2\pi_g^*$$

$$(10c) \quad 1\pi_u \longrightarrow 3\sigma_g^{+*}$$
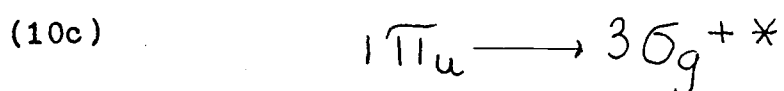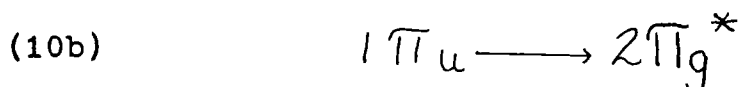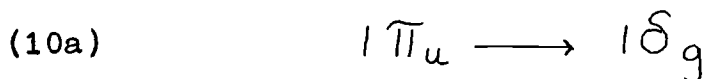
Transitions from the $2\sigma_u^+$ molecular orbital (See Figure
1) probably lie above 50,000 cm^{-1} (5).

Discussion will be focused on how spin-orbit splitting
of bands observed in the matrix-isolated dibromides and di-
iodides would be of use in assigning these one-electron
transitions. The observed splitting is expected to be due
primarily to spin-orbit coupling of the halogen, with the

splitting strongest in the matrix-isolated di-iodides.
Values for the spin-orbit coupling constants of the free
halogen atoms are: F, 269 cm^{-1}; Cl, 587 cm^{-1}; Br, 2457 cm^{-1};
and I, 5069 cm^{-1} (11, p. 159).

The polarization properties of an observed band can be
of aid in assignment and will also be considered. Kasai,
Whipple, and Weltner (12) have observed that CuF_2 isolated
in neon and argon matrices at 4°K is preferentially oriented
with the principle axis of symmetry (the ∞-fold z-axis)
parallel to the surface on which the matrix is deposited.
The principle axes of molecules in a given plane parallel to
the surface on which the matrix is deposited may assume any
orientation with respect to one another.

Plane polarized electric dipole radiation distinguishes
at most two types of transitions in gaseous linear dihalides:
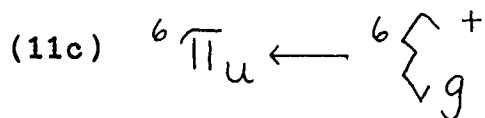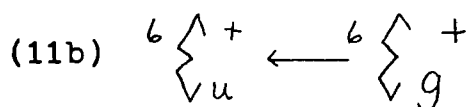
   (a) z-polarized, which occur when the electric vector is
       parallel to the z-axis of the molecule.

   (b) (x,y) - polarized, which occur when the electric
       vector is perpendicular to the z-axis.

Two orientations of the electric vector with respect to the
axis of rotation of the surface on which the matrix is de-
posited are of interest. The first is the case in which the
electric vector is collinear with the axis of rotation. For
those 3d transition-metal dihalides matrix-isolated in the
manner just described, no change in the intensities of ob-
served bands would occur as the surface is rotated. The

second is the case in which the electric vector is both
perpendicular to the axis of rotation and initially parallel
to the surface on which the matrix is deposited. As the
surface is rotated, a change in the intensities of the ob-
served bands would occur. The bands which decrease in in-
tensity are the z-polarized transitions, and the bands which
increase in intensity are the (x,y)-polarized transitions.

MnX_2

Three charge-transfer transitions at 43,900; 45,700;
and 50,000 cm^{-1} have been observed in matrix-isolated $MnCl_2$
(5). For sufficiently weak spin-orbit coupling in the di-
chloride, the observed bands are consistent with the three
spin and symmetry allowed transitions

(11a) $\quad {}^6\Pi_u \longleftarrow {}^6\Sigma_g^+$

(11b) $\quad {}^6\Sigma_u^+ \longleftarrow {}^6\Sigma_g^+$

(11c) $\quad {}^6\Pi_u \longleftarrow {}^6\Sigma_g^+$
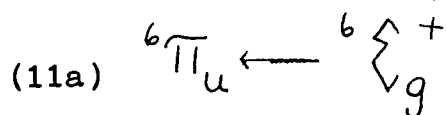
Transitions (11a,b,c) correspond to the one-electron transi-
tions (10a,b,c), respectively. The three bands are expected
to separate into spin-orbit components in the matrix-isola-
ted dibromide and di-iodide.

The $^6\Sigma_g^+$ ground state of gaseous $MnCl_2$ is formally split into three states by spin-orbit coupling. The splitting is due to higher order effects and will be small, on the order of a few wave numbers or less. Therefore, any splitting of the bands in matrix-isolated $MnBr_2$ and MnI_2 will be due to excited state term separation. The transition corresponding to (11b) is expected to remain single, since the excited $^6\Sigma_u^+$ term will be split by only a few wave numbers or less. The transitions corresponding to (11a,c) may each split into a maximum of six distinct transitions. The polarization properties of the two spin-orbit bands will be identical.

Appreciable overlapping of the transitions is probable in the matrix-isolated dibromide and di-iodide. The only definite statement which can be made on the basis of symmetry considerations alone is that thirteen transitions are expected in matrix-isolated $MnBr_2$ and MnI_2.

<u>CoX_2</u>

Eight charge-transfer bands at 30,800; 32,000, 33,700; 35,000; 36,400; 39,500; 42,000; and 45,800 cm^{-1} have been observed in matrix-isolated $CoCl_2$ (5). There is ambiguity about the ground state of gaseous $CoCl_2$. DeKock and Gruen (7) have found the $d^n \longleftarrow d^n$ transitions of high-temperature gaseous $CoCl_2$ consistent with a $^4\Phi_g$ ground state, although they did not exclude entirely the need for considering spin-
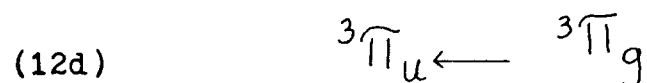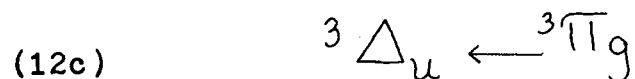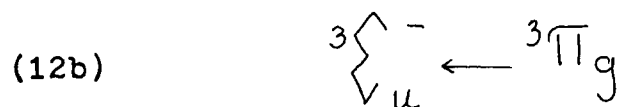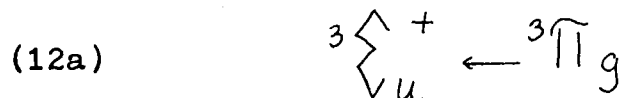
orbit coupling effects of the metal ion. The eight observed charge-transfer bonds are consistent with a $^4\Pi_g$ ground state if spin-orbit coupling at the metal ion and halogen is small. Recent calculations by Clifton and Gruen (4), including spin-orbit coupling of the metal ion, indicate that the ground state is an $E_{3/2 \, g}$. For sufficiently strong spin-orbit coupling at the halogen, an $E_{3/2 \, g}$ ground state is also consistent with the number of observed charge-transfer transitions.

For an $E_{3/2 \, g}$ ground state, eight charge-transfer transitions are expected in both matrix-isolated $CoBr_2$ and CoI_2. The eight transitions are the spin-orbit components of the three one-electron transitions (10a,b,c). Six of the transitions are expected to be (x,y)-polarized and two z-polarized in each case. No definite assignment of the one-electron transitions (10a,b,c) is possible with this information alone. However, observation of eight bands in both the matrix-isolated dibromide and di-iodide would lend support to an $E_{3/2 \, g}$ ground state for all three gaseous dihalides.

NiX_2

Four charge-transfer bands at 28,400; 32,000; 35,800; and 41,500 have been observed in matrix-isolated $NiCl_2$ (5). For sufficiently weak spin-orbit coupling in the dichloride,

the observed bands correspond to the spin and symmetry

allowed transitions

(12a) $\qquad ^3\left\{ \begin{array}{c} \Sigma^+ \\ \Sigma^- \end{array} \right\}_u \longleftarrow {}^3\Pi_g$

(12b) $\qquad ^3\left\{ \begin{array}{c} \Sigma^- \\ \Sigma^- \end{array} \right\}_u \longleftarrow {}^3\Pi_g$

(12c) $\qquad ^3\Delta_u \longleftarrow {}^3\Pi_g$

(12d) $\qquad ^3\Pi_u \longleftarrow {}^3\Pi_g$

Transitions (12a,b,c) and (12d) correspond to the one-elec-

tron transitions (10c) and (10b), respectively.

DeKock and Gruen (6) have made calculations which indi-

cate a Δ_g ground spin-orbit component of the ${}^3\Pi_g$ state

for the gaseous dihalides of Ni. Transitions (12a,b,c,d)

would exhibit the following behavior in matrix-isolated

$NiBr_2$ and NiI_2:

(a) transitions (12a,b) would remain single and are

(x,y)-polarized;

(b) transition (12c) would split into two (x,y)-polarized

components and one z-polarized component;

(c) transition (12d) would split into two (x,y)-polarized

components.

With this information, only two definite assignments are

possible. The bands which remain single in matrix-isolated

$NiBr_2$ and NiI_2 belong to the one-electron transition (10c), and the z-polarized band belongs to (10b).

CuX_2

One charge-transfer band at 19,000 cm^{-1} has been observed by DeKock and Gruen (5,7) for high-temperature gaseous $CuCl_2$. They assigned this band to the one-electron transition (10c). There is one other one-electron charge-transfer transition of interest for a gaseous copper dihalide

$$(10d) \qquad 2\,\sigma_u^+ \longrightarrow 3\,\sigma_g^+ {}^*$$
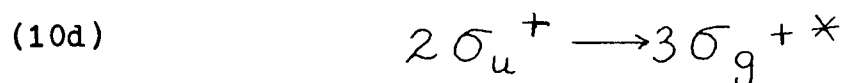
which is expected to lie above 50,000 cm^{-1}. Observation of both (10c) and (10d) in any gaseous copper dihalide would give an estimate of the separation of the $2\,\sigma_u^+$ and $1\,\pi_u$ one-electron molecular energy levels (See Figure 1).

Matrix-isolation of $CuCl_2$, $CuBr_2$, and CuI_2 is not possible due to the decomposition reaction

$$(13) \quad 2CuX_2 \longrightarrow 2CuX + X_2$$
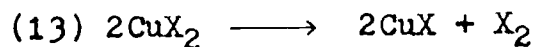
Study of the high-temperature spectra of gaseous $CuCl_2$, $CuBr_2$, and CuI_2 above 50,000 cm^{-1} with an overpressure of Cl_2, Br_2, or I_2 gas, respectively, would be difficult, if not impossible. Gaseous Cl_2, Br_2, and I_2 each possess several bands in the region above 50,000 cm^{-1} (10, p. 512, 519, 543). Reaction (13) does not occur for CuF_2. Study of

the ultraviolet spectrum of this molecule in matrix-isolation or at high temperatures could provide an estimate of the sigma-pi energy level separation.

There are two primary uncertainties in this analysis. The first is the assumption that the molecules are linear in the excited states. The second is the effect the matrix environment will have on the spin-orbit levels. Weltner, McLeod, and Kasai (21) have observed that the band spectra of matrix-isolated ScO, YO, and LaO are shifted by about one percent toward shorter wave lengths.

Symmetry considerations coupled with polarization studies alone do not provide enough information to assign all the bands expected in each of the molecules of interest. Estimates of transition intensities, total energy spread of the spin-orbit components of a transition allowed in the absence of spin-orbit coupling, and the unit of splitting of each zero-order state would prove useful. Bird and Day (1) have made estimates of such quantities in their analysis of the charge-transfer spectra of anionic tetrahalides of Fe, Co, and Ni in rigid glassy solutions at 77°K.

In conclusion, measurement of the charge-transfer spectra of matrix-isolated $MnBr_2$, MnI_2, $NiBr_2$, and NiI_2 coupled with calculations giving estimates of the quantities mentioned above would provide a good test of the model used in this analysis.

Table I. Spin-Orbit Terms for One-electron Transitions of MnX_2 Gas.

Electronic Configuration	Zero-order Term	Spin-orbit Term
1. Ground State: $(1\pi_u)^4(1\delta_g)^2(2\pi_g^*)^2(3\sigma_g^{+*})^1$	$^6\Sigma_g^+$	$E_{1/2\ g}\ ^FE_{3/2\ g}\ E_{5/2\ g}$
2. Excited State 1: $(1\pi_u)^3(1\delta_g)^3(2\pi_g^*)^2(3\sigma_g^{+*})^1$	$^6\Phi_u$	$E_{1/2u}\ ^FE_{3/2\ u}\ ^FE_{5/2u}\ ^FE_{7/2\ u}\ ^FE_{9/2u}\ E_{11/2\ u}$
	$^6\pi_u$	$(2)\,^*E_{1/2\ u}\ \ (2)\,^*E_{3/2\ u}\ ^*E_{5/2u}\ ^*E_{7/2u}$
3. Excited State 2: $(1\pi_u)^3(1\delta_g)^2(2\pi_g^*)^3(3\sigma_g^{+*})^1$	$^6\Sigma_u^+$	$^*E_{1/2\ u}\ \ ^*E_{3/2\ u}\ \ ^*E_{5/2\ u}$
	$^6\Sigma_u^-$	$E_{1/2\ u}\ \ E_{3/2\ u}\ \ E_{5/2\ u}$
	$^6\Delta_u$	$(2)\,E_{1/2\ u}\ ^FE_{3/2\ u}\ ^FE_{5/2u}\ ^FE_{7/2u}\ E_{9/2\ u}$
4. Excited State 3: $(1\pi_u)^3(1\delta_g)^2(2\pi_g^*)^2(3\sigma_g^{+*})^2$	$^6\pi_u$	$(2)\,^*E_{1/2\ u}\ (2)\,^*E_{3/2\ u}\ ^*E_{5/2\ u}\ ^*E_{7/2u}$

*These are the symmetry allowed transitions from the $E_{1/2\ g}$, $E_{3/2\ g}$, and

$E_{5/2\ g}$ states of gaseous MnX_2.

Table II.   Spin-orbit Terms for One-electron Transitions of CoX_2 Gas.

Electronic Configuration	Zero-order Term	Spin-orbit Term
1. Ground State:		
$(1\pi_u)^4(1\delta_g)^3(2\pi_g^*)^3(3\sigma_g^{+*})^1$	$^4\Phi_g$	$E_{3/2\ g}E_{5/2\ g}E_{7/2\ g}E_{9/2\ g}$
	$^4\pi_g$	$(2)E_{1/2\ g}E_{3/2\ g}E_{5/2\ g}$
2. Excited State 1:		
$(1\pi_u)^3(1\delta_g)^4(2\pi_g^*)^3(3\sigma_g^{+*})^1$	$^4\Sigma_u^+$	$E_{1/2\ u}\ E_{3/2\ u}$
	$^4\Sigma_u^-$	$E_{1/2\ u}\ E_{3/2\ u}$
	$^4\Delta_u$	$E_{1/2\ u}\ E_{3/2\ u}\ E_{5/2u}\ ^*E_{7/2\ u}$
3. Excited State 2:		
$(1\pi_u)^3(1\delta_g)^3(2\pi_g^*)^4(3\sigma_g^{+*})^1$	$^4\pi_u$	$(2)E_{1/2\ u}\ E_{3/2\ u}\ E_{5/2\ u}$
	$^4\Phi_u$	$E_{3/2\ u}\ E_{5/2\ u}\ ^*E_{7/2\ u}\ ^*E_{9/2\ u}$

*These are the symmetry allowed transitions from the $E_{9/2\ g}$ ground state of gaseous CoX_2.

Table II. (Continued)

Electronic Configuration	Zero-order Term	Spin-orbit Term

4. Excited State 3:

$(1\pi_u)^3(1\delta_g)^3(2\pi_g^*)^3(3\sigma_g^{+*})^2$ $^4\Sigma_u^+$ $E_{1/2\ u}\ E_{3/2\ u}$

$^4\Sigma_u^-$ $E_{1/2\ u}\ E_{3/2\ u}$

$^4\Delta_u$ $E_{1/2\ u}\ E_{3/2\ u}\ E_{5/2\ u}\ ^*E_{7/2\ u}$

$^4\Delta_u$ $E_{1/2\ u}\ E_{3/2\ u}\ E_{5/2\ u}\ ^*E_{7/2\ u}$

$^4\Gamma_u$ $E_{5/2\ u}\ ^*E_{7/2\ u}\ ^*E_{9/2\ u}\ ^*E_{11/2\ u}$

*These are the symmetry allowed transitions from the $E_{9/2\ g}$ ground state
of gaseous CoX_2.

Table III.   Spin-orbit Terms for One-electron Transitions of NiX_2 Gas.

Electronic Configuration	Zero-order Term	Spin-orbit Term

1. Ground State:

$$(1\pi_u)^4 (1\delta_g)^4 (2\pi_g^*)^3 (3\sigma_g^{+*})^1 \qquad {}^3\pi_g \qquad \Delta_g \ \pi_g \ \Sigma_g^+ \ \Sigma_g^-$$

2. Excited State 1:

$$(1\pi_u)^3 (1\delta_g)^4 (2\pi_g^*)^3 (3\sigma_g^{+*})^2 \qquad {}^3\Sigma_u^+ \qquad \Sigma_u^- \quad {}^*\pi_u$$

$$\phantom{(1\pi_u)^3 (1\delta_g)^4 (2\pi_g^*)^3 (3\sigma_g^{+*})^2 \qquad} {}^3\Sigma_u^- \qquad \Sigma_u^+ \quad {}^*\pi_u$$

$$\phantom{(1\pi_u)^3 (1\delta_g)^4 (2\pi_g^*)^3 (3\sigma_g^{+*})^2 \qquad} {}^3\Delta_u \qquad {}^*\Delta_u \quad {}^*\pi_u \quad {}^*\Phi_u$$

3. Excited State 2:

$$(1\pi_u)^3 (1\delta_g)^4 (2\pi_g^*)^4 (3\sigma_g^{+*})^1 \qquad {}^3\pi_u \qquad {}^*\pi_u \quad {}^*\Delta_u \quad \Sigma_u^+ \quad \Sigma_u^-$$

*These are the symmetry allowed transitions from the Δ_g ground state of gaseous NiX_2.

Table IV.   Spin-orbit Terms for One-electron Transitions of CuX_2 Gas.

Electronic Configuration	Zero-order Term	Spin-orbit Term
1. Ground State:		
$(2\sigma_u^+)^2 (1\pi_u)^4 (1\delta_g)^4 (2\pi_g^*)^4 (3\sigma_g^{+*})^1$	$^2\Sigma_g^+$	$E_{1/2\,g}$
2. Excited State 1:		
$(2\sigma_u^+)^2 (1\pi_u)^3 (1\delta_g)^4 (2\pi_g^*)^4 (3\sigma_g^{+*})^2$	$^2\Pi_u$	$^*E_{1/2\,u}$ $^*E_{3/2\,u}$
3. Excited State 2:		
$(2\sigma_u^+)^1 (1\pi_u)^4 (1\delta_g)^4 (2\pi_g^*)^4 (3\sigma_g^{+*})^2$	$^2\Sigma_u^+$	$^*E_{1/2\,u}$

*These are the symmetry allowed transitions from the $E_{1/2\,g}$ ground state of gaseous CuX_2.

Table V. Decomposition of $\Gamma_n \times \Gamma_u$ for MnX_2 Gas.

z-polarized   (x,y)-polarized

1. $E_{1/2\ g} \times \Sigma_u^+ \supset E_{1/2\ u}$ $E_{1/2\ g} \times \pi_u \supset E_{1/2\ u} + E_{3/2\ u}$

2. $E_{3/2\ g} \times \Sigma_u^+ \supset E_{3/2\ u}$ $E_{3/2\ g} \times \pi_u \supset E_{1/2\ u} + E_{5/2\ u}$

3. $E_{5/2\ g} \times \Sigma_u^+ \supset E_{5/2\ u}$ $E_{5/2\ g} \times \pi_u \supset E_{3/2\ u} + E_{7/2\ u}$

Table VI. Decomposition of $\Gamma_n \times \Gamma_u$ for CoX_2 Gas.

z-polarized   (x,y)-polarized

1. $E_{9/2\ g} \times \Sigma_u^+ \supset E_{9/2\ u}$ $E_{9/2\ g} \times \pi_u \supset E_{7/2\ u} + E_{11/2\ u}$

Table VII. Decomposition of $\Gamma_n \times \Gamma_u$ for NiX_2 Gas.

z-polarized   (x,y)-polarized

1. $\Delta_g \times \Sigma_u^+ \supset \Delta_u$ $\Delta_g \times \pi_u \supset \pi_u + \Phi_u$

Table VIII. Decomposition of $\Gamma_n \times \Gamma_u$ for CuX_2 Gas.

z-polarized   (x,y)-polarized

1. $E_{1/2\ g} \times \Sigma_u^+ \supset E_{1/2\ u}$ $E_{1/2\ g} \times \pi_u \supset E_{1/2\ u} + E_{3/2\ u}$

BIBLIOGRAPHY

1. Bird, B.D. and P. Day. Analysis of the charge-transfer spectra of some first-transition-series tetrahalide complexes. The Journal of Chemical Physics 49:392-403. 1968.

2. Büchler, Alfred, James L. Stauffer and William Klemperer. Geometry of the transition-metal dihalides: the fluorides of manganese, cobalt, nickel, copper, and zinc. The Journal of Chemical Physics 40:3471-3474. 1964.

3. Charkin, O.P. and M.E. Dyatkina. The energies of the valence states of atoms of transition metals in gaseous molecules of the halides MX_k I. The dihalides, MX_2. Journal of Structural Chemistry 6:550-560. 1965. (Translated from Zhurnal Strukturnoi Khimii)

4. Clifton, James and D.M. Gruen. Argonne National Laboratories, Chemistry Division. Personal communication. Argonne, Illinois. May 19, 1969.

5. DeKock, C.W. and D.M. Gruen. Charge-transfer spectra of matrix-isolated 3d transition-metal dichlorides. The Journal of Chemical Physics 49:4521-4526. 1968.

6. DeKock, C.W. and D.M. Gruen. Electronic-absorption spectra of gaseous $NiCl_2$, $NiBr_2$, and NiI_2. Axial ligand field calculations including spin-orbit coupling. The Journal of Chemical Physics 46:1096-1105. 1967.

7. DeKock, C.W. and D.M. Gruen. Electronic-absorption spectra of the gaseous 3d transition-metal dichlorides. The Journal of Chemical Physics 44:4387-4398. 1966.

8. Hastie, J.W., R.H. Hauge and J.L. Margrave. Infrared spectra and geometry of the difluorides of Co, Ni, Cu and Zn isolated in neon and argon matrices. Unpublished research. Houston, Tex., Rice University, Dept. of Chemistry. 1969.

9. Herzberg, Gerhard. Molecular spectra and molecular structure. Vol. 3. Electronic spectra of polyatomic molecules. Princeton, N.J., D. vanNostrand, 1967. 745 p.

10. Herzberg, Gerhard. Molecular spectra and molecular structure. Vol. 2. Spectra of diatomic molecules. 2d ed. Princeton, N.J., D. vanNostrand, 1950. 658 p.

11. Jørgensen, C.K. Absorption spectra and chemical bonding in complexes. London, Pergamon, 1962. 352 p.

12. Kasai, Paul H., Earl B. Whipple and William Weltner, Jr. ESR of $Cu(NO_3)_2$ and CuF_2 molecules oriented in neon and argon matrices at $4°K$. The Journal of Chemical Physics 44:2581-2591. 1966.

13. Leroi, George E. et al. Infrared spectra of gaseous transition-metal dihalides. The Journal of Chemical Physics 36:2879-2883. 1962.

14. Lohr, L.L., Jr. A molecular orbital study of vibronic interactions in the $CuCl_2$ molecule. Inorganic Chemistry 7:2093-2100. 1968.

15. McCreary, J.R. and R.J. Thorn. Heat and entropy of sublimation of Ni dichloride, dibromide, and di-iodide; dissociation energies of gaseous $NiCl_2$ and $NiBr_2$. The Journal of Chemical Physics 48:3290-3297. 1968.

16. Milligan, Dolphus E., Marilyn E. Jacox and John D. McKinley. Spectra of matrix-isolated NiF_2 and $NiCl_2$. The Journal of Chemical Physics 42:902-905. 1965.

17. Offenhartz, Peter O'Donnell. Molecular-orbital calculation of 10 Dq in some transition-metal fluorides. The Journal of Chemical Physics 47:2951-2960. 1967.

18. Pauling, Linus and E. Bright Wilson, Jr. Introduction to quantum mechanics. New York, McGraw-Hill, 1935. 468 p.

19. Schonland, David S. Molecular symmetry. Princeton, N.J., D. vanNostrand, 1965. 298 p.

20. Thompson, Kenneth R. and K. Douglas Carlson. Bending frequencies and new dimer modes in the far-infrared spectra of transition-metal dihalides. The Journal of Chemical Physics 49:4379-4384. 1968.

21. Weltner, W., Jr., D. McLeod, Jr. and P.H. Kasai. ESR and optical spectroscopy of ScO, YO, and LO in neon and argon matrices; establishment of their ground electronic states. The Journal of Chemical Physics 46:3172-3184. 1967.