

ion lone pairs. Linear I-I-O sequences with  $I_2$  bonds lengthened by complexation, as are commonly found in halogen ( $X_2$ ) charge-transfer complexes, occur here. The hope of finding the geometry of a sorbed molecule altered by sorption, perhaps so as to indicate the mechanism of a catalytic process or the electronic basis of sorption, is realized in this complex.

### Concluding Remarks

The reader has noted, perhaps with some impatience, that only a few of the many available ions have been studied, and that only a few of the available molecules have been sorbed onto these zeolites. In some cases problems in exchange or sorption have

prevented further work, but many combinations remain to be studied at various cation and sorbate compositions, pressures, and temperatures, as interest in new problems develops. Reduced metal ions, and perhaps clusters of metal atoms, may be studied inside zeolites. In the general sense, the choice of zeolite framework and composition are other variables, although, as discussed earlier, imprudent choices may lead to poor results.

Zeolites are widely appreciated for their many uses. The basis for this utility, their remarkable intravoid chemistry, is just beginning to be understood, as is their capacity to teach us about unusual interactions of interest far beyond their own realm.

## Interpretation of Potential Constants: Application to Study of Bonding Forces in Metal Cyanide Complexes and Metal Carbonyls

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A clear understanding of the interatomic forces in molecules and complex ions, as well as the weaker crystal-lattice forces in solids, is of fundamental importance to chemists. While there are several experimental methods which help clarify our concepts of bonding, few probe interatomic forces directly.

Vibrational spectra, as observed by infrared absorption and Raman scattering, are direct manifestations of these forces. Interatomic forces can be expressed as force constants (or compliance constants, which may be more appropriate in some cases) which determine the vibrational frequencies of the system.

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Observation and correct interpretation of the vibrational frequencies, using infrared and Raman spectroscopy, can lead to an evaluation of the force constants which describe the details of bonding forces.

As a simple example, let us consider a diatomic molecule, AB. The force resisting distortion from the equilibrium bond length can, in general, be expressed as a power series in the displacement from equilibrium,  $X = R - R_e$ :  $f = -kX + lX^2 + \dots$ . The potential energy is then  $V = -\int f dX = \frac{1}{2}kX^2 - \frac{1}{3}lX^3 + \dots + V_0$ . The zero of potential energy is arbitrary, and thus the integration constant  $V_0 = 0$ . Near the equilibrium bond length terms higher than  $X^2$  can be neglected. We then have the potential function of a harmonic oscillator,  $V = \frac{1}{2}kX^2$ , with  $k$  the "quadratic" force constant at the equilibrium bond length. Solution of the equations of motion yields the relationship between the frequency of vibration,  $\nu$ , and the quadratic force constant,  $k = 4\pi^2\nu^2c^2\mu$ , where  $c$  is the velocity of light and  $\mu$  is the reduced mass  $[M_A M_B / (M_A + M_B)]$ . The direct relationship between  $\nu$  and  $k$  for diatomics has led to the use of frequencies of vibration as a direct probe of bonding in polyatomic molecules.

While the simplicity of correlating observed frequencies with bond strength is appealing, it has severe limitations. Even for diatomics, the frequency alone is not a direct measure of bond strength as a mass factor,  $\mu$ , is included. For example, the observed fundamental vibrational frequency is  $2885\text{ cm}^{-1}$  for  $\text{H}^{35}\text{Cl}$  and  $2143\text{ cm}^{-1}$  for  $^{12}\text{C}^{16}\text{O}$ ; the respective quadratic force constants at equilibrium are 5.2 and  $19.0\text{ mdyn/\AA}$ . Thus, the CO bond is almost four times as strong as the HCl bond (it requires four times as much force to stretch it a unit distance); however, the CO bond has a lower vibrational frequency.

The situation for polyatomic molecules is more complex. In the quadratic approximation (near the equilibrium configuration) the potential energy is expressed as  $2V = \sum F_{ij}R_iR_j$ , where the  $F_{ij}$  are force constants and the  $R_i$  are displacements of coordinates which describe the atomic configuration of the system. One can describe the atomic configuration of a system of  $N$  atoms with  $3N - 6$  coordinates, which are referred to as *internal coordinates*. Unfortunately, the relationship between frequencies of vibration and coordinate strengths for polyatomics is complicated. One problem is that the fundamental or normal modes of vibration are made up of linear combinations of all of the internal coordinates and thus the frequencies cannot be associated with particular well-defined internal coordinates. Furthermore, in addition to the primary force constants analogous to those in diatomic molecules, we now have interaction force constants representing mutual interactions of the various coordinates. However, knowing the masses of the atoms and the equilibrium structure of the system one can evaluate force constants from vibrational frequencies. The end result in such calculations is the evaluation of force constants, which can be used to discuss bonding, and a description of the normal modes of vibration in terms of the internal coordinates.

One can also express the potential function in terms of compliance constants,  $C_{ij}$ , and generalized forces applied to the various internal coordinates,  $\mathcal{F}_i$ ;  $2V = \sum_{ij} C_{ij}\mathcal{F}_i\mathcal{F}_j$ . Again, using structural information and the observed frequencies of vibration, one can evaluate compliance constants. In the following paragraphs we hope to clarify the meaning of force and compliance constants with regard to interatomic forces. The results for a number of metal cyanide complexes and metal carbonyls will also be discussed as examples of the type of bonding information one can obtain from such studies.

This discussion is limited to quadratic potential constants which describe the interatomic forces for a molecule in its equilibrium configuration. A number of workers, particularly Overend,<sup>1</sup> have determined cubic and quartic constants for some of the simpler molecules. Though these are certainly of interest to describe changes in bonding as the molecule is distorted from equilibrium, they do not relate directly to the equilibrium electronic forces. We are concerned with harmonic frequencies (fundamental frequencies corrected for anharmonicity—the hypothetical frequencies of infinitesimal vibrations).

Table I  
Force Constants of Nitrosyl Halides<sup>a</sup>

	ONF	ONCl	ONBr
$F_{\text{NO}}$	15.93 (4) <sup>b</sup>	15.26 (3)	15.25 (4)
$\Upsilon_{\text{NO}}(C_{\text{NO}}^{-1})$	13.64 (21)	13.41 (13)	13.35 (90)
$F_{\text{NX}}$	2.22 (4)	1.27 (1)	1.13 (5)
$\Upsilon_{\text{NX}}(C_{\text{NX}}^{-1})$	1.89 (1)	1.10 (0)	0.99 (2)
$F_{\alpha}$	1.83 (1)	1.32 (1)	1.13 (2)
$\Upsilon_{\alpha}(C_{\alpha}^{-1})$	1.81 (1)	1.31 (1)	1.12 (3)

<sup>a</sup> Units are  $\text{mdyn/\AA}$  for stretch and  $\text{mydn A rad}^{-2}$  for bend. <sup>b</sup> Numbers in parentheses are least-squares standard deviations in units of last decimal place.

From these, harmonic potential constants of a general quadratic potential function can be calculated.

### The Meaning of Force and Compliance Constants

The primary force constant provides a measure of the steepness of the potential well,  $F_{ii} = (\partial^2 V / \partial R_i^2)_{R_j=0}$ , for a molecule in its equilibrium configuration. In a strict sense, the primary force constant is the force required to distort a coordinate a unit amount *while holding all other coordinates fixed in their equilibrium configurations*. On the other hand, a primary compliance constant,  $C_{ii}$ , gives the displacement of coordinate  $i$  resulting from a unit force imposed on coordinate  $i$  while all other coordinates are allowed to relax to the minimum energy configuration with  $i$  displaced.

As the units for compliance constants are the reciprocal of those of force constants, it is difficult to compare the two directly. For this reason, it is convenient to introduce the relaxed force constant  $\Upsilon_{ii} = 1/C_{ii}$ . The term "relaxed" is appropriate as  $\Upsilon_{ii}$  measures the force required to distort coordinate  $i$  a unit amount *while allowing all other coordinates  $j$  to relax to a minimum energy configuration*:  $\Upsilon_{ii} = (\partial^2 V / \partial R_i^2)_{\mathcal{F}_j=0}$  (see above). Thus,  $F_{ii}$  is a measure of bond strength with the remainder of the molecule constrained while  $\Upsilon_{ii}$  measures bond strength, allowing the remainder of the molecule to relax so as to minimize potential energy. Indeed, the difference  $F_{ii} - \Upsilon_{ii}$  provides a measure of the force required to constrain all coordinates  $j$  while distorting  $i$  a unit amount.

In many systems the difference between the relaxed and regular force constants is substantial. For the nitrosyl halides<sup>2</sup>  $F_{\text{NO}}$  and  $F_{\text{NX}}$  are considerably larger than  $\Upsilon_{\text{NO}}$  and  $\Upsilon_{\text{NX}}$  (see Table I). Thus, the force required to constrain the NX bond length and the XNO angle while stretching the NO bond is quite large. This implies a substantial change in the electronic configuration as the NO bond is deformed. In general, the relaxed force constant is *always* less than the regular or rigid force constant.

While rigid force constants are used almost exclusively to discuss bonding there are several problems associated with their interpretation. The most telling criticism is that the magnitude of a force constant depends on the nature of the internal coordinates used to describe the problem. Consider water, which can be described in terms of the two O-H bonds and the H-O-H angle,  $GQVFF$ , or the two O-H bonds and the nonbonded H-H distance,  $GQCFF$ . The primary

(1) See, for example, V. K. Wang and J. Overend, *Spectrochim. Acta, Part A*, **29**, 1623 (1973), and references cited therein.

(2) L. H. Jones, "Inorganic Vibrational Spectroscopy", Vol. 1, Marcel Dekker, New York, N.Y., 1971.

constant for the O–H bond increased by 0.7 mdyne/Å (9%) in going from the GQVFF description to the GQCF model.<sup>2</sup> This dependence on coordinate selection is troublesome, as the measure of the O–H bond strength varies dramatically. The compliance constant formalism enjoys a considerable advantage here as the compliances, and thus the relaxed force constants, do not change with the choice of coordinates used to define the configuration.

An equally worrisome problem occurs when the number of internal coordinates used to describe the system exceeds the degrees of internal freedom,  $3N - 6$ . Methane offers an example: there are six H–C–H angles and four C–H bonds, and only nine degrees of freedom. Essentially, the internal coordinates are not linearly independent (in the case of CH<sub>4</sub> the relationship relating H–C–H angles, referred to as the redundancy condition, is  $\sum_i^6 \Delta\alpha_i = 0$ ). In this case, none of the force constants involved in the redundancy condition can be evaluated independently. As  $F_\alpha$  cannot be evaluated for methane, there is no reliable measure of the H–C–H coordinate strength. Again, compliance constants offer an advantage since they are uniquely defined *even in the case of a redundancy among internal coordinates*.

While the primary force and compliance constants provide a measure of bond strengths, the interaction constants,  $F_{ij}$  and  $C_{ij}$ , where  $i \neq j$ , give us information about changes in electronic configuration as a given coordinate is distorted. That is, as one coordinate is distorted the change in electronic structure leads to changes in the bonding forces in all other coordinates. An interaction force constant,  $F_{ij}$ , is the force instilled in coordinate  $j$  when coordinate  $i$  is displaced a unit amount *while  $j$  and all other coordinates except  $i$  remain fixed at their equilibrium values*. Alternatively,  $C_{ij}$  represents the displacement of coordinate  $j$  which would accompany a unit displacement of coordinate  $i$ , *while allowing the remainder of the molecule to relax to a minimum of energy*.

In the case of interaction constants the reciprocal units for compliances allows them a conceptually simple physical interpretation. Thus,  $C_{ij}$  is directly related to the physically significant interaction displacement coordinate  $(j)_i = C_{ij}/C_{ii}$ . The quantity  $(j)_i$  gives the change in coordinate  $j$  required to minimize the potential energy when coordinate  $i$  is distorted a unit amount. Thus,  $(j)_i$  measures the change in  $j$ th bond strength in the distorted molecule resulting from weakening one particular bond,  $i$ .

The importance of  $(j)_i$  cannot be overemphasized: consider the simple molecule CH<sub>4</sub>. The constant  $(CH)_CH$  is negative, implying that as one C–H bond is weakened, all the others get stronger. This observation is explicable from hybrid theory. As one C–H bond is weakened we expect more s character in the remaining bonds since, in the limit of infinite distortion, the CH<sub>3</sub> fragment is sp<sup>2</sup> rather than sp<sup>3</sup>. Clearly,  $(j)_i$  and therefore  $C_{ij}$  are significant constants which can help clarify our ideas about bonding. As shown below, interaction displacement coordinates provide invaluable information concerning bonding in metal cyanides and metal carbonyls.

In this section, we have tried to compare force and compliance constants while pointing to some of the

problems associated with the usual force-constant description. While compliance constants appear to have a mathematical and descriptive advantage over force constants, they have generally been neglected in the past. It is not known which type of constant is more transferable between molecules, and we encourage others to address themselves to this question. For the present, we feel that it is best to report both force and compliance functions, and urge that workers consider interaction displacement coordinates as part of the bonding information provided by vibrational studies.

### Problems Associated with Evaluation of Potential Constants

The calculation of force constants or compliance constants from vibrational frequencies is generally referred to as a normal coordinate analysis or normal mode calculation. The theory behind the calculations and the mechanics involved are discussed by a number of authors.<sup>2-9</sup> One uses an iteration procedure whereby the vibrational frequencies are calculated from a trial force field. The force constants are then adjusted by a least-squares procedure to converge on the best fit of calculated to observed frequencies.

Unfortunately there are generally more quadratic force constants than there are vibrational frequencies for a molecular species, so one requires additional data. The observable/parameter ratio can be increased by using frequency data from isotopically substituted species, Coriolis coupling constants, centrifugal distortion constants, mean-square amplitudes of vibration, and intensity data. Isotopic frequency shifts provide the most generally available auxiliary data since Coriolis constants and centrifugal distortion data can be obtained only for gas-phase species, and mean amplitudes of vibration are found to be rather insensitive to the force field.<sup>2</sup> Intensity data, which have been used sparingly, should probably receive more attention as they give information concerning the eigenvectors for a given vibrational mode and can be used to help define the force field.

In principle it should be possible to determine all of the potential constants in a general quadratic force field if there are at least as many observables as there are potential constants. However, it is often true that the observables are quite insensitive to some of the off-diagonal (interaction) constants. For example, six isotopic species of Co(CO)<sub>3</sub>NO were studied, yielding 78 frequencies to determine 49 potential constants.<sup>10</sup> Even though the number of frequencies was in excess of the number of potential constants, several constraints were necessary in order to converge on a solution. One problem here is that the calculated frequencies (or other vibrational data) are insensitive

(3) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1046 (1939).

(4) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.

(5) W. J. Taylor and K. S. Pitzer, *J. Res., Natl. Bur. Stand.*, **38**, 1 (1974); P. G. Maslow, *Dokl. Acad. Nauk SSSR*, **67**, 819 (1949); **71**, 867 (1950).

(6) J. C. Decius, *J. Chem. Phys.*, **38**, 241 (1963).

(7) L. H. Jones and R. R. Ryan, *J. Chem. Phys.*, **52**, 2003 (1970).

(8) L. H. Jones, Proceedings, 13th International Conference on Coordination Chemistry, Crakow and Zakopane, Poland, Sept 1970.

(9) T. Shimanouchi, "Physical Chemistry, An Advanced Treatise", Vol. 4, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N.Y., 1970.

(10) L. H. Jones, R. S. McDowell, and B. I. Swanson, *J. Chem. Phys.*, **58**, 3757 (1973).

to changes in a particular interaction constant,  $F_{ij}$ . Inclusion of this  $F_{ij}$  in a least-squares refinement results in a singularity or near-singularity in the inversion of the normal equation.<sup>11</sup> In this event,  $F_{ij}$  must be fixed to a predetermined value.

Constraints are also required when two or more potential constants are highly correlated.<sup>11</sup> That is, the parameters are not linearly independent and, therefore, cannot be refined simultaneously. High correlation of potential constants is particularly worrisome since the constants involved are often quite important. For example, the Li-N primary force constant in  $\text{Cs}_2\text{LiFe}(\text{CN})_6$  is highly correlated with the Li-N, C-N interaction constant (the Fe-C-N-Li framework is linear).<sup>12</sup> The result is that one of the constants must be constrained to a predetermined value to achieve solution. However, the Jacobian elements relating  $F_{\text{LiN,CN}}$  to the calculated frequencies are quite large, indicating that this constant is important.

One method for applying constraints is to use an approximate force field where the number of force constants is less than that needed to define a completely general potential function. There are a number of these approximations which vary from slight to extreme. It is important to remember that the results are biased by the constraints involved. If the constraints are justified, and not purely arbitrary, the results are meaningful.

Within the framework of a general valence potential function a number of approaches can be used to justify certain necessary constraints. It is often appropriate to transfer some potential constants from a similar molecule for which they have been determined uniquely. This is an important approach worthy of careful study. In many cases interaction coordinates which do not share a common atom are essentially indeterminate and can be constrained over a rather wide range without seriously influencing the values calculated for the other constants. The neglect of interaction constants between internal coordinates which do not share a common atom is not always appropriate. For example, in metal carbonyls the interaction potentials between C-O and M-C stretch coordinates which are trans to one another are significant and well determined.<sup>13</sup> However, the interactions of the CO stretches with the bending coordinates of the hexacarbonyls are essentially indeterminate and can be constrained over a rather wide range without influencing the calculation of the other constants.<sup>13</sup> Perhaps an even more attractive approach would be to calculate some of the interaction coordinates through a suitable molecular orbital calculation; however, at present there are few results to encourage such a tactic, though Pulay<sup>14</sup> appears to be making progress in this direction.

Finally, under constraints, it is appropriate to mention those methods which are advertised to give a "unique" potential function of  $n$  potential constants

from less than  $n$  frequencies.<sup>15</sup> The term unique implies that all of the primary and interaction constants are determined. Clearly, in any unique determination of a set of parameters one needs an equal number or more observables than parameters to be determined. While it is inappropriate to discuss these methods in detail at this point, it is important to recognize that they all involve some sort of constraint which is not always obvious. A critical discussion of these constraints is given by Averbukh et al.<sup>16</sup>

### Interpretation of Potential Constants for Some Metal Cyanide Complexes

Before discussing some of the results we have obtained over the past few years on transition-metal cyanides and carbonyls, it is appropriate to discuss the current bonding models. Both  $\text{CN}^-$  and CO are  $\pi$ -acceptor ligands.<sup>17</sup> That is, the usual M-L  $\sigma$  bond formed by electron donation from the ligand to the metal may be augmented by a  $\pi$  interaction formed through back-donation of electron density from the metal d orbitals to the  $\pi^*$  level of the ligand. MO calculations<sup>18</sup> on cyano and carbonyl complexes indicate that the ligand  $\sigma$  orbitals involved in forming the M-L  $\sigma$  bond are slightly antibonding with respect to the C-N or C-O moieties. The  $\pi^*$  C-O and C-N levels are strongly antibonding. Thus, an increase in M-L  $\sigma$  bonding should result in a slight increase in the C-N bond strength. Conversely, an increase in  $d\pi-p\pi^*$  overlap should result in a decrease in the C-N bond order.

We start with discussion of the results on the stretching potential constants of the linear ion  $\text{Au}(\text{CN})_2^-$  (N-C-Au-C-N) which are well determined. In the quadratic field we can discuss the stretching modes without considering the bending modes as they fall in a different symmetry class. From the stretching frequencies of the three isotopic species,  $\text{Au}^{(12}\text{C}^{14}\text{N})_2^-$ ,  $\text{Au}^{(13}\text{C}^{14}\text{N})_2^-$ , and  $\text{Au}^{(12}\text{C}^{15}\text{N})_2^-$ , force constants have been calculated as given in Table II. Solution A we believe to be the best as it uses the harmonic CN stretching frequencies. The main difference between B and A is a lowering in the CN force constant because the observed frequencies uncorrected for anharmonicity have been used. Note from the values of  $\Delta\nu_i$  in Table II that the frequency fit for solution B is somewhat poorer than for A, indicating that harmonic corrections should be made when possible. Solutions C and D are those of an "energy-factored" force field, applied to the normal isotope species, in which the CN stretching modes are factored out from the others because the frequencies are so much greater. This amounts to constraining all force constants to zero except those for CN stretches and their mutual interactions. A

(15) See for example R. L. Redington and A. L. K. Aljibury, *J. Mol. Spectrosc.*, **57**, 494 (1971); W. Sawodney, A. Fadini, and K. Ballein, *Spectrochim. Acta*, **21**, 995 (1965); F. Billés, *Acta Chim. Acad. Sci. Hung.*, **47**, 53 (1965).

(16) B. S. Averbukh, L. S. Mayants, and G. B. Shaltuper, *J. Mol. Spectrosc.*, **30**, 310 (1969).

(17) Many chemists are of the opinion that " $\pi$ -back bonding is the last refuge of a scoundrel!" (R. T. Burwell, private communication). However, the  $d\pi-p\pi^*$  bonding model has been quite successful in describing M-L interactions for complexes containing so-called  $\pi$ -acceptor ligands. It is appropriate, therefore, to discuss the bonding information obtained from normal coordinate analyses in terms of the  $\pi$ -acceptor model.

(18) R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **10**, 38 (1971).

(11) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964.

(12) L. H. Jones, B. I. Swanson, and G. J. Kubas, *J. Chem. Phys.*, **61**, 4650 (1974).

(13) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

(14) P. Pulay, *Mol. Phys.*, **18**, 473 (1970); *J. Mol. Spectrosc.*, **40**, 59 (1971), and more recent papers.

Table II  
Force Constant Solutions for  $\text{Au}(\text{CN})_2^-$

	A <sup>a</sup>	B	C	D
$F_{\text{CN}}$	17.65 <sup>b</sup> (6) <sup>c</sup>	17.29 (11)	18.14 (2)	17.68 (2)
$F_{\text{MC}}$	2.77 (2)	2.76 (4)	[0]	[0]
$F_{\text{CN},\text{C}'\text{N}'}$	0.02 (6)	0.03 (11)	0.15 (2)	0.15 (2)
$F_{\text{CN},\text{MC}}$	0.31 (5)	0.39 (10)	[0]	[0]
$F_{\text{CN},\text{MC}'}$	0.00 (5)	0.01 (10)	[0]	[0]
$F_{\text{MC},\text{MC}'}$	0.42 (2)	0.41 (4)	[0]	[0]
$\Delta\nu_1(12,14)_2$	-0.1 <sup>d</sup>	-0.1	0.3	0.0
$\Delta\nu_3$	-0.2	-0.5	-0.1	-0.5
$\Delta\nu_1(13,14)_2$	-0.1	0.1	-3.3	-3.0
$\Delta\nu_3$	0.1	0.3	-2.1	-1.8
$\Delta\nu_1(12,15)_2$	-0.1	0.1	3.0	3.0
$\Delta\nu_3$	0.1	0.3	2.2	2.3

<sup>a</sup> Solution A uses the harmonic CN frequencies,  $\omega_i$ , and  $\omega_2$ . B uses observed frequencies. C is the  $\nu_{\text{CN}}$  energy factored field using harmonic  $\omega_i$ . D is the  $\nu_{\text{CN}}$  energy factored field using observed  $\nu_i$ . <sup>b</sup> Units are  $\text{mdyn } \text{Å}^{-1}$ . <sup>c</sup> Numbers in parentheses are least-squares standard deviations in units of the last decimal place. <sup>d</sup> Deviation,  $\nu_{\text{obsd}} - \nu_{\text{calcd}}$ , in  $\text{cm}^{-1}$ .

simplified force field such as this has been used often in the past to discuss bonding trends in metal carbonyls.<sup>19</sup> From the frequency discrepancies listed in Table II it is apparent that this is a poor approximation, as it has also been shown to be for metal carbonyls.<sup>13</sup>

Let us compare the results for  $\text{Au}(\text{CN})_2^-$  with those of  $\text{Hg}(\text{CN})_2$  with attention to compliance constants and interaction coordinates in order to illustrate their usefulness in interpretation of bonding. Based on the frequencies of Smith and Jones,<sup>20</sup> a least-squares refinement of compliance constants has been made for  $\text{Hg}(\text{CN})_2$ . The compliance constants for both complexes are presented in Table III along with the interaction displacement coordinates (see above). The M-C bond is slightly stronger in  $\text{Au}(\text{CN})_2^-$  than in  $\text{Hg}(\text{CN})_2$  (as evidenced by the smaller compliance constant) even though we might expect a weaker M-C  $\sigma$  bond on the basis of formal oxidation states. It is possible that in going from  $\text{Hg}(\text{CN})_2$  to  $\text{Au}(\text{CN})_2^-$  the decrease in M-C bond order resulting from decreased M-C  $\sigma$  bonding is offset by increased M-CN back  $\pi$  bonding. This is also supported by the observation of a weaker C-N bond in the gold complex, as pointed out previously.<sup>21</sup>

The interaction displacement coordinate  $(\text{CN})_{\text{MC}}$  also is informative about the relative importance of  $d\pi-p\pi^*$  bonding in these two complexes. The quantity  $(\text{CN})_{\text{MC}}$  measures the change in the C-N bond length required to minimize potential energy when the M-C bond is stretched a unit amount. In the gold complex, as the M-C bond is stretched, to achieve minimum energy the CN bond would contract by 1.8% of the M-C stretch. This significant effect of increase in CN bond strength can only be attributed to decreased M-CN  $\pi$  bonding since a decrease of M-C  $\sigma$  bonding should result in a weakening of the C-N bond because the  $5\sigma$  C orbital is antibonding.<sup>18</sup> For  $\text{Hg}(\text{CN})_2$  both  $(\text{CN})_{\text{MC}}$  and  $(\text{MC})_{\text{CN}}$  are essentially zero, indicating very little  $d\pi-p\pi^*$  back-bonding. This finding is consistent with our general ideas

Table III  
Valence Compliance Constants and Interaction Displacement Coordinates for  $\text{Au}(\text{CN})_2^-$  and  $\text{Hg}(\text{CN})_2$

	$\text{Au}(\text{CN})_2^-$	$\text{Hg}(\text{CN})_2$
$C_{\text{CN}}$	0.05677 <sup>a</sup> (14) <sup>b</sup>	0.05545 <sup>a</sup> (9) <sup>b</sup>
$C_{\text{MC}}$	0.3698 (29)	0.3863 (23)
$C_{\text{CN},\text{C}'\text{N}'}$	-0.00008 (14)	0.00005 (9)
$C_{\text{CN},\text{MC}}$	-0.0066 (10)	-0.0004 (5)
$C_{\text{CN},\text{MC}'}$	0.0011 (10)	-0.0004 (5)
$C_{\text{MC},\text{MC}'}$	-0.0556 (29)	-0.0175 (23)
$(\text{MC})_{\text{CN}}$	-0.116 (18)	-0.007 (10)
$(\text{CN})_{\text{MC}}$	-0.018 (3)	-0.001 (1)
$(\text{CN})_{\text{C}'\text{N}'}$	-0.001 (2)	+0.001 (2)
$(\text{MC})_{\text{MC}'}$	-0.150 (8)	-0.045 (6)
$(\text{MC})_{\text{C}'\text{N}'}$	0.019 (18)	-0.007 (10)
$(\text{CN})_{\text{MC}'}$	0.003 (3)	-0.001 (1)

<sup>a</sup> Units are  $\text{Å mdyn}^{-1}$  for  $C_i$  and  $C_{ij}$ . <sup>b</sup> Numbers in parentheses are least-squares standard deviations in units of last decimal place given.

about the lack of d-orbital participation in bonding for complexes of the zinc group.

The meaning of  $(\text{MC}')_{\text{MC}}$  is more difficult to assess, since stretching an M-C bond should result in enhancement of both  $\sigma$  and  $\pi$  overlap to the trans M-C'. From the results of Table III it is apparent that the trans M-C' bond strengthens as M-C is stretched; however, it is not clear why this effect is three times as great for  $\text{Au}(\text{CN})_2^-$  as for  $\text{Hg}(\text{CN})_2$ .

The foregoing illustrates the utility of interaction displacement coordinates in clarifying our ideas about bonding. We feel that the  $(l)_k$  provide direct information about how the various coordinates interact and are, therefore, very useful in discussing electronic bonding forces.

A comparison of the bonding among different CN-containing species is of interest. As noted above, we prefer discussion in terms of compliance constants and interaction coordinates. However, since at present chemists are more familiar with force constants, we present in Table IV a list of stretching force constants which have been observed. The interpretation is roughly the same, though not as direct.

As pointed out above, the force constants indicate that  $\pi$  "back-bonding" is more important for  $\text{Au}(\text{CN})_2^-$  than for  $\text{Hg}(\text{CN})_2$ . This gives rise to a weaker CN bond and stronger MC,CN interaction for the gold compound. The low value for free  $\text{CN}^-$  is in line with the theoretical work of DeKock et al.<sup>18</sup> in which they find significant antibonding character in the lone pair of electrons ( $5\sigma$ ) on the C atom. When these are used in bond formation they deplete the antibonding C-N orbitals and the CN bond becomes stronger. The maximum increase is noted for HCN as there are no compensating effects such as  $\pi$  back-bonding into the CN antibonding  $\pi^*$  orbitals.

The tetracyanides and hexacyanides also have the possibility of cis interactions which are not given here. They are small and essentially zero within their standard deviations. The solutions for these more complex species involve  $4 \times 4$  secular determinants. It is found that for problems of this size at least two and often more potential constants must be constrained at some predetermined value in order to achieve convergence. Thus the constants and their standard deviations have meaning only with the specification of the constraints applied. The values in

(19) F. A. Cotton and C. J. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); C. J. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(20) J. M. Smith and L. H. Jones, *J. Chem. Phys.*, **44**, 3643 (1966).

(21) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

Table IV  
Stretching Force Constants of Some Cyanide Complexes

Ref	$F_{CN}$	$F_{MC}$	$F^{t_{CN,C'N'}}$	$F^{t_{MC,MC'}}$	$F_{MC,CN}$	$F^{t_{MC,C'N'}}$
CN	8	16.29 (1)				
CN <sup>-</sup>	8	16.89 (4)				
C <sub>2</sub> N <sub>2</sub>	33	18.03 (2)		-0.26 (2)		
HCN	8	18.8				
Au(CN) <sub>2</sub> <sup>-</sup>	31	17.65 (6)	2.77 (2)	0.02 (6)	0.42 (2)	0.31 (5)
Hg(CN) <sub>2</sub>	32	18.03 (3)	2.59 (2)	-0.01 (3)	0.12 (3)	0.02 (3)
Ni(CN) <sub>4</sub> <sup>2-</sup>	34	17.20 (5)	2.25 (2)	0.10 (5)	0.41 (2)	0.23 (5)
Pd(CN) <sub>4</sub> <sup>2-</sup>	34	17.44 (6)	2.32 (2)	0.06 (6)	0.58 (2)	0.25 (5)
Pt(CN) <sub>4</sub> <sup>2-</sup>	34	17.41 (4)	2.75 (1)	0.02 (4)	0.76 (1)	0.34 (3)
Co(CN) <sub>6</sub> <sup>3-</sup>	23	17.43 (5)	2.09 (13)	-0.07 (5)	0.45 (13)	0.24 (7)
Fe(CN) <sub>6</sub> <sup>3-</sup>	13	17.2	2.0	-0.2	0.4	0.2

<sup>a</sup> Units are mdyn Å<sup>-1</sup>. Numbers in parentheses are least-squares standard deviations in units of the last digit given.

Table IV do suggest, however, that it may be justified to constrain the interactions  $F^{t_{CN,C'N'}}$ , and  $F^{t_{MC,C'N'}}$ , to zero along with the three cis interactions  $F^{c_{CN,C'N'}}$ ,  $F^{c_{MC,C'N'}}$ , and  $F^{c_{MC,MC'}}$ . Unfortunately the bending constants are much more uncertain than the stretching constants.

Much interesting bonding information is available from solid-state studies of metal cyanide complexes. However, care must be taken in using solid-state frequencies for normal mode calculations; coupling with lattice modes must be considered. It has been shown<sup>22</sup> that solid-state vibrational frequency data for Cs<sub>2</sub>LiCo(CN)<sub>6</sub> would give a completely erroneous potential function if based on an isolated ion molecule. The perturbation of internal modes of vibration by interatomic forces is even greater for Cs<sub>2</sub>MgFe(CN)<sub>6</sub><sup>23</sup> and greater yet for Prussian Blue systems.<sup>24</sup>

A preliminary treatment of the pseudo-Prussian Blue Mn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>·xH<sub>2</sub>O, where the N end of the cyanide is linearly bound to the manganese atom, has shown that the Mn-N interaction is unusually strong. In comparison with the Mg-N interaction in Cs<sub>2</sub>MgFe(CN)<sub>6</sub>, the Mn-N bond is roughly twice as strong even though both metals are divalent. The implication is that there is a dπ-pπ\* interaction present in the Prussian Blue which cannot exist in Cs<sub>2</sub>MgFe(CN)<sub>6</sub>. This observation is also supported by the calculated changes in the CN bond strength for both ions in going to their crystalline lattices. This finding is consistent with the insolubility of Prussian Blue. It implies extended overlap between sites via the π\* level on the CN<sup>-</sup> moiety.

#### Interaction Coordinates and Bonding in M(CO)<sub>6</sub>

The potential functions for M(CO)<sub>6</sub> (M = Cr, Mo, and W) which have been determined from isotopic frequency data (<sup>12</sup>C<sup>16</sup>O, <sup>13</sup>C<sup>16</sup>O, <sup>12</sup>C<sup>18</sup>O) are no doubt the best determined of the transitional-metal carbonyls.<sup>13</sup> The bonding implications of the potential functions have already been discussed in some detail.<sup>13,25</sup> We limit this discussion to the interaction displacement coordinates, most of which were found<sup>25</sup> to be the same for the three molecules within experimental error. The average values for the three metals are presented in Table V.

Table V

Interaction Coordinates <sup>a</sup> for M(CO) <sub>6</sub> , M = Cr, Mo, W	
(C <sub>2</sub> O <sub>2</sub> )C <sub>1</sub> O <sub>1</sub> (cis)	-0.0129 (3) <sup>b</sup>
(C <sub>2</sub> O <sub>2</sub> )C <sub>1</sub> O <sub>1</sub> (trans)	-0.011 (4)
(MC <sub>1</sub> )C <sub>1</sub> O <sub>1</sub>	-0.401 (9) <sup>c</sup>
(MC <sub>2</sub> )C <sub>1</sub> O <sub>1</sub> (cis)	0.037 (2)
(MC <sub>6</sub> )C <sub>1</sub> O <sub>1</sub> (trans)	0.164 (9)
(MC <sub>2</sub> )MC <sub>1</sub> (cis)	-0.005 (9) <sup>d</sup>
(MC <sub>6</sub> )MC <sub>1</sub> (trans)	-0.228 (6)
(C <sub>1</sub> O <sub>1</sub> )MC <sub>1</sub>	-0.045 (1)
(C <sub>2</sub> O <sub>2</sub> )MC <sub>1</sub> (cis)	0.0040 (3)
(C <sub>2</sub> O <sub>2</sub> )MC <sub>1</sub> (trans)	0.019 (1)
(β <sub>21</sub> )MC <sub>1</sub>	0.21 (4) rad Å <sup>-1</sup>
(α <sub>12</sub> )MC <sub>1</sub>	0.16 (3) rad Å <sup>-1</sup>
(β <sub>12</sub> )α <sub>12</sub>	0.30 (5)

<sup>a</sup> From ref 25. <sup>b</sup> Numbers in parentheses are least-squares standard deviations in units of the last decimal place. <sup>c</sup> This constant was statistically different for gas and solution. An average and range are given. <sup>d</sup> This constant was statistically different for Cr(CO)<sub>6</sub>; an average range is given.

Consider first those interaction coordinates associated with stretching the M-C<sub>1</sub> bond. The C<sub>1</sub>-O bond is observed to strengthen (shorten for minimum energy), (CO)<sub>MC</sub> = -0.045 (1), as is consistent with the dπ-pπ\* bonding model. As the M-C<sub>1</sub> bond is weakened, the reduced π back-bonding to the C<sub>1</sub>-O moiety is expected to result in a stronger C-O bond. It should be noted that a reduction in M-C<sub>1</sub> σ bonding has the opposite effect, as the ligand σ orbital is slightly antibonding. Therefore, it appears that changes in the π bonding as a M-C bond is stretched are much more important in determining the various (CO)<sub>MC</sub> interactions than changes in the σ-bonding framework. Thus, both (C'O)<sub>MC</sub><sup>t</sup> and (C'O)<sub>MC</sub><sup>c</sup> are observed to be positive, as is consistent with increased π back-bonding to the remaining ligands.

Decreases in either the M-C<sub>1</sub>O σ or π bonding should result in enhanced σ or π interactions to the remaining ligands: thus, from bonding considerations we expect both (MC')<sub>MC</sub><sup>c</sup> and (MC')<sub>MC</sub><sup>t</sup> to be negative. As shown in Table V, the M-C bond trans to M-C<sub>1</sub> tends to shorten ca. 23% of the amount that M-C<sub>1</sub> is stretched, as is consistent with the above arguments. However, the M-C bonds cis to M-C<sub>1</sub> do not exhibit any change; (MC')<sub>MC</sub><sup>c</sup> is essentially zero.

The absence of any change in the M-C bonds cis to M-C<sub>1</sub> is at first surprising, since the shortening of the cis M-C bonds is expected to be about half that of the trans M-C bond on the basis of orbital participation arguments.<sup>26</sup> The reasoning for the π-bonding

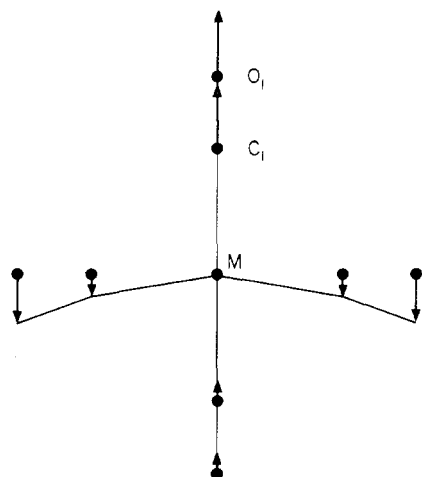
(22) B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, **55**, 4174 (1971); *Inorg. Chem.*, **13**, 313 (1974).

(23) B. I. Swanson and J. Rafalko, submitted for publication.

(24) B. I. Swanson, submitted for publication.

(25) L. H. Jones, *J. Mol. Spectrosc.*, **36**, 398 (1970).

(26) F. A. Cotton, W. T. Edwards, F. C. Ranch, M. A. Graham, R. N. Perutz, and J. J. Turner, *J. Coord. Chem.*, **2**, 247 (1973).



**Figure 1.** Schematic representation of interaction displacement coordinates,  $(k)_{MC_1}$ , for  $M(CO)_6$ . The lengths of the arrows represent the relative displacements of the atoms to achieve minimum energy when the  $MC_1$  bond is constrained to a unit positive displacement as indicated. The four atoms out of the plane of the paper are not shown.

framework is as follows. We expect the two d orbitals which are involved in  $d\pi-p\pi^*$  bonding to  $C_1O$  to be destabilized as  $\pi$  back-donation is reduced. Since both orbitals are involved in  $\pi$  back-bonding to the trans CO ligand, while only one is involved in the  $\pi$  interaction to each cis ligand, we expect the change in the cis M-C bonds to be one-half as great as that in the trans M-C bond. Clearly, changes in the electronic structure following distortion of the  $M-C_1$  bond are complex, and simplified orbital participation arguments are not applicable in this case.

Changes in bonding as one M-C bond is weakened are almost entirely trans directive. While these observations cannot be explained using orbital participation arguments, they do agree well with MO calculations which have been carried out on  $Mn(CO)_6^+$  and  $Mn(CO)_5X$  ( $X = Cl, Br, \text{ and } I$ ).<sup>27</sup> The idea here is that in going from  $Mn(CO)_6^+$  to  $Mn(CO)_5X$  there is an extreme reduction in one of the M-L  $\pi$  interactions (this is somewhat analogous to the reduction of  $M-C_1O$   $d\pi-p\pi^*$  bonding which results from stretching the  $M-C_1$  bond). MO calculations for the manganese complexes show an almost exclusive trans effect.<sup>27</sup>

One problem with the orbital participation model is that a localized bonding change is anticipated by consideration of only the metal d-orbital perturba-

tion. We are not taking into account any possible change in geometry which may accompany a specific distortion: i.e., the stretching of  $M-C_1$ . In this regard it is interesting to note the angle changes which accompany a weakening of the  $M-C_1$  bond. As shown in Figure 1 the cis CO ligands bend away from the leaving CO group while the  $M-C-O$  angle becomes non-linear. In discussion of a localized bond, i.e., the M-C bonds cis to  $M-C_1$ , one must include the geometry change as well as the energy change in the metal d orbitals.

On intuitive grounds one expects the M-CO  $d\pi-p\pi^*$  interaction to weaken as the  $M-C-O$  framework is distorted from equilibrium. It is possible, then, that the increase expected in the M-C  $\pi$  interaction arising from destabilization of some of the d orbitals is offset by a decrease in  $\pi$  bonding as a result of CMC and M-C-O bend. While this explanation supports the observation reported here [ $(MC')^c_{MC} \approx 0$  and  $(MC')^t_{MC} = 0.24$ ], it in no way explains why the M-C-O angles for cis carbonyl groups tend to distort in the first place.

These results are highly significant as they probe the intimacies of bonding forces and suggest that the usual localized molecular orbital model is deficient in discussing the interactions. Through further vibrational studies of this sort one can hope to develop a more sophisticated picture of molecular orbitals. It is certainly of interest to compare metal cyanide complexes with the analogous metal carbonyls. There are many similarities, but also significant differences. The major difference appears to be that the  $CN^-$  ions form somewhat stronger M-C  $\sigma$  bonds and definitely weaker M-ligand  $\pi$  bonds than the metal carbonyls. This is largely because of the difference in valence state of the metal. Presumably a zerovalent metal cyanide such as  $Ni(CN)_4^{4-}$  or  $Cr(CN)_6^{6-}$  would bear greater resemblance to  $Ni(CO)_4$  and  $Cr(CO)_6$  than do  $Ni(CN)_4^{2-}$  and  $Cr(CN)_6^{3-}$ . Thorough studies of such species would be interesting.

There are, of course, many more binary metal cyanide complexes than there are binary metal carbonyls. It is these relatively simple and symmetric species which can yield reasonably unique force fields. Thus continued studies on general force fields of metal cyanide complexes can be expected eventually to yield an abundance of bonding information which should be of great interest in describing a pattern and giving information to transfer to more complex bonding systems.

(27) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).