

THE SIGNIFICANCE OF FORCE CONSTANTS OF A GENERAL QUADRATIC VALENCE FORCE FIELD: APPLICATION TO $\text{Au}(\text{CN})_2^-$, PtCl_4^{2-} , AuCl_4^- , AuBr_4^- , and $\text{Au}(\text{CN})_2\text{Cl}_2^-$ *

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CONTENTS

- A. Introduction
- B. The meaning of force constants
 - (i) Primary stretching force constants
 - (ii) Primary bending force constants
 - (iii) The interaction constants, F_{ij}
- C. Force constants of $\text{Au}(\text{CN})_2^-$
 - (i) Stretching force constants of $\text{Au}(\text{CN})_2^-$
 - (ii) Bending force constants of $\text{Au}(\text{CN})_2^-$
- D. Force constants for molecules with redundant coordinates
- E. Potential function and force constants for square-planar MX_4
 - (i) Stretching force constants for planar MX_4
 - (ii) Stretch-bend interaction constants for planar MX_4
 - (iii) In-plane bending force constants for MX_4
- F. Force constants of PtCl_4^{2-} , AuCl_4^- and AuBr_4^-
- G. Force constants of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$
 - (i) A_{1g} vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$
 - (ii) B_{1g} vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$
 - (iii) B_{2u} vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$
 - (iv) B_{3u} vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$
- H. Summary

A. INTRODUCTION

In recent years there have been many contributions to the literature dealing with the calculation of force constants in coordination compounds and correlation

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of these force constants with electronic structure and the nature of bonding. In the course of these investigations it has generally been necessary to make several approximations concerning the force field in order to make the problem solvable. Furthermore, the actual meaning of force constants, especially the interaction constants, has not always been crystal clear. This review is intended to elucidate the meaning of force constants and to illustrate detailed calculations for some square-planar complexes of trivalent gold and PtCl_4^- , taking into account reasonable ranges of interaction constants. As an example, the linear ion, $[\text{Au}(\text{CN})_2]^-$, is also considered.

Before delving into the calculations it seems pertinent to make some general remarks about the meaning of force constants, especially with regard to their correlation with electronic structure.

B. THE MEANING OF FORCE CONSTANTS

The interatomic forces within a molecule or complex ion* are, of course, determined by the existing electronic configuration. Such forces are manifested by the vibrational frequencies of the molecule. By means of infrared absorption spectra and Raman spectra we can observe most, if not all, of the fundamental vibrational frequencies of the molecule of interest. In order to derive relations between these frequencies and the interatomic forces it is necessary to assume a potential function.

A completely general potential function is given by

$$V = V_0 + \sum_i f_i S_i + \frac{1}{2} \sum_{ij} F_{ij} S_i S_j + \sum_{ijk} F_{ijk} S_i S_j S_k + \text{higher terms.} \quad (1)$$

The f_i , F_{ij} , F_{ijk} , etc. are constants. The S_i , S_j , etc. are internal displacement coordinates such as changes in interatomic distances, changes in bond angles, etc., which serve to define changes in configuration of the molecule. There must be at least $3N-6$ of these S_i for a molecule of N atoms as there are $3N-6$ degrees of freedom.

The potential energy zero is arbitrary so we can choose the zero as the energy of the equilibrium configuration, in which case $V_0 = 0$. The cubic and higher terms are generally quite small and are rightfully neglected for small displacements. Their importance is reflected in the degree of anharmonicity observed. By extrapolating to vibrational frequencies of infinitesimal amplitude, these higher order terms can certainly be neglected.

If all the coordinates are independent, since at equilibrium the potential energy must be at a minimum, then

* Henceforth we shall refer to a complex ion as a molecule.

$$\left(\frac{\partial V}{\partial S_i}\right)_0 = 0$$

and thus $f_i = 0$. However, if we include more than $3N-6$ coordinates, in order to make use of symmetry, some of these coordinates are not independent. There then exists a relation among certain of the coordinates which is referred to as a redundancy. In this case, for these redundant coordinates we cannot say

$$\left(\frac{\partial V}{\partial S_i^R}\right)_0 = 0$$

and the f_i^R are not necessarily zero, but are really undetermined multipliers[†].

First let us consider only configurations without redundancies in which case the first order term in (1) vanishes. We then express the potential energy, to a good approximation, as

$$V = \frac{1}{2} \sum_{ij} F_{ij} S_i S_j. \quad (2)$$

It is convenient to break this up into two terms

$$V = \frac{1}{2} \sum_i F_{ii} S_i^2 + \frac{1}{2} \sum_{i \neq j} F_{ij} S_i S_j \quad (3)$$

The F_{ii} we call primary force constants while the F_{ij} are interaction constants. In order to attach a physical meaning to these constants we must specify what sort of internal coordinates they are associated with.

For correlation with electronic structure and bonding properties, the most pertinent force field is the General Quadratic Valence Force Field (GQVFF), for which the S_i are changes in bond lengths or changes in angles included by bonds. Any other quadratic force field* can be correlated with the GQVFF.

(i) Primary stretching force constants

The bond stretching force constants are included in the first term of Eq. (3). As with diatomic molecules, such a force constant is a measure of the strength of the bond at the equilibrium electronic configuration. Mathematically it is expressed by

$$F_{ii} = \left(\frac{\partial^2 V}{\partial S_i^2}\right)_0$$

and represents the force tending to restore the bond to its equilibrium configuration after a small displacement has occurred. Often in diatomic molecules the dissocia-

* A popular force field is the Urey-Bradley Field which stresses interaction of non-bonded atoms. This is a somewhat restrictive force field which reduces the force constants to a solvable number. However, it does not represent the true situation for most coordination compounds and will not be considered here. It can be correlated with a GQVFF.

tion energy is used as a measure of the bond strength. However, in the process of dissociation a bond goes through considerable change in the electronic structure and thus the dissociation energy is not directly related to the strength of the bond at the equilibrium electronic configuration. The force constant, when calculated from the frequency of infinitesimal vibration, is a direct measure of the strength of the bond at the equilibrium configuration. Thus, the force constant is the logical quantity to correlate with the binding forces.

(ii) *Primary bending force constants*

Analogous to the stretching force constants, a primary bending force constant not involving redundant coordinates is a measure of the force tending to restore an angle to its equilibrium value after it has undergone a small displacement. As such, a bending force constant measures the strength of the directional forces which determine the equilibrium configuration of the angle.

(iii) *The interaction constants, F_{ij}*

Mathematically the interaction constant F_{ij} equals

$$\left(\frac{\partial^2 V}{\partial S_i \partial S_j} \right)_0$$

for S_i and S_j not involved in redundancies. However, the physical meaning is somewhat obscure. The following procedure helps to define these quantities*.

Consider a forced small displacement of one particular coordinate, $S_k = +1$; the potential energy is now, from (3),

$$V = \frac{1}{2} F_{kk} + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq k}}^{\alpha} F_{ii} S_i^2 + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq k}}^{\alpha} (F_{ik} + F_{ki}) S_i + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j \neq k}}^{\alpha} F_{ij} S_i S_j \quad (4)$$

$$\text{with } \alpha = 3N - 6$$

Now allow the molecule to achieve minimum potential energy with the constraint that $S_k = +1$. All the other coordinates will change to achieve this minimum and the displacements we express by $(S_i)_k$, meaning a change in coordinate i caused by a small unit change of coordinate k .

Since we are again at an energy minimum, for any given non-redundant displacement coordinate, S_i , we know that

$$\left(\frac{\partial V}{\partial S_i} \right)_0 = 0.$$

* This is similar to an argument developed by Coulson *et al.*², in discussing triatomic molecule interaction constants.

Applying this to (4) gives the result

$$0 = F_{ii}(S_i)_k + \frac{1}{2}(F_{ik} + F_{ki}) + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq k, l}}^n (F_{il} + F_{li})(S_i)_k \quad (5)$$

The interaction of coordinate j with coordinate i must be the same as interaction of i with j ; therefore, $F_{ij} = F_{ji}$. With this equality (5) can be rearranged as

$$F_{ki} = -F_{ii}(S_i)_k - \sum_{\substack{i=1 \\ i \neq k, l}}^n F_{il}(S_i)_k \quad (6)$$

Generally the F_{il} are small compared with F_{ii} . Then, since the $(S_i)_k$ are usually of the same order of magnitude, the last term above can be considered second order and we have the approximation

$$F_{ki} \approx -F_{ii}(S_i)_k \quad (7)$$

This serves as an approximate definition of the interaction constant F_{ki} . In other words, the constant for interaction between two non-redundant coordinates is approximately equal to the negative of the product of the primary force constant of one coordinate, i , times the displacement of that coordinate caused by unit small displacement of the other coordinate, k .

In order to determine how good an approximation (7) is for a given pair of coordinates one must first determine approximate values of the F_{ii} , the F_{ki} , and the $(S_i)_k$ for all coordinates involved in (6). Then by substitution in (6) one can determine the relative importance of the summation terms.

We shall now consider the force constants of the relatively simple complex ion $[\text{Au}(\text{CN})_2]^-$ as an illustrative example.

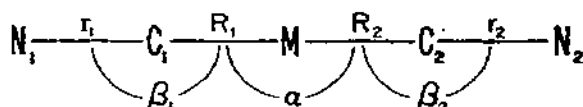
C. FORCE CONSTANTS OF $[\text{Au}(\text{CN})_2]^-$

A general quadratic valence force potential function* for $[\text{Au}(\text{CN})_2]^-$ is given by

$$\begin{aligned} V = & \frac{1}{2}F_{\text{CN}}(r_1^2 + r_2^2) + \frac{1}{2}F_{\text{MC}}(R_1^2 + R_2^2) + \frac{1}{2}F_{\beta}(\beta_1^2 + \beta_2^2) + \frac{1}{2}F_{\alpha}\alpha^2 + \\ & + F_{\text{CN}, \text{CN}'}r_1r_2 + F_{\text{MC}, \text{MC}'}R_1R_2 + F_{\text{MC}, \text{CN}}(r_1R_1 + r_2R_2) + \\ & + F_{\text{MC}, \text{CN}'}(r_1R_2 + r_2R_1) + F_{\beta\beta'}\beta_1\beta_2 + F_{\alpha\beta}(\alpha\beta_1 + \alpha\beta_2) \end{aligned} \quad (8)$$

The r_i , R_i , β_i , and α are short for Δr_i , ΔR_i , $\Delta\beta_i$, and $\Delta\alpha$. These coordinates are defined in Fig. 1. There are no interactions between stretching and bending coordinates as they occur in different symmetry blocks.

* In Equation (3) the primary force constants are referred to as F_{ii} . To be consistent we should label the primary force constants as $F_{\text{CN}, \text{CN}}$, $F_{\text{MC}, \text{MC}}$, $F_{\beta\beta}$, and $F_{\alpha\alpha}$. However, for simplicity and to distinguish easily from interaction constants, we use only the single subscript for primary force constants.

Figure 1. Schematic diagram of internal coordinates of $[\text{Au}(\text{CN})_2]^-$.

The observed vibrational frequencies for this linear complex ion are given in Table I. The calculated symmetry force constants are given in Table 2. The bond-stretching interaction constants were determined from a Raman and infrared study of the ^{13}C - and ^{15}N -enriched species³. The limits of error arise from un-

TABLE I

OBSERVED VIBRATIONAL FREQUENCIES FOR $[\text{Au}(\text{CN})_2]^-$

The Σ_g , Σ_u , and π_g frequencies are for aqueous solutions³. The π_u frequencies are somewhat uncertain, being estimated from combination bands in the solid state⁴.

Σ_g	ν_1	$2164.0 \pm 0.4 \text{ cm}^{-1}$
	ν_2	448 ± 2
Σ_u	ν_3	2145.7 ± 0.2
	ν_4	436 ± 2
π_g	ν_5	304 ± 2
π_u	ν_6	368 ± 5
	ν_7	$\approx 100 \pm 10$

certainties in observed frequencies (including those of the enriched species). The range of values for $F_{\alpha\beta}$ was estimated as discussed in a following section on bending force constants. From Table 2 we can calculate the valence force constants for the various internal coordinate. They are given in Table 3.

TABLE II

SYMMETRY FORCE CONSTANTS^a OF $[\text{Au}(\text{CN})_2]^-$

$F_{11} = F_{\text{CN}} + F_{\text{CN}, \text{C}'\text{N}'}$	$17.19 \pm 0.18 \text{ mdynes } \text{\AA}^{-1}$
$F_{22} = F_{\text{MC}} + F_{\text{MC}, \text{MC}'}$	3.19 ± 0.03
$F_{12} = F_{\text{MC}, \text{CN}} + F_{\text{MC}, \text{C}'\text{N}'}$	0.3 ± 0.15^b
$F_{33} = F_{\text{CN}} - F_{\text{CN}, \text{C}'\text{N}'}$	17.15 ± 0.18
$F_{44} = F_{\text{MC}} - F_{\text{MC}, \text{MC}'}$	2.36 ± 0.02
$F_{34} = F_{\text{MC}, \text{CN}} - F_{\text{MC}, \text{C}'\text{N}'}$	0.3 ± 0.15^b
$F_{55} = F_{\beta} - F_{\beta\beta'}$	$0.266 \pm 0.004 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$
$F_{46} = F_{\beta} + F_{\beta\beta'}$	0.38 ± 0.15
$F_{77} = F_{\alpha}$	0.60 ± 0.25
$F_{47} = \sqrt{2} F_{\alpha\beta}$	0.1 ± 0.1^c

^a The stretching force constants are calculated using the equations of reference 3. The bending constants are calculated by the usual methods (reference 1, chapter 4).

^b Determined from spectra of ^{13}C and ^{15}N enriched species (see Ref. 3).

^c Estimated range of values (see text).

TABLE III

VALENCE FORCE CONSTANTS OF $[\text{Au}(\text{CN})_2]^-$

F_{CN}	$17.17 \pm 0.18 \text{ mdynes } \text{\AA}^{-1}$
F_{MC}	2.775 ± 0.025
$F_{\text{CN}, \text{C}'\text{N}'}$	0.02 ± 0.18
$F_{\text{MC}, \text{MC}'}$	0.415 ± 0.025
$F_{\text{MC}, \text{CN}}$	0.3 ± 0.15
$F_{\text{MC}, \text{C}'\text{N}'}$	0.0 ± 0.15
F_β	$0.33 \pm 0.08 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$
F_α	0.60 ± 0.25
$F_{\beta\beta'}$	0.05 ± 0.08
$F_{\alpha\beta}$	$(0.07 \pm 0.07)^*$

* This range of values was assumed for $F_{\alpha\beta}$ for reasons given in the text.(i) *Stretching force constants of $[\text{Au}(\text{CN})_2]^-$*

The CN-stretching force constant of Table 3 shows about $\pm 1\%$ uncertainty based on the isotopic frequency shifts. There is probably no hope of decreasing the error limits; thus, when CN-stretching force constants are within 1% of each other they are the same within experimental error. In fact, the uncertainty is actually greater as the anharmonicity has been neglected in the figures of Table 3. If it is included, the CN-stretching force constant is about 2.6% greater, raised from 17.2 to 17.6 mdynes \AA^{-1} (see references 3 and 4). The anharmonic corrections are not known very accurately for $[\text{Au}(\text{CN})_2]^-$. For most cyanide complexes the anharmonic corrections are even more uncertain. For this reason it appears that for comparison of one cyanide complex with another it is better to use the CN-stretching force constant uncorrected for anharmonicity, as given in Table 3, at least until more-complete anharmonic corrections are available.

The metal-carbon force constant also shows about 1% uncertainty as given in Table 3. It appears from observed combination bands that the anharmonic corrections for metal-carbon stretching vibrations are probably negligible.

For a discussion of the interactions of coordinates, we refer back to (6). Application of this equation leads to the relations*

$$\begin{aligned}
 F_{\text{CN}, \text{C}'\text{N}'} &= -F_{\text{CN}}(\text{C}_2\text{N}_2)_{\text{C}_1\text{N}_1} - F_{\text{MC}, \text{CN}}(\text{MC}_2)_{\text{C}_1\text{N}_1} - F_{\text{MC}, \text{C}'\text{N}'}(\text{MC}_1)_{\text{C}_1\text{N}_1} \\
 F_{\text{MC}, \text{MC}'} &= -F_{\text{MC}}(\text{MC}_2)_{\text{MC}_1} - F_{\text{MC}, \text{CN}}(\text{C}_2\text{N}_2)_{\text{MC}_1} - F_{\text{MC}, \text{C}'\text{N}'}(\text{C}_1\text{N}_1)_{\text{MC}_1} \\
 F_{\text{MC}, \text{CN}} &= -F_{\text{MC}}(\text{MC}_1)_{\text{C}_1\text{N}_1} - F_{\text{MC}, \text{MC}'}(\text{MC}_2)_{\text{C}_1\text{N}_1} - F_{\text{MC}, \text{C}'\text{N}'}(\text{C}_2\text{N}_2)_{\text{C}_1\text{N}_1} \\
 &= -F_{\text{CN}}(\text{C}_1\text{N}_1)_{\text{MC}_1} - F_{\text{CN}, \text{C}'\text{N}'}(\text{C}_2\text{N}_2)_{\text{MC}_1} - F_{\text{MC}, \text{C}'\text{N}'}(\text{MC}_2)_{\text{MC}_1} \\
 F_{\text{MC}, \text{C}'\text{N}'} &= -F_{\text{MC}}(\text{MC}_2)_{\text{C}_1\text{N}_1} - F_{\text{MC}, \text{MC}'}(\text{MC}_1)_{\text{C}_1\text{N}_1} - F_{\text{MC}, \text{CN}}(\text{C}_2\text{N}_2)_{\text{C}_1\text{N}_1} \\
 &= -F_{\text{CN}}(\text{C}_2\text{N}_2)_{\text{MC}_1} - F_{\text{CN}, \text{C}'\text{N}'}(\text{C}_1\text{N}_1)_{\text{MC}_1} - F_{\text{MC}, \text{CN}}(\text{MC}_2)_{\text{MC}_1}
 \end{aligned} \quad (9)$$

* In equation 6, $(S_l)_k$ was used for the displacement of coordinate l caused by constraining k to a value of ± 1 from its equilibrium value. Rather than write the cumbersome expression $(S_{\text{C}_1\text{N}_1})_{\text{C}_1\text{N}_1}$, we abbreviate to $(\text{C}_1\text{N}_1)_{\text{C}_1\text{N}_1}$, etc.

The six equations (9) contain six interaction displacement coordinates (S_i)_j. Thus, if we know all the stretching force constants we can calculate the (S_i)_j from these equations. For this purpose we use the values of Table 3. The results are given in Table 4. If the approximate relation (7) is used we arrive at the same values except that $(MC_2)_{C_1N_1} = 0$; thus, (7) is a good approximation for this molecule.

TABLE IV

STRETCHING-INTERACTION DISPLACEMENT COORDINATES FOR $[Au(CN)_2]^-$

$(C_2N_2)_{C_1N_1}$ ^a	0
$(MC_2)_{C_1N_1}$	+0.02
$(MC_1)_{C_1N_1}$	-0.11
$(MC_2)_{MC_1}$	-0.15
$(C_2N_2)_{MC_1}$	0
$(C_1N_1)_{MC_1}$	-0.02

^a The meaning of this term is the "displacement of bond C_2N_2 which minimizes the potential energy after bond C_1N_1 is given a small unit positive displacement."

These quantities in Table 4 are quite interesting. For example, the fact that $(MC_1)_{C_1N_1} = -0.11$ means that if bond C_1N_1 is stretched by a small positive unit amount, bond MC_1 tends to shorten by 0.11 units to minimize the potential energy. This means that stretching C_1N_1 causes a slight rearrangement of electrons which tends to tighten the MC_1 bond. Perhaps the most appealing explanation, which has been put forth many times⁵, is that the metal- d electrons form π bonds to the CN antibonding π orbitals. When the CN bond is stretched these antibonding π orbitals decrease in energy so that a stronger M-CN π bond is formed. This explanation is not unique; further evidence is required to support it or refute it.

(ii) *Bending force constants of $[Au(CN)_2]^-$*

From (6) we can write:

$$\begin{aligned} F_{\beta\beta'} &= -F_{\beta}(\beta_2)_{\beta_1} - F_{\alpha\beta}(\alpha)_{\beta_1} \\ F_{\alpha\beta} &= -F_{\alpha}(\alpha)_{\beta_1}/[1 + (\beta_2)_{\beta_1}] \\ &= -(F_{\beta} + F_{\beta\beta'}) (\beta_1)_{\alpha} \end{aligned} \quad (10)$$

As before $(\beta_1)_{\alpha}$ stands for the displacement of angle β_1 arising from minimization of energy when α is increased by +1 (small unit displacement). When α is increased we expect β_1 and β_2 to decrease slightly in order to equalize the π overlap of the gold- d orbitals with the carbon- π orbitals. If this were the only consideration, to minimize the energy, β_1 and β_2 would each change by about $-\frac{1}{2}$ when α changes by +1. However, the bending of β_1 and β_2 is resisted by the directional forces of the sp σ -bonding system on the carbon atom so we expect $-(\beta_1)_{\alpha}$ to be considerably less than $\frac{1}{2}$. Preliminary calculations show that $F_{\beta} + F_{\beta\beta'}$ is about 0.3 mdynes Å rad⁻². Then from the last of (10) above, $F_{\alpha\beta} = -0.3 (\beta_1)_{\alpha}$. Allowing a generous

range of values for $(\beta_1)_\alpha$ we say $(\beta_1)_\alpha = -0.25 \pm 0.25$ in which case $F_{\alpha\beta} = +0.07 \pm 0.07$ mdynes Å rad⁻². It is probable that a detailed knowledge of the electronic structure would enable one to estimate $(\beta_1)_\alpha$, and thus $F_{\alpha\beta}$, more precisely and thus greatly reduce the limits of uncertainty given in Table 3.

One further consideration helps us to reduce the uncertainties. Let us look again at (10).

As discussed previously $(\beta_1)_\alpha$ should be negative so $F_{\alpha\beta}$ should be positive. From the second of these equations this tells us that $(\alpha)_{\beta_1}$ is also negative. If we choose our maximum value, $F_{\alpha\beta} = +0.14$ mdynes Å rad⁻², then we calculate $(\alpha)_{\beta_1} \approx -0.23$ and $F_{\beta\beta'} = -0.33 (\beta_2)_{\beta_1} + 0.03$. By the arguments presented previously when β_1 is increased, α should decrease slightly and β_2 should then increase, perhaps negligibly. Thus, $(\beta_2)_{\beta_1}$ should have a zero or slightly positive value and $F_{\beta\beta'}$ is limited to the range 0 to $+0.03$ mdynes Å rad⁻². From the value of F_{55} in Table 2, then, $F_\beta = 0.283 \pm 0.019$ and $F_{66} = F_\beta + F_{\beta\beta'} = 0.298 \pm 0.019$. Fixing F_{66} limits the range of F_α and $F_{\alpha\beta}$ and we arrive at the force constants in Table 5.

TABLE V

BENDING FORCE CONSTANTS OF $[\text{Au}(\text{CN})_2]^-$

F_β	0.281 ± 0.019
$F_{\beta\beta'}$	0.015 ± 0.015
F_α	0.65 ± 0.25
$F_{\alpha\beta}$	0.025 ± 0.025

Thus, by a little reasoning concerning the interaction displacements, it has been possible to greatly increase the precision of F_β , $F_{\beta\beta'}$, and $F_{\alpha\beta}$. The large uncertainty in the force constant, F_α , remains because of the uncertainty in the observed frequency, ν_7 .

D. FORCE CONSTANTS FOR MOLECULES WITH REDUNDANT COORDINATES

In order to discuss other complexes, such as $[\text{AuCl}_4]^-$ etc., it is often convenient to use redundant coordinates as mentioned earlier. These are coordinates which are not independent; they occur in sets such that one cannot change one of the coordinates without changing at least one other in the set. As mentioned previously, in this case the first-order coefficients in (1), namely the f_i , are not necessarily zero.

In order to remove the first-order terms in (1) it is necessary to express the redundancy to the second order.

$$\sum a_i S_i + \sum b_{ij} S_i S_j = 0 \quad (11)$$

One can then solve for one of the coordinates in the redundant set in terms of the others as

$$S_k = -\sum_{ij} \frac{b_{ij}}{a_k} S_i S_j - \sum_{i \neq k} \frac{a_i}{a_k} S_i \quad (12)$$

Substitution of (12) into (1), with omission of V_0 and third- and higher-order terms, yields

$$V = \sum_{i \neq k} \left(f_i - \frac{f_k a_i}{a_k} \right) S_i + \frac{1}{2} \sum_{ij} \left(F_{ij} - 2f_k \frac{b_{ij}}{a_k} \right) S_i S_j \quad (13)$$

Now all the S_i in the first-order term are independent, provided all redundancies are removed by equation (12), so

$$\left(\frac{\partial V}{\partial S_i} \right)_0 = 0$$

and thus

$$f_i = \frac{a_i}{a_k} f_k.$$

The potential energy is then

$$V = \frac{1}{2} \sum_{ij} (F_{ij} - f_k B_{ij}) S_i S_j \quad (14)$$

where $B_{ij} = 2b_{ij}/a_k$.

In Eq. (14), for the coefficients of $S_i S_j$, where either S_i or S_j is not involved in the redundancy, $B_{ij} = 0$. This problem is treated in an excellent paper by Crawford and Overend⁶.

For a discussion of the meaning of the force constants involving redundancies it is convenient to break up the potential energy into several terms.

$$\begin{aligned} V = & \frac{1}{2} \sum_{i=1}^{\alpha} F_{ii} S_i^2 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{\alpha} F_{ij} S_i S_j \\ & + \frac{1}{2} \sum_{i=\alpha+1}^{\beta} \bar{F}_{ii} (S_i^R)^2 + \frac{1}{2} \sum_{\substack{i,j=\alpha+1 \\ i \neq j}}^{\beta} \bar{F}_{ij} S_i^R S_j^R \\ & + \frac{1}{2} \sum_{\substack{i=1 \\ j=\alpha+1}}^{\substack{j=\beta \\ i=\alpha}} (F_{ij} + F_{ji}) S_i S_j^R \end{aligned} \quad (15)$$

$\bar{F}_{ii} = F_{ii} - f_k B_{ii}$; $\bar{F}_{ij} = F_{ij} - f_k B_{ij}$ as defined by (14).

The coordinate indices in (15) are ordered so that the non-redundant coordinates run from 1 to α , while the redundant coordinates run from $\alpha+1$ to β . The quantity

β is equal to $3N-6+p$, where p is the number of excess coordinates giving rise to redundancies. The coordinates involved in redundancies are specified by the superscript R .

Again we shall assume a General Quadratic Valence Force Field for which the S_i are changes in bond lengths or changes in angles included by bonds. The first two expressions, not involving redundancies, are the same as in (3). The previous discussion applies here also.

For the force constants of redundant coordinates, such as \bar{F}_{ii} , \bar{F}_{ij} , and F_{ij} , with either i or j from a redundant set [see (15)], the physical meaning of the force constants is less clear. Their interpretation is best discussed for each individual case and this is the approach taken here.

E. POTENTIAL FUNCTION AND FORCE CONSTANTS FOR SQUARE-PLANAR MX_4

This is a fairly-simple molecule and will serve as an example for investigation of the meaning of force constants for redundant coordinates. The valence-type internal coordinates of this D_{4h} molecule are defined in Fig. 2. The potential energy for a General Quadratic Valence Force Field for MX_4 is expressed as

$$\begin{aligned} 2V = & f_a[\alpha_{12} + \alpha_{23} + \alpha_{34} + \alpha_{14}] + F_R(R_1^2 + R_2^2 + R_3^2 + R_4^2) \\ & + 2F_{RR'}(R_1R_2 + R_2R_3 + R_3R_4 + R_1R_4) \\ & + 2F_{RR''}(R_1R_3 + R_2R_4) + F_a(\alpha_{12}^2 + \alpha_{23}^2 + \alpha_{34}^2 + \alpha_{14}^2) \\ & + 2F_{aa'}(\alpha_{12}\alpha_{23} + \alpha_{23}\alpha_{34} + \alpha_{34}\alpha_{14} + \alpha_{14}\alpha_{12}) + 2F_{aa''}(\alpha_{12}\alpha_{34} + \alpha_{14}\alpha_{23}) \\ & + 2F_{Ra'}[R_1(\alpha_{12} + \alpha_{14}) + R_2(\alpha_{12} + \alpha_{23}) + R_3(\alpha_{23} + \alpha_{34}) + R_4(\alpha_{34} + \alpha_{14})] \\ & + 2F_{Ra''}[R_1(\alpha_{23} + \alpha_{34}) + R_2(\alpha_{34} + \alpha_{14}) + R_3(\alpha_{14} + \alpha_{12}) + R_4(\alpha_{12} + \alpha_{23})] \\ & + F_\pi[\pi_{13}^2 + \pi_{24}^2] + 2F_{\pi\pi'}\pi_{13}\pi_{24} \end{aligned} \quad (16)$$

The α_{ij} , R_i , etc., in (16) represent small displacements, $\Delta\alpha_{ij}$ and ΔR_i . The first-order term with coefficient f_a is included because we have a redundancy among the four XMX angles—they are not independent. To the second order the relation among the angles, as derived by the method of Cihla and Pliva⁷, is given by

$$\alpha_{12} + \alpha_{23} + \alpha_{34} + \alpha_{14} + \pi_{13}\pi_{24} = 0 \quad (17)$$

These, again, are short for $\Delta\alpha_i$ and $\Delta\pi_i$. In this case we can eliminate the first-order term in (16) by the substitution

$$\alpha_{12} + \alpha_{23} + \alpha_{34} + \alpha_{14} = -\pi_{13}\pi_{24}$$

This changes the coefficient of $\pi_{13}\pi_{24}$ in Eq. (16) to $2\bar{F}_{\pi\pi} = (2F_{\pi\pi'} - f_a)$; all other quadratic terms remain the same.

The meaning of the force constants can now be discussed for this case.

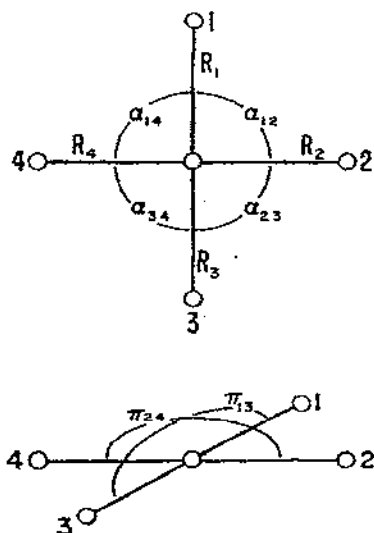


Figure 2. Schematic Representation of Internal Coordinates of Square-Planar MX_4 .

Eq. (16) can be simplified somewhat by making use of the first-order redundancy, $\alpha_{12} + \alpha_{23} + \alpha_{34} + \alpha_{14} = 0$. Thus, we can substitute $-(\alpha_{12} + \alpha_{14})$ for $\alpha_{23} + \alpha_{34}$ (and vice versa) in the $F_{R\alpha}$ terms which then can be collected as $2(F_{R\alpha}' - F_{R\alpha}'')$ $[R_1(\alpha_{12} + \alpha_{14}) + R_2(\alpha_{12} + \alpha_{23}) + R_3(\alpha_{23} + \alpha_{34}) + R_4(\alpha_{34} + \alpha_{14})]$. This shows that $F_{R\alpha}'$ and $F_{R\alpha}''$ cannot be determined by themselves but only as their difference. In fact, it is hard to give a meaning to them individually*. Therefore, the difference is here abbreviated as $H_{R\alpha} = F_{R\alpha}' - F_{R\alpha}''$.

To investigate force constants involving α_{ij} it is necessary to remove the redundancy as we wish to use the relation

$$\left(\frac{\partial V}{\partial \alpha_{kl}} \right)_0 = 0$$

which is true only if the α are independent. This can be done by substituting for $\alpha_{34} = -\alpha_{12} - \alpha_{23} - \alpha_{14}$ in Eq. (16), which then becomes,

$$\begin{aligned} 2V = & F_R(R_1^2 + R_2^2 + R_3^2 + R_4^2) + 2F_{RR}'(R_1R_2 + R_2R_3 + R_3R_4 + R_1R_4) \\ & + 2F_{RR}''(R_1R_3 + R_2R_4) \\ & + 2F_{\alpha\alpha}[\alpha_{12}^2 + \alpha_{23}^2 + \alpha_{14}^2 + \alpha_{12}\alpha_{23} + \alpha_{12}\alpha_{14} + \alpha_{23}\alpha_{14}] \\ & - 2F_{\alpha\alpha}'(\alpha_{23}^2 + \alpha_{14}^2 + 2\alpha_{23}\alpha_{14}) + 2F_{\alpha\alpha}''(\alpha_{14}\alpha_{23} - \alpha_{12}\alpha_{23} - \alpha_{12}\alpha_{14} - \alpha_{12}^2) \\ & + 2H_{R\alpha}[(R_1 - R_3)(\alpha_{12} + \alpha_{14}) + (R_2 - R_4)(\alpha_{12} + \alpha_{23})] \\ & + F_{\pi}(\pi_{13}^2 + \pi_{24}^2) + 2F_{\pi\pi}\pi_{13}\pi_{24} \end{aligned} \quad (18)$$

* Some authors prefer to think of terms like $F_{R\alpha}'$ as an interaction constant which would pertain if the redundancy did not exist. This is somewhat of an artifice but is often necessary if one wishes to transfer force constants from one molecule to another.

All the coordinates in (18) are, of course, displacement coordinates; all are now independent variables.

(i) *Stretching force constants for planar MX₄*

First let us look at F_R . Since all R_i can vary independently,

$$\left(\frac{\partial^2 V}{\partial R_k^2}\right)_0 = F_R,$$

which is then a measure of the force resisting a small displacement (stretching or compressing) of an MX bond from its equilibrium length. Thus, F_R is a measure of the strength of the MX bond at the equilibrium electronic configuration.

To investigate the other constants let us first assume a forced displacement $R_1 = +1$ and follow the procedure of (4), (5), and (6). Thus, +1 is substituted for R_i in (18)*. Then we shall take the partial derivative

$$\begin{aligned} \left(\frac{\partial V}{\partial R_2}\right)_0 = 0 = & F_R(R_2)_{R_1} + F_{RR}'[1 + (R_3)_{R_1}] \\ & + F_{RR}''(R_4)_{R_1} + H_{R\alpha}[(\alpha_{12})_{R_1} + (\alpha_{23})_{R_1}] \end{aligned} \quad (19)$$

By symmetry, when we make $R_1 = +1$

$$(R_2)_{R_1} = (R_4)_{R_1} \text{ and } (\alpha_{12})_{R_1} = (\alpha_{14})_{R_1} = -(\alpha_{23})_{R_1} = -(\alpha_{34})_{R_1} \quad (20)$$

Substituting this in (19) gives

$$F_{RR}' = \frac{-(F_R + F_{RR}'')(R_2)_{R_1}}{1 + (R_3)_{R_1}} \quad (21)$$

Taking the partial,

$$\left(\frac{\partial V}{\partial R_3}\right)_0 = 0$$

leads to

$$F_{RR}'' = -F_R(R_3)_{R_1} - 2F_{RR}'(R_2)_{R_1} + 2H_{R\alpha}(\alpha_{12})_{R_1} \quad (22)$$

In these relations, as before, $(R_i)_{R_j}$ is the change in R_i caused by small positive unit change in R_j , to minimize the potential energy.

(ii) *Stretch-bend interaction constants for planar MX₄*

To derive a relation for $H_{R\alpha}$ we take the partial derivative

* Here again R_i is really ΔR_i and in (19) $(R_2)_{R_1}$ is really $(S_{R_2})_{R_1}$, etc.

$$\left(\frac{\partial V}{\partial \alpha_{12}}\right)_0 = 0$$

after substituting $R_1 = +1$ in (18). Making use of the relations (20) we arrive at the expression

$$H_{R\alpha} = \frac{-2(F_\alpha - F_{\alpha\alpha}'')(\alpha_{12})_{R_1}}{1 - (R_3)_{R_1}} \quad (23)$$

Next we return to (18) and let $\alpha_{12} = +1$. We then take the partial derivatives

$$\left(\frac{\partial V}{\partial R_1}\right)_0 = 0 \quad \text{and} \quad \left(\frac{\partial V}{\partial R_3}\right)_0 = 0.$$

These lead to two relations for $H_{R\alpha}$:

$$H_{R\alpha} = \frac{-F_R(R_1)_{\alpha_{12}} - F_{RR}'[(R_2)_{\alpha_{12}} + (R_4)_{\alpha_{12}}] - F_{RR}''(R_3)_{\alpha_{12}}}{1 + (\alpha_{14})_{\alpha_{12}}} \quad (24)$$

$$H_{R\alpha} = \frac{F_R(R_3)_{\alpha_{12}} + F_{RR}'[(R_2)_{\alpha_{12}} + (R_4)_{\alpha_{12}}] + F_{RR}''(R_1)_{\alpha_{12}}}{1 + (\alpha_{14})_{\alpha_{12}}} \quad (25)$$

For this to be true it is apparent that $(R_3)_{\alpha_{12}} = -(R_1)_{\alpha_{12}}$. It is also obvious from Fig. 2, that $(R_1)_{\alpha_{12}} = (R_2)_{\alpha_{12}}$ and $(R_3)_{\alpha_{12}} = (R_4)_{\alpha_{12}}$. Thus, we have the relation:

$$(R_1)_{\alpha_{12}} = (R_2)_{\alpha_{12}} = -(R_3)_{\alpha_{12}} = -(R_4)_{\alpha_{12}} \quad (26)$$

and

$$H_{R\alpha} = \frac{-(F_R - F_{RR}'')(R_1)_{\alpha_{12}}}{1 + (\alpha_{14})_{\alpha_{12}}} \quad (27)$$

(iii) In-plane bending force constants for MX_4

Now let us take the partial derivative

$$\left(\frac{\partial V}{\partial \alpha_{14}}\right)_0 = 0$$

for (18) with $\alpha_{12} = +1$. Using the fact that $(\alpha_{14})_{\alpha_{12}} = (\alpha_{23})_{\alpha_{12}}$ this leads to the relation

$$F_\alpha - F_{\alpha\alpha}'' = \frac{-4(F_\alpha - F_{\alpha\alpha}')(\alpha_{14})_{\alpha_{12}} - 2H_{R\alpha}(R_1)_{\alpha_{12}}}{1 - (\alpha_{14})_{\alpha_{12}}} \quad (28)$$

F_α always occurs as linear combinations of $F_\alpha - F_{\alpha\alpha}''$ and $F_\alpha - F_{\alpha\alpha}'$. Thus F_α , $F_{\alpha\alpha}'$, and $F_{\alpha\alpha}''$ cannot be determined independently. They have no real meaning individually*.

* Here again one might identify F_α as a hypothetical force constant of α angle bending which would pertain in the absence of the redundancy.

One could also define these combinations as follows [from (16)].

$$\left(\frac{\partial^2 V}{\partial \alpha_{12}^2}\right)_{\substack{\alpha_{23}=0 \\ \alpha_{14}=0 \\ \alpha_{34}=-\alpha_{12}}} = 2(F_\alpha - F_{\alpha\alpha}) \quad (29)$$

$$\left(\frac{\partial^2 V}{\partial \alpha_{23}^2}\right)_{\substack{\alpha_{12}=0 \\ \alpha_{14}=0 \\ \alpha_{34}=-\alpha_{23}}} = 2(F_\alpha - F_{\alpha\alpha}') \quad (30)$$

To summarise this section, the relations among the force constants for square-planar MX_4 are given below.

$$\begin{aligned} F_R &= \left(\frac{\partial^2 V}{\partial R_k^2}\right)_0 \\ F_{RR'} &= \frac{-(F_R + F_{RR'}) (R_2)_{R_1}}{1 + (R_3)_{R_1}} \\ F_{RR''} &= -F_R (R_3)_{R_1} - 2F_{RR'} (R_2)_{R_1} + 2H_{R\alpha} (\alpha_{12})_{R_1} \\ H_{R\alpha} &= \frac{-2(F_\alpha - F_{\alpha\alpha}) (\alpha_{12})_{R_1}}{1 - (R_3)_{R_1}} = \frac{-(F_R - F_{RR'}) (R_1)_{\alpha_{12}}}{1 + (\alpha_{14})_{\alpha_{12}}} \\ F_\alpha - F_{\alpha\alpha} &= \frac{-4(F_\alpha - F_{\alpha\alpha}') (\alpha_{14})_{\alpha_{12}} - 2H_{R\alpha} (R_1)_{\alpha_{12}}}{1 - (\alpha_{14})_{\alpha_{12}}} \end{aligned} \quad (31)$$

In the above, the expression $(q)_{q_j}$ is displacement of coordinate q_i caused by unit positive displacement of coordinate q_j .

The out-of-plane bending constants are not considered here. They do not affect the in-plane vibrations or force constants.

These relations will now be used to discuss the vibrational spectra and force constants of PtCl_4^{2-} , AuCl_4^- , and AuBr_4^- .

F. FORCE CONSTANTS OF PtCl_4^{2-} , AuCl_4^- , AND AuBr_4^-

There are seven different fundamental vibrations for these square-planar MX_4 ions of point group D_{4h} . They are divided among the representations $A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$. For all but the E_u vibrations we can calculate the symmetry force constants of a general quadratic valence force field without any assumptions about the interactions because each representation contains only one vibration. For the E_u vibrations only two frequencies are available to calculate three force constants so some assumptions about the interactions are necessary as will be discussed below.

The Raman-active A_{1g} , B_{1g} , and B_{2g} frequencies have been observed in aqueous solution by Stammreich and Forneris⁸. The infrared-active E_u and A_{2u}

frequencies were observed by Sabatini *et al.*⁹ on nujol mulls and pressed polyethylene disks of solid CsAuCl_4 , RbAuCl_4 , CsAuBr_4 , RbAuBr_4 , Cs_2PtCl_4 , Rb_2PtCl_4 , and K_2PtCl_4 . The results are given in Table 6. For the A_{2u} and E_u vibrations the values reported are averages of the observations for the complex with different cations.

TABLE VI

FREQUENCY ASSIGNMENTS IN cm^{-1} FOR SOME MX_4 COMPLEXES

Assignment ^{a,b}			PtCl_4^{2-}	AuCl_4^-	AuBr_4^-
ν_1	A_{1g}	ν_{MX}	335	347	212
ν_2	B_{1g}	ν_{MX}	304	324	196
ν_3	B_{2g}	δ_{XMX}	164	171	102
ν_4	A_{2u}	π_{XMX}	167	144	—
ν_5	B_{2u}	π_{XMX}	—	—	—
ν_6	E_u	ν_{MX}	320	360	252
ν_7	E_u	δ_{XMX}	189	177	100

^a Column 2 gives the representation and column 3 gives an approximate characterization of the vibration with ν for stretching, δ for in-plane bending, and π for out-of-plane bending.

^b Here the ordering of frequencies and representation nomenclature is different from that in references (8) and (9). In this paper it is arranged to conform to that of Wilson, Decius and Cross [reference 1, page 327].

The B_{2u} vibrations are inactive and were not observed. The assignments of ν_4 and ν_7 are not conclusive; they are based on the expectation that the out-of-plane bending-force constant should be lower than the in-plane bending force constant.

Anharmonicity corrections are not known. However, it has been observed¹⁰ that diatomic molecules containing a halide atom and a heavy metal atom have small anharmonicity*. Thus, the anharmonic corrections are negligible—a few cm^{-1} at the most. Of greater significance is the possible phase shift. Thus, the g frequencies are for aqueous solutions whereas the u frequencies are averages of solid-state spectra. This leads to an uncertainty of several cm^{-1} .

The symmetry force constants are calculated from the frequencies listed in Table 6. The values are given in Table 7. The definition of the various force constants is given in the previous section ((29), (30) and (31)).

In arriving at the values of Table 7 for F_{66} and F_{77} it was necessary to assume values for $H_{R\alpha}$. The following argument was used in arriving at a reasonable range of values. From the approximate value of F_{66} for AuCl_4^- it is apparent that the interaction constant for opposite AuCl bonds ($F_{RR''}$) is about 0.2 mdynes \AA^{-1} and F_R is about 2 mdynes \AA^{-1} . From (22) we have the approximate relation $(R_3)_{R1} \approx -F_{RR''}/F_R \approx -0.1$. This means that if the bond $(\text{AuCl})_1$ is stretched by a small unit displacement, d , the bond $(\text{AuCl})_3$ contracts by about 0.1 d to mini-

* In particular, for AuCl , $\omega_e x_e = 1.3 \text{ cm}^{-1}$ and for AgBr , $\omega_e x_e = 0.7 \text{ cm}^{-1}$ as reported in reference 10, pages 502 and 505.

TABLE VII

FORCE CONSTANTS OF MX_4 IONS

		$PtCl_4^{2-}$	$AuCl_4^-$	$AuBr_4^-$
F_{11}	$F_R + 2F_{RR'} + F_{RR''}$	2.343	2.514	2.115 mdynes \AA^{-1}
F_{22}	$F_R - 2F_{RR'} + F_{RR''}$	2.136	2.192	1.808 mdynes \AA^{-1}
F_{33}	$F_\alpha - 2F_{\alpha\alpha'} + F_{\alpha\alpha''}$	0.770	0.767	0.704 mdynes $\text{\AA} \text{ rad}^{-2}$
F_{44}	$F_\phi + F_{\phi\phi'}$	0.925	0.633	— mdynes $\text{\AA} \text{ rad}^{-2}$
F_{55}	$F_\phi - F_{\phi\phi'}$	—	—	— mdynes $\text{\AA} \text{ rad}^{-2}$
F_{66}	$F_R - F_{RR''}$	1.667 -0.006 -0.060	2.103 $+0.033$ -0.160	1.897 $+0.10$ mdynes \AA^{-1} -0.25
F_{77}	$F_\alpha - F_{\alpha\alpha''}$	1.685 $+0.46$ -0.05	1.358 $+0.34$ -0.05	0.8 $+0.33$ mdynes $\text{\AA} \text{ rad}^{-2}$ -0.03
F_{67}	$\sqrt{2} H_{R\alpha}$	$+0.5 \pm 0.5^a$	$+0.5 \pm 0.5^a$	$+0.5 \pm 0.5^a$ mdynes rad^{-1}

^a This was an assumed reasonable range following arguments given in text.

mize the energy. A look at Fig. 1 suggests that stretching of R_1 and contraction of R_3 would tend to decrease the angle, α_{12} , for more than one reason. First, any repulsion of Cl atoms for each other would lead to this conclusion. In fact, if we maintain the same Cl-Cl distance, we arrive at the conclusion that $(\alpha_{12})_{R_1} \approx -0.25$ radians per Angstrom. Also, if we stretch R_1 , assuming that the bonding electron pair remains primarily with the Cl_1 atom, the *orbital-following* concept¹¹ leads to the prediction that the remaining three bonds would approach a trigonal sp^2 structure and, thus, α_{12} and α_{14} would decrease. It would be difficult to say what the magnitude of $(\alpha_{12})_{R_1}$ would be in this case without further empirical data. However, we would not expect α_{12} to change so much that the Cl_1 - Cl_2 distance becomes less than the Cl_2 - Cl_3 distance when $AuCl_4$ is stretched. Therefore, we take 0.25 as the maximum for $-(\alpha_{12})_{R_1}$. Since $F_\alpha - F_{\alpha\alpha''}$ is around 1.4 mdynes $\text{\AA} \text{ rad}^{-2}$, (23) tells us that $H_{R\alpha} \approx -2.5 (\alpha_{12})_{R_1}$. Thus, $H_{R\alpha} \approx 0.32 \pm 0.32$ or $F_{67} = \sqrt{2} H_{R\alpha} \approx 0.5 \pm 0.5$ mdynes rad^{-1} . Similar arguments apply for $PtCl_4^{2-}$ and $AuBr_4^-$. This reasoning leads to the calculations of Table 7.

It is enlightening to examine the calculations more closely. For this purpose, we give in Table 8 the values calculated for the various valence-force stretching

TABLE VIII

VALENCE STRETCHING CONSTANTS FOR MX_4 IONS

	$H_{R\alpha}^a$	F_R	$F_{RR'}$	$F_{RR''}$
$PtCl_4^{2-}$	0	1.87	0.05	0.37
$AuCl_4^-$	0	2.15	0.08	0.21
$AuBr_4^-$	0	1.80	0.08	0.16
$PtCl_4^{2-}$	0.5	1.95	0.05	0.29
$AuCl_4^-$	0.5	2.23	0.08	0.13
$AuBr_4^-$	0.5	1.93	0.08	0.03
$PtCl_4^{2-}$	1.0	1.95	0.05	0.29
$AuCl_4^-$	1.0	2.24	0.08	0.11
$AuBr_4^-$	1.0	1.98	0.08	-0.02

^a Assumed values.

constants assuming three different values for $H_{R\alpha}$; namely, 0, 0.5, and 1.0 mdynes rad^{-1} . These are calculated from F_{11} , F_{22} , and F_{66} of Table 7. Of particular interest are the opposite bond interactions, $F_{RR'}$, for the AuBr_4^- ion. This value we expect to be *slightly smaller* than that for AuCl_4^- as the vibrations are similar and the AuBr force constant a little smaller than the AuCl force constant. This expectation is born out only for $H_{R\alpha}$ near zero. Thus, the most satisfactory solution is that with $H_{R\alpha} \approx 0$ and the valence force constants are then as in Table 9.

TABLE IX

VALENCE FORCE CONSTANTS OF SOME MX_4 IONS

	PtCl_4^{2-}	AuCl_4^-	AuBr_4^-
F_{MCl}	1.87	2.15	1.80
$F_{\text{MCl, MCl}'}$	0.05	0.08	0.08
$F_{\text{MCl, MCl}''}$	0.37	0.21	0.16
$F_{\alpha} - F_{\alpha\alpha'}$	1.71	1.31	0.77
$F_{\alpha} - F_{\alpha\alpha''}$	1.24	1.04	0.74
$H_{R\alpha}$	0	0	0
$F_{\phi} + F_{\phi\phi'}$	0.925	0.633	—

As expected, the MCl bonds in PtCl_4^{2-} are weaker than the AuCl bonds in AuCl_4^- , yet it is surprising that the opposite bond interaction is stronger for the Pt compound, as is the bending constant. Perhaps this implies weaker MCl σ bonding but an appreciable amount of MCl π bonding for the PtCl_4^{2-} ion. This might also explain the greater out-of-plane bending constant ($F_{\phi} + F_{\phi\phi'}$) for PtCl_4^{2-} .

It is interesting to investigate the interaction displacements which arise from the force constants of Table 9. For example, application of (7) leads to the results of Table 10.

TABLE X

INTERACTION DISPLACEMENTS FOR MX_4

	$(\text{MX}_3)_{\text{MX}_1}^a$ (Opposite bonds)	$(\text{MX}_2)_{\text{MX}_1}$ (adjacent)	$(\alpha_{11})_{\alpha_{12}}$
PtCl_4^{2-}	-0.20	-0.03	-0.38
AuCl_4^-	-0.10	-0.04	-0.36
AuBr_4^-	-0.09	-0.04	-0.34

^a $(\text{MX}_3)_{\text{MX}_1}$ means the displacement of bond MX_3 caused by unit displacement of the opposite bond, MX_1 . $(\text{MX}_2)_{\text{MX}_1}$ is the analogous term for adjacent bonds.

Application of the more exact equations, (21) and (22), leads to the same values for $(\text{MX}_3)_{\text{MX}_1}$ but slightly smaller values for $(\text{MX}_2)_{\text{MX}_1}$. If we accept the conclusion that $H_{R\alpha} = 0$, it follows from equations (23) and (27) that $(\alpha_{12})_{R_1} = (R_1)\alpha_{12} = 0$.

From (28) we can investigate the displacement term $(\alpha_{14})_{a_{12}}$. With $H_{R_{\alpha}} = 0$, (28) can be rearranged to give

$$(\alpha_{14})_{a_{12}} = \frac{F_{\alpha} - F_{\alpha\alpha'}}{(F_{\alpha} - F_{\alpha\alpha'}) - 4(F_{\alpha} - F_{\alpha\alpha'})}$$

The values of Table 9 then give the displacements in the last column of Table 10. The results for $(\alpha_{14})_{a_{12}}$ are interesting in that they are close to the value of $-1/3$ which would pertain if no α, α -interactions occur other than the redundancy.

The results for AuCl_4^- are of value in the treatment of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ to follow.

TABLE XI

FUNDAMENTAL FREQUENCIES IN cm^{-1} FOR $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

A_{1g}	$\nu_1(\nu_{\text{CN}})^a$	2199	B_{2u}	$\nu_{10}(\nu_{\text{CN}})$	2181
	$\nu_2(\nu_{\text{MC}})$	461		$\nu_{11}(\nu_{\text{MC}})$	430
	$\nu_3(\nu_{\text{MX}})$	342		$\nu_{12}(\delta_{\text{XMC}})$	126
B_{1g}	$\nu_4(\delta_{\text{MCN}})$	[368] ^b	B_{3u}	$\nu_{13}(\nu_{\text{MX}})$	364
	$\nu_5(\delta_{\text{XMC}})$	126		$\nu_{14}(\delta_{\text{MCN}})$	456
B_{2g}	$\nu_6(\pi_{\text{MCN}})$	297		$\nu_{15}(\delta_{\text{XMC}})$	[97] ^c
B_{1u}	$\nu_7(\pi_{\text{MCN}})$	—			
	$\nu_8(\pi_{\text{CMC}})$	—			
	$\nu_9(\pi_{\text{XMX}})$	—			

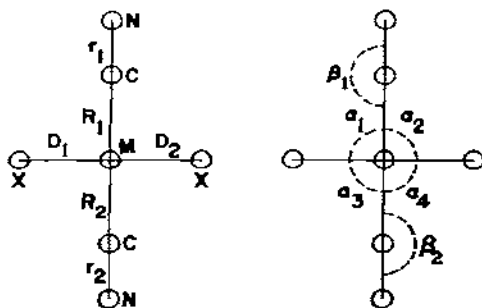
^a Approximate description of vibration; ν for stretching, δ for in-plane bending, π for out-of-plane bending.

^b From a combination band.

^c Not observed. Calculated assuming $F_{\text{XMC}B_{2u}} = F_{\text{XMC}B_{3u}}$.

G. FORCE CONSTANTS OF $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

The fifteen fundamental vibrations of the planar $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ ion of D_{2h} symmetry fall in the representations $3A_{1g} + 2B_{1g} + B_{3g} + 3B_{1u} + 3B_{2u} + 3B_{3u}$. Most of the fundamental frequencies have been assigned¹². They are repeated in Table 11 for convenience. A schematic diagram of the structure is shown in Fig. 3.

Figure 3. Schematic diagram of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$.

(i) A_{1g} Vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

The different symmetry blocks will be treated separately. For the $3A_{1g}$ frequencies there are six symmetry force constants¹³ for the general quadratic valence-force field.

$$\begin{aligned} F_{11} &= F_{\text{CN}} + F_{\text{CN}, \text{C}'\text{N}'} \\ F_{22} &= F_{\text{MC}} + F_{\text{MC}, \text{MC}'} \\ F_{33} &= F_{\text{MX}} + F_{\text{MX}, \text{MX}'} \\ F_{12} &= F_{\text{MC}, \text{CN}} + F_{\text{MC}, \text{C}'\text{N}'} \\ F_{13} &= 2F_{\text{CN}, \text{MX}} \\ F_{23} &= 2F_{\text{MC}, \text{MX}} \end{aligned} \quad (32)$$

(the X stands for halogen atom)

Calculations were made on an IBM 7094 computer*. In order to make these calculations it is necessary to assume values, or ranges of values, for three of the force constants. The approach used here involves an estimation of a reasonable range for the three interaction constants followed by calculation of the primary force constants for this range of interaction constants.

From a study³ of the isotopically enriched ^{13}C and ^{15}N species of $\text{KAu}(\text{CN})_2$ it was found that for the $[\text{Au}(\text{CN})_2]^-$ ion, $F_{\text{MC}, \text{CN}} = 0.3 \pm 0.1$ mdynes \AA^{-1} while $F_{\text{MC}, \text{C}'\text{N}'} = 0.0 \pm 0.1$ mdynes \AA^{-1} . However, for $\text{Hg}(\text{CN})_2$ it was found¹⁴ that $F_{\text{MC}, \text{CN}} = 0.05 \pm 0.1$ mdynes \AA^{-1} and $F_{\text{MC}, \text{C}'\text{N}'} = 0.0 \pm 0.1$ mdynes \AA^{-1} . Probably the $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ ion is more like $\text{Hg}(\text{CN})_2$ than $[\text{Au}(\text{CN})_2]^-$ with respect to MC, CN interactions as the AuC bond in $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ appears to have strong σ -bond character with very little M-CN π bonding as in $\text{Hg}(\text{CN})_2$. In $[\text{Au}(\text{CN})_2]^-$ much greater metal-cyanide π bonding is present⁵. For these calculations we shall allow for this uncertainty and consider the range $F_{\text{MC}, \text{CN}} = 0.2 \pm 0.2$ mdynes \AA^{-1} .

Since $F_{\text{MC}, \text{C}'\text{N}'}$ is much smaller than $F_{\text{MC}, \text{CN}}$ for $[\text{Au}(\text{CN})_2]^-$ it seems appropriate to assume that the same holds true for $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$. In fact, since we do not expect much Au-CN π -bonding, it is expected that a change in C_2M arising from a change in C_1N_1 is effected through the change in C_1M . Thus, $(C_2M)_{C_1N_1} = (C_1M)_{C_1N_1} \cdot (C_2M)_{C_1M}$. With (7) this leads to the approximate relation $F_{\text{MC}, \text{C}'\text{N}'} = -F_{\text{MC}, \text{MC}'} F_{\text{MC}, \text{CN}} / F_{\text{MC}}$. The force constants $F_{\text{MC}, \text{MC}'}$ and F_{MC} were previously determined¹² to be about 0.6 mdynes \AA^{-1} and 2.9 mdynes \AA^{-1} , respectively. These values lead to the relations:

$$F_{\text{MC}, \text{C}'\text{N}'} = -0.2 F_{\text{MC}, \text{CN}}$$

and

$$F_{12} = 0.8 F_{\text{MC}, \text{CN}} = 0.16 \pm 0.16 \text{ mdynes } \text{\AA}^{-1}.$$

* The author is extremely grateful to Dr. J. H. Schachtschneider of the Shell Development Co., Emeryville, California, for supplying the eigenvalue program for these calculations.

Now consider F_{13} which is $2 F_{MX,CN}$. This is an interaction of a CN bond with a non-connected MX bond at right angles. Since $F_{MC,C'N'}$ is small we expect $F_{MX,CN}$ to be even smaller as bonds at 90° generally show less interaction than bonds at 180° to each other. Furthermore, calculations show that the other force constants are quite insensitive to $F_{MX,CN}$. Thus, even if it is as much as ± 0.2 mdynes \AA^{-1} it does not appreciably affect the other calculated F_{ij} .

Finally consider $F_{23} = 2 F_{MX,MC}$. This interaction is again for bonds at right angles though they both involve the same atom, M. From $[\text{Au}(\text{CN})_4]^-$ studies¹² it was found that $F_{MC,MC}$ for interaction of AuC bonds at 90° was about $+0.035$ mdynes \AA^{-1} . We shall then assume a maximum of $+0.04$ mdynes \AA^{-1} for $F_{MX,MC}$.

Using the above ranges of interaction constants we calculate the ranges of force constants given in Table 12.

TABLE XII

CALCULATED^a A_{1g} FORCE CONSTANTS FOR $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

$$F_{11} = F_{CN} + F_{CN,C'N'} = 17.55 \pm 0.19 \text{ mdynes } \text{\AA}^{-1}$$

$$F_{22} = F_{MC} + F_{MC,MC'} = 3.40 \pm 0.05$$

$$F_{33} = F_{MX} + F_{MX,MX'} = 2.46 \pm 0.02$$

^a Assuming $F_{12} = +0.16 \pm 0.16$ mdynes \AA^{-1} ; $F_{13} = 0 \pm 0.2$ mdynes \AA^{-1} ; $F_{23} = 0.04 \pm 0.04$ mdynes \AA^{-1} as discussed in text. The range ± 0.2 for F_{13} is much larger than reasonable—it should be smaller than F_{23} ; however, as mentioned in the text, in this range F_{13} has negligible effect on the other force constants.

(ii) B_{1g} Vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

There are two B_{1g} frequencies determined by the three general quadratic valence-force constants

$$F_{44} = F_\beta + F_{\beta\beta}'$$

$$F_{55} = (F_\alpha - F_{\alpha\alpha}') + (F_\alpha - F_{\alpha\alpha}'') - (F_\alpha - F_{\alpha\alpha}''')$$

$$F_{45} = F_{\alpha\beta}' + F_{\alpha\beta}''$$

where the β are in-plane MCN angles and the α are CMCl angles. There is really no evidence at present for an estimate of the magnitude of $F_{\alpha\beta}'$ and $F_{\alpha\beta}''$. A treatment similar to that of (19)–(22) leads to the conclusion that

$$\begin{aligned} F_{\alpha\beta}' &\approx -\frac{3}{2}F_\beta(\beta_1)_{\alpha_1} \\ F_{\alpha\beta}'' &\approx -\frac{3}{2}F_\beta(\beta_2)_{\alpha_1} \end{aligned} \quad (34)$$

From an inspection of Fig. 2 one would predict that increasing α_1 might lead to a small decrease in β_1 to maintain equal overlap of the π orbitals of Au and C_1 . A similar argument was discussed previously for octahedral $\text{X}(\text{YZ})_6$ molecules¹⁵ and earlier in this paper for $[\text{Au}(\text{CN})_2]^-$. The change $(\beta_2)_{\alpha_1}$ should be smaller

and of opposite sign than $(\beta_1)_{\alpha_1}$. We shall arbitrarily say $(\beta_1)_{\alpha_1} = 0$ to -0.4 and $(\beta_2)_{\alpha_1} = 0$ to $+0.2$. Since F_β is about 0.4 this leads to:

$$F_{\alpha\beta}' = +0.06 \pm 0.06$$

$$F_{\alpha\beta}'' = -0.03 \pm 0.03$$

$$F_{45} = F_{\alpha\beta}' + F_{\alpha\beta}'' = 0.03 \pm 0.03 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$$

We then calculate the force constants of Table 13.

TABLE XIII

B_{1g} FORCE CONSTANTS^a OF $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$
(in mdynes $\text{\AA} \text{ rad}^{-2}$)

$$F_{44} = F_\beta + F_{\beta\beta}' = 0.33 \pm 0.04$$

$$F_{55} = (F_\alpha - F_{\alpha\alpha}') + (F_\alpha - F_{\alpha\alpha}'') - (F_\alpha - F_{\alpha\alpha}''') = 0.52 \begin{matrix} +0.06 \\ -0.04 \end{matrix}$$

Calculated assuming $F_{45} = 0.03 \pm 0.03$.

(iii) B_{2u} Frequencies of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

As listed in Table 11 there are three B_{2u} frequencies which determine the six B_{2u} force constants

$$\begin{aligned} F_{10,10} &= F_{\text{CN}} - F_{\text{CN},\text{CN}'} \\ F_{11,11} &= F_{\text{MC}} - F_{\text{MC},\text{MC}'} \\ F_{12,12} &= (F_\alpha - F_{\alpha\alpha}'') + (F_\alpha - F_{\alpha\alpha}''') - (F_\alpha - F_{\alpha\alpha}') \\ F_{10,11} &= F_{\text{MC},\text{CN}} - F_{\text{MC},\text{CN}'} \\ F_{10,12} &= 2(F_{\text{CN},\alpha}' - F_{\text{CN},\alpha}'') = 2H_{\text{CN},\alpha} \\ F_{11,12} &= 2(F_{\text{MC},\alpha}' - F_{\text{MC},\alpha}'') = 2H_{\text{MC},\alpha} \end{aligned} \quad (35)$$

The discussion of A_{1g} frequencies leads, for consistency, to the relation

$$F_{10,11} = +0.24 \pm 0.24 \text{ mdynes } \text{\AA}^{-1}$$

Analogous to (23) we find

$$\begin{aligned} H_{\text{CN},\alpha} &= \\ &= \frac{-2[F_\alpha + F_{\alpha\alpha}' - F_{\alpha\alpha}'' - F_{\alpha\alpha}'''](\alpha_1)_{\text{C}_1\text{N}_1} - H_{\text{MC},\alpha}[(\text{MC}_1)_{\text{C}_1\text{N}_1} - (\text{MC}_2)_{\text{C}_1\text{N}_1}]}{1 - (\text{C}_2\text{N}_2)_{\text{C}_1\text{N}_1}} \end{aligned} \quad (36)$$

$$\begin{aligned} H_{\text{MC},\alpha} &= \\ &= \frac{-2[F_\alpha + F_{\alpha\alpha}' - F_{\alpha\alpha}'' - F_{\alpha\alpha}'''](\alpha_1)_{\text{MC}_1} - H_{\text{CN},\alpha}[(\text{C}_1\text{N}_1)_{\text{MC}_1} - (\text{C}_2\text{N}_2)_{\text{MC}_1}]}{1 - (\text{MC}_2)_{\text{MC}_1}} \end{aligned} \quad (37)$$

We can estimate many of these displacement coordinates from other interaction constants. For example, we know¹² $F_{\text{MC},\text{MC}'} \approx 0.6$, $F_{\text{CN},\text{CN}'} \approx -0.03$, $F_{\text{MC},\text{CN}} \approx$

0.2 ± 0.2 , $F_{MC,CN'} \approx -0.04 \pm 0.04$, $F_{MC} \approx 2.9$, and $F_{CN} \approx 17.4$ mdynes \AA^{-1} . Use of (7) with these numbers gives the following results:

$$(MC_1)_{C_1N_1} = -0.07$$

$$(MC_2)_{C_1N_1} = +0.014$$

$$(C_2N_2)_{C_1N_1} = -0.002$$

$$(C_1N_1)_{MC_1} = -0.011$$

$$(C_2N_2)_{MC_1} = +0.002$$

$$(MC_2)_{MC_1} = -0.21$$

Substitution of these values into (36) and (37) leads to the equations

$$H_{CN,\alpha} = -2 \tilde{F}_\alpha(\alpha_1)_{C_1N_1} + 0.084 H_{MC,\alpha} \quad (38)$$

$$H_{MC,\alpha} = -1.7 \tilde{F}_\alpha(\alpha_1)_{MC_1} + 0.01 H_{CN,\alpha} \quad (39)$$

where $\tilde{F}_\alpha = F_\alpha + F_{\alpha\alpha}' - F_{\alpha\alpha}'' - F_{\alpha\alpha}'''$

Thus, it appears to be a good approximation to say

$$\begin{aligned} H_{CN,\alpha} &= -2 \tilde{F}_\alpha(\alpha_1)_{C_1N_1} \\ H_{MC,\alpha} &= -1.7 \tilde{F}_\alpha(\alpha_1)_{MC_1} \end{aligned} \quad (40)$$

Stretching C_1N_1 would tend to compress MC_1 thus increasing α_1 . This is a second-order effect so we expect $(\alpha_1)_{C_1N_1}$ to be quite small. Furthermore, if $H_{CN,\alpha}$ is assigned a value as large as 0.2, it has negligible effect on the other force constants.

As discussed previously, in the section on $AuCl_4^-$, stretching MC_1 should cause α_1 to decrease. The magnitude of $(\alpha_1)_{MC_1}$ is quite uncertain. However, for $AuCl_4^-$ the analogous term, $(\alpha_1)_{MCl_2}$, is apparently close to zero. This is based on one piece of evidence so may be subject to doubt, but certainly the results indicate it is small. We shall somewhat arbitrarily adopt a range of about 0.2 ± 0.2 for $H_{MC,\alpha}$ and a smaller range for $H_{CN,\alpha}^*$.

$$F_{10,12} = \sqrt{2} H_{CN,\alpha} = 0 \pm 0.1 \text{ mdynes rad}^{-1}$$

$$F_{11,12} = \sqrt{2} H_{MC,\alpha} = 0.3 \pm 0.3 \text{ mdynes rad}^{-1}$$

The B_{2u} force constants calculated from these ranges of interaction constants are given in Table 14.

TABLE XIV

B_{2u} FORCE CONSTANTS^a OF $[Au(CN)_2Cl_2]^-$

$F_{10,10} = F_{CN} - F_{CN,CN'}$	$17.67 \pm 0.30 \text{ mdynes } \text{\AA}^{-1}$
$F_{11,11} = F_{MC} - F_{MC,MC'}$	$2.35 \pm 0.09 \text{ mdynes } \text{\AA}^{-1}$
$F_{12,12} = (F_\alpha - F_{\alpha\alpha}') + (F_\alpha - F_{\alpha\alpha}'') - (F_\alpha - F_{\alpha\alpha}')$	$0.71 \pm 0.06 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$

^a These force constants are calculated assuming $F_{10,11} = 0.24 \pm 0.24 \text{ mdynes } \text{\AA}^{-1}$, $F_{10,12} = 0 \pm 0.1 \text{ mdynes rad}^{-1}$; $F_{11,12} = 0.3 \pm 0.3 \text{ mdynes rad}^{-1}$.

* It is interesting to note from (38) that even if $(\alpha_1)_{C_1N_1}$ is zero, $H_{CN,\alpha}$ is not necessarily zero, though it will certainly be quite small.

(iv) B_{3u} Vibrations of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

There are three B_{3u} vibrations as seen in Table 6. The B_{3u} C≡C bending frequency was not observed. For purposes of calculation we have fixed the force constant for this frequency at $0.6 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$ which is a rough average of the other α bending force constants, F_{55} and $F_{12,12}$. The symmetry force constants are given by

$$\begin{aligned} F_{13,13} &= F_{\text{MX}} - F_{\text{MX},\text{MX}}' \\ F_{14,14} &= F_{\beta} - F_{\beta\beta}' \\ F_{15,15} &= (F_{\alpha} - F_{\alpha\alpha}') + (F_{\alpha} - F_{\alpha\alpha}'') - (F_{\alpha} - F_{\alpha\alpha}''') \\ F_{13,14} &= 2 F_{D\beta}' \\ F_{13,15} &= \sqrt{2} H_{D\alpha} \\ F_{14,15} &= \sqrt{2} (F_{\alpha\beta}' - F_{\alpha\beta}'') \end{aligned} \quad (41)$$

Using (6) one can derive the relation

$$F_{D\beta}' = \frac{-(F_{\beta} - F_{\beta\beta}')(\beta_1)_{D_1} + 2(F_{\alpha\beta}' - F_{\alpha\beta}'')(\alpha_1)_{D_1}}{1 - (D_2)_{D_1}} \quad (42)$$

When AuCl_1 is stretched ($D_1 = +1$) we expect α_1 to decrease. For AuCl_4^- we found that this change was quite small. As with $(\alpha_1)_R$ (see B_{2u} section) we shall allow a range of values from 0 to -0.15 for $(\alpha_1)_{D_1}$. The quantity $(D_2)_{D_1}$ is approximately $-F_{DD}/F_D \approx -0.1$. From our discussion of the B_{1g} frequencies of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ we decided $F_{\alpha\beta}' = +0.06 \pm 0.06$ and $F_{\alpha\beta}'' = -0.03 \pm 0.03$. This leads to $F_{\alpha\beta}' - F_{\alpha\beta}'' = 0.09 \pm 0.09$. $F_{\beta} - F_{\beta\beta}'$ is approximately 0.4. Inserting into (42) leads to $F_{D\beta}' = -0.4(\beta_1)_{D_1} - 0.012 \pm 0.012$.

The decrease in α_1 arising from $D_1 = +1$ should result in a slight increase in β_1 . However, this is a second-order effect so that we expect $(\beta_1)_{D_1}$ to be quite small though positive. We shall adopt a range for $F_{D\beta}'$ of $-0.02 \pm 0.02 \text{ mdynes rad}^{-1}$, and $F_{13,14} = 2 F_{D\beta}' = -0.04 \pm 0.04 \text{ mdynes rad}^{-1}$.

For (AuCl, α) interaction one can derive the relation

$$H_{D\alpha} = \frac{-2[F_{\alpha} - F_{\alpha\alpha}' - F_{\alpha\alpha}'' + F_{\alpha\alpha}'''](\alpha_1)_{D_1} - 2[F_{\alpha\beta}' - F_{\alpha\beta}''](\beta_1)_{D_1}}{1 - (D_2)_{D_1}} \quad (43)$$

If we again say $(\alpha_1)_{D_1} = -0.075 \pm 0.075$ radians per angstrom, (43) leads to $H_{D\alpha} = 0.1 \pm 0.1 \text{ mdynes rad}^{-1}$ and $F_{13,15} = \sqrt{2} H_{D\alpha} = 0.15 \pm 0.15 \text{ mdynes rad}^{-1}$.

As discussed above we assign the range $F_{\alpha\beta}' - F_{\alpha\beta}'' = 0.09 \pm 0.09 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$. Therefore,

$$F_{14,15} = \sqrt{2}(F_{\alpha\beta}' - F_{\alpha\beta}'') = 0.13 \pm 0.13 \text{ mdynes } \text{\AA} \text{ rad}^{-2}$$

TABLE XV

 B_{22} FORCE CONSTANTS^a FOR $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

$F_{13, 13} = F_{\text{MCl}} - F_{\text{MCl}, \text{MCl}'}$	2.21 ± 0.20 mdynes \AA^{-1}
$F_{14, 14} = F_{\beta} - F_{\beta\beta'}$	0.54 ± 0.10 mdynes $\text{\AA} \text{ rad}^{-2}$

^a Calculated assuming $F_{12, 12} = 0.04 \pm 0.04$ mdynes rad^{-1} ; $F_{13, 14} = 0.15 \pm 0.15$ mdynes rad^{-1} ; $F_{14, 15} = 0.13 \pm 0.13$ mdynes $\text{\AA} \text{ rad}^{-2}$; and $F_{15, 16} = 0.6$ mdynes $\text{\AA} \text{ rad}^{-2}$.

With these ranges of interaction constants, the calculated primary-force constants are as given in Table 15.

From Tables 12–15 we can now calculate the individual valence force constants. The results are summarized in Table 16.

The uncertainties in F_{CN} , F_{MC} , and $F_{\text{MC}, \text{MC}'}$ depend primarily on the MC, CN interactions. Hopefully $F_{\text{MC}, \text{CN}}$ and $F_{\text{MC}, \text{C}'\text{N}'}$ can be determined to 0.1 mdynes \AA^{-1} from studies of the ^{13}C and ^{15}N species. This would reduce the uncertainty in F_{CN} to about 0.12 mdynes \AA^{-1} or 0.7%.

TABLE XVI

VALENCE FORCE CONSTANTS OF $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$

Assumed ^a		Calculated	
$F_{\text{MC}, \text{CN}}$	0.2 ± 0.2 mdynes \AA^{-1}	F_{CN}	17.61 ± 0.25 mdynes \AA^{-1}
$F_{\text{MC}, \text{C}'\text{N}'}$	-0.04 ± 0.04	F_{MC}	2.88 ± 0.08
$F_{\alpha\beta'}$	0.06 ± 0.06 mdynes $\text{\AA} \text{ rad}^{-2}$	F_{MCl}	2.34 ± 0.12
$F_{\alpha\beta''}$	-0.03 ± 0.03	$F_{\text{CN}, \text{C}'\text{N}'}$	-0.06 ± 0.25
$H_{\text{CN}, \alpha}$	0 ± 0.07 mdynes rad^{-1}	$F_{\text{MC}, \text{MC}'}$	0.53 ± 0.07
$H_{\text{MC}, \alpha}$	0.2 ± 0.2	$F_{\text{MCl}, \text{MCl}'}$	0.13 ± 0.11
$F_{\text{MCl}, \beta}$	-0.012 ± 0.012	F_{β}	0.44 ± 0.07 mdynes $\text{\AA} \text{ rad}^{-2}$
$H_{\text{MCl}, \alpha}$	0.1 ± 0.1	$F_{\beta\beta'}$	-0.11 ± 0.08
		$F_{\alpha} - F_{\alpha\alpha''}$	0.62 ± 0.06
		$F_{\alpha\alpha''} - F_{\alpha\alpha'}$	0.10 ± 0.05

^a See text for argument.

The most discouraging result is that for the MCl force constants, particularly for MCl, MCl' interaction. This depends primarily on the value chosen for $H_{\text{MCl}, \alpha}$. However, $F_{\text{AuCl}, \text{AuCl}'}$ can be narrowed down somewhat. For AuCl_4^- the corresponding opposite interaction constant had a minimum value of 0.11 mdynes \AA^{-1} (see Table 3), with a probable value of 0.2 mdynes \AA^{-1} . Since the structure of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ is similar to that of AuCl_4^- we expect similar $\text{AuCl}, \text{AuCl}'$ interaction. Thus it is probably appropriate to limit this interaction to the range

$$F_{\text{AuCl}, \text{AuCl}'} = 0.15 \pm 0.05 \text{ mdynes } \text{\AA}^{-1}$$

This would narrow down the range for the primary AuCl force constant to

$$F_{\text{AuCl}} = 2.31 \pm 0.07 \text{ mdynes } \text{\AA}^{-1}$$

A comparison of these AuCl stretching constants with those of Table 9 shows that the AuCl bond is slightly stronger in $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ than in AuCl_4^- . Also, it is apparent from Tables 16 and 9 that it is easier to bend a ClAuC angle of $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ than to bend a ClAuCl angle of AuCl_4^- .

When more molecules of the same type are studied and their interatomic forces are analyzed it should be possible to narrow down the range of values for some of these interactions. Hopefully it will also be possible to predict from a knowledge of electronic structure and bonding what the interactions will be among the various coordinates. Thus, some day it may be possible to predict fairly accurately how the Cl_1MC_1 angle will change when the Cl_1M bond is given a small unit displacement.

Detailed calculations on ranges of force constants for $[\text{Au}(\text{CN})_4]^-$ have not been made. They are more complicated as there are four frequencies in the E_u symmetry block. However, a comparison of Table 16 with previous results¹² on $[\text{Au}(\text{CN})_4]^-$ shows that within our limits of uncertainty we cannot determine any difference in corresponding force constants. Thus, the MCN bonding in $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ and $[\text{Au}(\text{CN})_4]^-$ is essentially the same.

In this study we have neglected anharmonicity corrections. These are, as discussed for AuCl_4^- and $[\text{Au}(\text{CN})_2]^-$, no doubt quite small except for the CN-stretching vibrations. From observed combination bands it is apparent that the true ω for the CN-stretching vibrations may be 30 cm^{-1} higher than given in Table 6. The net effect would be to raise the calculated CN-stretching force constant by about 2.7% (to $18.09\text{ mdyne } \text{\AA}^{-1}$). However, as discussed in the section on $[\text{Au}(\text{CN})_2]^-$, until we can determine the anharmonicity better, it is perhaps wiser to neglect it and recognize that the calculated force constants are for the observed fundamental frequencies. Hopefully the anharmonic corrections will some day be shown to be similar for different cyanide complexes and comparisons of CN-stretching force constants among different complexes without the anharmonic corrections will be proven to be valid.

H. SUMMARY

The first part of this paper explains the meaning of force constants for a General Quadratic Valence Force Field in which all displacement coordinates are independent. This is followed by a detailed treatment of the force constants of the linear complex ion, $[\text{Au}(\text{CN})_2]^-$. In particular it is shown how the interaction constants are related to changes in bond lengths or bond angles arising from changes in other bond lengths or bond angles. Such changes, here called "interaction coordinates", are related to the electronic structure. They are interesting quantities for correlation with bonding properties.

For most coordination compounds there are sets of coordinates which are

not independent among themselves (called redundant coordinates). The rather obscure meaning of force constants involving redundancies is discussed after the treatment of $[\text{Au}(\text{CN})_2]^-$. Following this discussion, calculated ranges of force constants are given for PtCl_4^{2-} , AuCl_4^- , and AuBr_4^- . These are based on ranges of certain interaction constants estimated from the $\text{Au}(\text{CN})_2^-$ studies and from our knowledge of molecular orbitals. By noting that AuCl_4^- and AuBr_4^- are no doubt similar in bonding properties it is shown that it is possible to narrow down the reasonable ranges of force constants.

Some of the force constants are comparable among the different species. These are listed in Table 17. It is seen that the CN-stretching force constant, F_{CN} , is about the same for the two trivalent gold complexes, $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ and $[\text{Au}(\text{CN})_4]^-$, but definitely lower for $[\text{Au}(\text{CN})_2]^-$. However, the AuC bond is

TABLE XVII

Force constant ^a	$[\text{Au}(\text{CN})_2]^-$	$[\text{AuCl}_4]^-$	$[\text{Au}(\text{CN})_2\text{Cl}_2]^-$	$[\text{Au}(\text{CN})_4]^-$ ¹²
F_{CN}	17.17 ± 0.18		17.61 ± 0.25	~ 17.5
F_{MC}	2.775 ± 0.025		2.88 ± 0.08	~ 2.8
F_{MCl}		2.18 ± 0.03	2.31 ± 0.07	
$F_{\text{MC, MC}}^{\text{b}}$	0.415 ± 0.025		0.53 ± 0.07	~ 0.57
$F_{\text{MC, CN}}$	0.3 ± 0.15			
$F_{\text{MCl, MCl}}^{\text{b}}$		0.2	0.15	
F_{ClAuCl}		~ 1		
F_{ClAuC}			~ 0.6	
F_{CAuC}	0.65 ± 0.25			~ 0.5
F_{NCM}	0.28 ± 0.02		0.44 ± 0.07	~ 0.45

^a The CN, CN interactions are essentially zero and are thus not listed. The other constants not listed occur only in one species.

^b The double prime refers to opposite bond interactions.

about the same strength for all three CN species. This suggests that the trivalent gold complexes have stronger Au-C σ bonds but weaker AuC π bonds. The AuC π bonds tend to lower the CN force constant by using the antibonding CN orbitals. This argument has been given before⁵ in explaining the data for $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ which apparently have similar metal-carbon bond strengths, though F_{CN} is much lower for the iron complex. The opposite MC, MC interaction is definitely greater for the trivalent gold complexes even though the M-C π bonding is less than for $[\text{Au}(\text{CN})_2]^-$. Thus, the magnitude of the MC, MC opposite bond interaction is not dependent primarily on the strength of MC π bonding.

The AuCl bond strength is perhaps somewhat greater for $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ than for AuCl_4^- though the difference is barely significant. Thus, the evidence suggests very little change in bonding to the gold atom from AuCl_4^- to $[\text{Au}(\text{CN})_2\text{Cl}_2]^-$ to $[\text{Au}(\text{CN})_4]^-$.

It is interesting that it appears to require considerably more force to bend a ClAuCl angle of AuCl_4^- than to bend a CAuC angle of $[\text{Au}(\text{CN})_4]^-$. The ClAuC bending force constant lies in between the other two.

The results of this article show that considerable uncertainties exist in most force-constant calculations. Often quite arbitrary assumptions are made concerning interaction constants. It is hoped that more authors will consider the effects of interaction constants within reasonable ranges now that good computer programs are available. The resulting force constants, when reliable, are quite important for correlation with electronic structure and the nature of bonding.

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