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Why the C–O Factored Force Field Works So Well

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The infrared spectra in the C–O stretching region of isotopically enriched matrix-isolated transition-metal carbonyls and carbonyl fragments can be fitted very accurately using the simple energy factored force field. The best match of experiment and theory is obtained with $^{12}C^{16}O/^{13}C^{16}O$ substitution (rather than $^{12}C^{16}O/^{12}C^{18}O$ or $^{12}C^{16}O/^{13}C^{18}O$). We examine the reasons for this and show how the inclusion of a "variable reduced mass ratio", which in effect modifies the force constant with isotope, leads to even closer agreement.

Introduction

Several authors, including ourselves, have investigated the vibrational spectra and structure of transition-metal carbonyl fragments (e.g., $Mo(CO)_4$[1]) and unusual species (e.g., $Pt(CO)_4$[2]) trapped in low-temperature matrices. All such authors have made extensive use of the energy factored ("Cotton–Kraihanzel") force field in which the carbonyl groups are considered sufficiently removed in energy to be treated independently of the other groups. Such methods have also been investigated by inorganic chemists on more conventional systems, and there has been much discussion on the value of this approximate method.

Quoting some of our work on $Mo(CO)_5$[3] and $Fe(CO)_4$[4] fragments, Braterman[5] has said, "These matrix studies embody the results of both high and low degrees of isotopic labelling. The degree of self-consistency and overproof achieved both for the frequencies and the relative intensities of the bands involved is impressive; so much so as to provide the best possible demonstration of the usefulness of the energy factored force field."

In the course of such matrix studies, and as a test of the method, we also examined in detail the spectra of matrix-isolated hexacarbonyls with ^{13}CO substitution, $Cr(^{12}C^{16}O)_n(^{13}C^{16}O)_{6-n}$. Jones,[6] in a recent note, comments on this work "It is quite remarkable that they were able to fit 19 observed IR-active CO stretching peaks with a mean error of 0.3 cm^{-1} and maximum error of 0.9 cm^{-1} using the CO factored force field. It is difficult to present an analytical expression for the applicability of this approximate force field." Jones goes on to question the "meaningfulness" of the force field and comments on the much worse fit for the species with $^{12}C^{18}O$ substitution, $Cr(^{12}C^{16}O)_n(^{12}C^{18}O)_{6-n}$. We have published a brief note[7] in reply to Jones' comments and included the statement "The reasons for these surprising differences (i.e. between isotopic fitting) lie in fortuitous or less fortuitous cancellation of terms." We also commented that we were not so much concerned with the "nuances of various force fields" but "to use isotopic data to determine structures of carbonyl fragments".

In this paper we are concerned with the reliability and significance of approximate force fields for metal carbonyls and related species. The reliability of intensity measurements for structure determinations will be assessed elsewhere.[8] The most extensive available data for stable metal carbonyl molecules are for the *completely* isotopically enriched species (e.g., $Cr(^{12}C^{16}O)_6$, $Cr(^{13}C^{16}O)_6$, and $Cr(^{12}C^{18}O)_6$). Thus as a starting point we consider the effectiveness of various approximations in predicting the isotopic shifts of the three "C–O stretching" modes of $Cr(^xC^yO)_6$ and compare with published solution data.[9,10] Of course the best overall results are obtained with a full general quadratic valence force field (GQVFF) but very good agreement is obtained for carbonyl vibrations by modifying the energy factored force field by allowing for both anharmonicity and for vibrational coupling between M–C and C–O bands. These calculations show that, in contrast to $^{12}C^{18}O$ and $^{13}C^{18}O$ substitution, for $^{13}C^{16}O$ substitution the two effects work in *opposite* directions, so that the crudest predictions work best for $^{13}C^{16}O$ substitution.

For the *partially* substituted hexacarbonyls we have extended our earlier matrix data and have examined, in the CO stretching region, the infrared spectra of the sets of molecules $Cr(^{12}C^{16}O)_n(^xC^yO)_{6-n}$ (x,y = 13,16; 12,18; 13,18) trapped in low-temperature matrices to obtain a complete set of data on the effect of substitution by each of the three readily available $^xC^yO$ isotopes. The matrix isolation method is ideally suited to the task since we have sharp bands (<1 cm^{-1} fwhm), the positions of which may be more accurately located than those of gas phase or solution. In addition, the spectra of the partially substituted molecules are far better resolved than in other phases.

With an energy factored force field the best fit is obtained for x,y = 13,16; this is not surprising in view of the behavior of the *completely* substituted species. It is shown how the fit can be further improved with a "variable reduced mass ratio" and why.

The paper concludes with some comments on N_2, O_2, and CN complexes.

Results and Discussion

A. Vibrational Shifts on Complete Isotopic Substitution. 1. General Quadratic Valence Force Field (GQVFF). Jones and his colleagues have accurately measured the IR and Raman spectra throughout the vibrational range of several carbonyls[9,11-13] and, using these data, have performed extensive GQVFF calculations. We here concentrate on $Cr(CO)_6$[9] (very similar results are obtained for $Mo(CO)_6$ and $W(CO)_6$). For ease of comparison with approximate methods we represent the method diagrammatically in Figure 1. The GQVFF, with certain approximations, produces a very good fit of all the $M(CO)_6$ vibrations as shown in Table I (column $\Delta\bar{\omega}^d$). To be acceptable, any approximate method will have to calculate the "carbonyl" frequencies with errors comparable to those of GQVFF calculations. The errors of the various approximations to be discussed are set out in Table I.

2. The Anharmonic, Energy-Factored Force Field. This method, introduced by Cotton and Kraihanzel[15,16] into transition-metal carbonyl chemistry, simplifies the Wilson[17] *GF* eigenvalue problem (1) by assuming the C–O stretching

$$|GF - \lambda E| = 0 \qquad (1)$$

vibrations are so far removed from other molecular vibrations that the complete *GF* matrix can be factored into one representing CO stretches (2).[18] The λ_{CO}'s are almost invariably

$$|g_{CO}k_{CO} - \lambda_{CO}E| = 0 \qquad (2)$$

derived from the anharmonic "CO-stretching" vibrations. The g_{CO} matrix is a diagonal matrix containing the inverse reduced masses of the CO groups. There are no off-diagonal terms since no CO groups have a common atom. The k_{CO} matrix consists of diagonal elements (CO stretching force constants)

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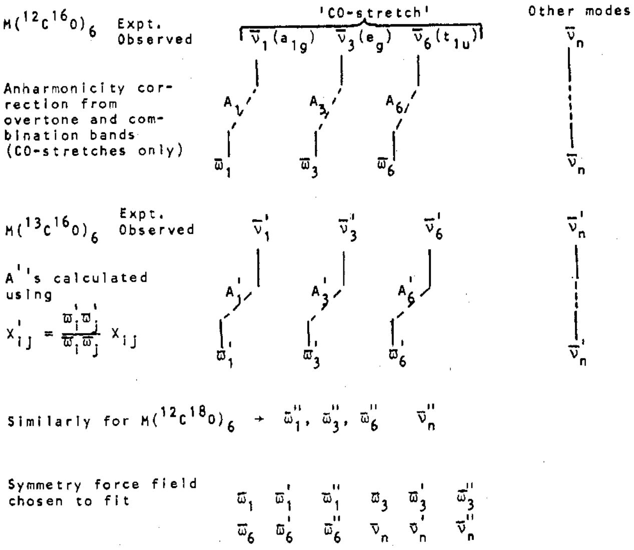

Figure 1. Schematic representation of GQVFF for $M(CO)_6$ in inert solvent. (This method ignores any Fermi resonance; some authors believe it may be important in such systems.)

Table I. Comparison of C-O Stretching Isotopic Shift Predictions[a] in cm^{-1} for $Cr(CO)_6$ in Solution and Matrix

	Γ	$\Delta\bar{\omega}^d$	$\Delta\bar{\nu}^e$	$\Delta\bar{\omega}^f$	$\Delta\bar{\omega}^g$	(P^h	S^h)	$\Delta\bar{\nu}^h$
			Solution[b]					
$Cr(^{13}C^{16}O)_6$	a_{1g}	0.5	−2.3	−1.7	0.4	(−2.6	0.5)	0.4
	e_g	0.1	−1.6	−1.1	0.0	(−1.6	0.4)	0.1
	t_{1u}	−0.5	−0.3	0.1	0.0	(−0.3	0.9)	−0.5
$Cr(^{12}C^{18}O)_6$	a_{1g}	0.3	4.3	4.8	0.3	(4.0	0.5)	0.3
	e_g	0.1	2.7	3.1	0.1	(2.5	0.4)	0.2
	t_{1u}	−0.4	0.6	1.1	0.0	(0.6	1.0)	−0.5
			Matrix[c]					
$Cr(^{13}C^{16}O)_6$	t_{1u}		0.6			(−0.3	0.9)	0.0
$Cr(^{12}C^{18}O)_6$	t_{1u}		1.9			(0.6	1.0)	0.3
$Cr(^{13}C^{18}O)_6$	t_{1u}		1.9			(0.2	1.9)	−0.2

[a] $\bar{\nu},\bar{\omega}$ refer to $Cr(^{12}C^{16}O)_6$; $\bar{\nu}',\bar{\omega}'$ to $Cr(^{13}C^{16}O)_6$; $\bar{\nu}'',\bar{\omega}''$ to $Cr(^{12}C^{18}O)_6$; $\bar{\nu}''',\bar{\omega}'''$ to $Cr(^{13}C^{18}O)_6$. [b] Data from ref 9. [c] Data from this work and ref 3. [d] GQVFF; $\Delta\bar{\omega} = [\bar{\omega}(\text{exptl}) - \bar{\omega}(\text{calcd})] - [\bar{\omega}'(\text{exptl}) - \bar{\omega}'(\text{calcd})]$, etc.; see Tables XII and XIV of ref 9. [e] $\Delta\bar{\nu}$ ($\equiv\bar{\nu}'(\text{exptl}) - \nu'(\text{calcd})$ etc.) from $\bar{\nu}'(\text{calcd}) = \bar{\nu}(\text{exptl})R'$. [f] $\Delta\bar{\omega}$ ($\equiv\bar{\omega}'(\text{exptl}) - \bar{\omega}'(\text{calcd})$ etc.) from $\bar{\omega}'(\text{calcd}) = \bar{\omega}(\text{exptl})R'$. [g] $\Delta\bar{\omega}$ ($\equiv\bar{\omega}'(\text{exptl}) - \bar{\omega}'(\text{calcd})$ etc.) from $\bar{\omega}' = \bar{\omega}(K_{CO'(\text{harmonic})}/K_{CO(\text{harmonic})})^{1/2}R'$; see Table II for values of K_{CO}'s. [h] $\Delta\bar{\nu}$ from $\bar{\nu}' = \bar{\nu}R' + \bar{\nu}R'Q' + AR'(1-R') \equiv \bar{\nu}R' + P + S$, therefore $\Delta\bar{\nu} = \bar{\nu}(\text{exptl}) - [\nu R' + P + S] = \Delta\bar{\nu}^e - P - S$.

which, in general, are different for CO groups unrelated by symmetry, and off-diagonal elements (CO–CO interaction force constants) which are, also, usually different for CO groups unrelated by symmetry. An initial suggestion[19] that, in octahedral and pseudooctahedral molecules, $k_{CO,CO}^{cis} \approx {}^1/_2 k_{CO,CO}^{trans}$ is an unnecessary and restrictive over-simplification which we do not use in our calculations. $g_{CO}k_{CO}$ or k_{CO} may be symmetrized (to give $G_{CO}K_{CO}$ or K_{CO})[18] to reduce calculation times for matrix diagonalization. In particular, for a molecule in which the carbonyl vibrations are all in different symmetry classes (e.g., for $M(CO)_6$: a_{1g}, e_g, t_{1u}) the symmetrized matrix ($G_{CO}K_{CO}$) is diagonal and the relationship between the C–O frequencies of "parent" molecule and the completely isotopically substituted molecule depends, in this approximation, only on the inverse reduced masses of the CO groups, i.e.,

$$\bar{\nu}_i'/\bar{\nu}_1 = (\mu_{CO}'/\mu_{CO})^{1/2} \equiv R'$$

The atomic masses and R values used in these calculations are given in the footnote 20. The values of the frequencies of the completely enriched molecules can be obtained by multiplying the $M(^{12}C^{16}O)_6$ frequencies ($\bar{\nu}$) by the appropriate R factor (R' for $^{13}C^{16}O$, R'' for $^{12}C^{18}O$, and R''' for $^{13}C^{18}O$ substitution[20]). The results are compared with the GQVFF calculations in Table I (column $\Delta\bar{\nu}^e$); the overall fit is very poor. However, it should be noted that the best fit is obtained for the $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$ shifts.

Table II. Values of K_{CO} (in N m^{-1} for $Cr(CO)_6$) Calculated Using Equation 3

	Mode		
	a_{1g}	e_g	t_{1u}
K_{CO} (12, 16)	1836	1675	1659
K_{CO}' (13, 16)	1831	1672	1658
K_{CO}''(12, 18)	1843	1679	1660
K_{CO}'''(13, 18)	1838	1676	1659

3. Harmonic, Energy-Factored Force Field. The effect of operating with the appropriate R factor on the *harmonic* frequencies (i.e., assuming $\bar{\omega}_i' = \bar{\omega}_i R'$, etc.) is also shown in Table I (column $\Delta\bar{\omega}^f$). The errors are again very large. Thus, as is well known, energy factoring is an inadequate approximation, whether harmonic or anharmonic frequencies are used.

4. Modified, Energy-Factored Force Field. Substitution of some of the GQVFF force constants (in particular F_{CO}, $F_{MC,CO}$, and F_{MC}) into eq 1 tells us that the value of λ_{CO} is determined to about 98–99%, in general, by the value of F_{CO}. However, this is merely a consequence of the high CO force constant compared to that for M–C stretching. The eigenvectors describing the "CO stretching vibration" indicate that a substantial contribution from the M–C stretching internal coordinate is in this mode. Miller[21] has derived an expression which takes this into account

$$K_{CO} = F_{CO} - 2xF_{MC,CO} + x^2F_{MC} \tag{3}$$

K_{CO} represents the symmetrized force constant (e.g., for $M(CO)_6$, $K_{t_{1u}} = k_{CO} - k_{CO,CO}^{trans}$) in terms of the symmetry F matrix elements of eq 1 (e.g., $F_{CO}(t_{1u}) = F_{66}$; $F_{MC}(t_{1u}) = F_{77}$; $F_{MC,CO}(t_{1u}) = F_{67}$ of Table IX of ref 9). It is important to note that there must be only one mode, of symmetry (Γ), in the energy factored force field description. The parameter x is given by the simple expression

$$x = \frac{\mu_C}{\mu_C + \mu_O} \equiv \frac{M_O}{M_C + M_O} \tag{4}$$

where μ's refer to reciprocal masses and M's to atomic masses. An equation very similar to eq 3 has been derived numerically by Jones for the $^{12}C^{16}O$ case and also examined by Bor et al.[22] We give a derivation of eq 3 via a different but illuminating route in the Appendix.

Equation 3 indicates two important facts: (i) the energy factored force constant (K_{CO}, etc.) will be different from the corresponding GQVFF values (F_{CO}, etc.) as demonstrated by several studies; (ii) the energy factored force constants will, in addition, depend on the CO isotope used, via the "x factor" of eq 3 although we expect this to be a smaller factor than (i).

So, for example, we may write an equation (5) relating the

$$\frac{\bar{\omega}_i'}{\bar{\omega}_i} = \left(\frac{K_{CO}'}{K_{CO}}\frac{\mu_{CO}'}{\mu_{CO}}\right)_i^{1/2} \equiv \left(\frac{K_{CO}'}{K_{CO}}\right)_i^{1/2} R' \tag{5}$$

harmonic frequencies of the single mode of given symmetry (Γ) in parent and totally isotopically substituted ($^xC^yO$) molecules (and similar expressions involving K_{CO}'', K_{CO}''', R'', R'''), where the K_{CO}'s are derived from eq 3 using *harmonic* F_{CO}'s and, using the data of ref 9, are listed in Table II. Using these values in eq 5 the isotopic shifts are calculated and compared with the experimental shifts in Table I (column $\Delta\bar{\omega}^g$). The errors are strikingly small, thus confirming how good an approximation is eq 3. A similar calculation using *an*harmonic K_{CO}'s derived from *an*harmonic F_{CO}'s produces a much worse fit. Clearly, therefore, both anharmonicity and vibrational coupling of M–C with C–O are important. This is readily seen by deriving a new expression; eq 5 can be rewritten

$$\bar{\omega}_i'/\bar{\omega}_i = (1 + Q_i')R'$$

where

$$Q_i' = (K_{CO'}/K_{CO})_i^{1/2} - 1 \approx 0$$

Since

$$\bar{\nu}_i = \bar{\omega}_i - A_i \qquad (6)$$

and assuming[23]

$$A_i' \approx A_i R'^2 \qquad (7)$$

$$\bar{\nu}_i' = \bar{\omega}_i' - A_i R'^2 \qquad (8)$$

it is easy to show (ignoring small second-order terms) that

$$\bar{\nu}_i' = \bar{\nu}_i R' + \bar{\nu}_i Q_i' R' + A_i R'(1 - R')$$

Defining $\bar{\nu}_i Q_i' R' \equiv P_i$ and $A_i R'(1 - R') \equiv S_i$

$$\bar{\nu}_i'(\text{exptl}) - \bar{\nu}_i'(\text{calcd}) = \bar{\nu}_i'(\text{exptl}) - \bar{\nu}_i(\text{exptl})R' - P_i - S_i \qquad (9)$$

$\bar{\nu}_i'(\text{exptl}) - \bar{\nu}_i(\text{exptl})R'$ is the error in applying the crude anharmonic energy factored force field—see Table I (column $\Delta\bar{\nu}^e$), P_i is a correction for M–C/C–O vibrational coupling, and S_i is the anharmonicity correction.[24] Table I gives the details of the calculations for $Cr(CO)_6$ (for the matrix-isolated species we use the K_{CO}'s calculated for the solution data); the column headed $\Delta\bar{\nu}^h$ gives the overall error. The errors are small and confirm the applicability of eq 9. We can now see why, overall, the "crude" approximation (Table I, $\Delta\bar{\nu}^e$) works better for $Cr(^{13}C^{16}O)_6$ shifts than for $Cr(^{12}C^{18}O)_6$ and $Cr(^{13}C^{18}O)_6$ shifts. It is simply that for $^{13}C^{16}O$, $K_{CO'}/K_{CO}$, as calculated using eq 3, is <1 so P is negative, while the anharmonic correction S is always positive so the P and S terms tend to cancel. Of course this argument will probably not apply to isocarbonyls, but there are no known binary metal isocarbonyls.

The method can be extended to other carbonyls for which a complete vibrational analysis is available. Strictly speaking, this simple analysis can only be done for vibrations which are unique in a symmetry class.

However, in practice the method works fairly well for mixed vibrations (e.g., the two a_1' modes of $Fe(CO)_5$). The results for $M(CO)_6$ (M = Cr, Mo, W), $Ni(CO)_4$, $Fe(CO)_5$, and $Co(CO)_3NO$ are given in Table III, available as additional material. Once again the anharmonic energy factored approach works best for $^{13}C^{16}O$ substitution.

Using eq 9 the isotopic shifts for all 61 frequencies in Table III are predicted with a root mean square error of 0.46 cm^{-1} and with a maximum error of 1.2 cm^{-1}, to be compared with a root mean square error of 2.62 cm^{-1} and maximum error of 5.4 cm^{-1} using the crudest energy-factored force field.

5. The Effective Reduced Mass. Bor[25] has introduced the concept of "effective" reduced mass. In its simplest application this is defined by

$$\bar{\nu}_i'/\bar{\nu}_i = R'_{\text{eff}} \equiv (\mu'_{\text{eff}}/\mu_{12,16})^{1/2} \qquad (10)$$

When this is compared with eq 9 it is clear that R'_{eff} contains a correction for both M–C/C–O coupling and anharmonicity. A more subtle application is to use "R_{eff}" ($\equiv R_{\text{variable}} \equiv R_v$), as a "floating" variable in calculations involving partially substituted species (e.g., $Cr(^{12}C^{16}O)_n(^{13}C^{16}O)_{6-n}$) and we shall return to this application shortly.

Table V. Anharmonic Energy Factored Force Field Constants (N m^{-1}) and Errors (cm^{-1}) between Calculated and Observed Band Positions of $Cr(^{12}C^{16}O)_n(^xC^yO)_{6-n}$

	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{13}C^{18}O$
	(A) Fixed Reduced Mass Ratio, R		
k_{CO}	1645.09	1647.56	1647.07
$k_{CO,CO}^{cis}$	26.59	27.05	26.5
$k_{CO,CO}^{trans}$	52.38	52.49	52.14
Std dev	0.31	0.67	0.61
Max error	0.9	1.6	1.6
R	0.977709	0.975855	0.953001
	(B) Variable Reduced Mass Ratio, R_v		
k_{CO}	1645.43	1645.65	1645.6
$k_{CO,CO}^{cis}$	26.61	26.81	26.51
$k_{CO,CO}^{trans}$	52.22	53.5	53.01
Std dev	0.29	0.21	0.14
Max error	0.8	0.4	0.3
No. of obsd bands	19	15	20
R_v	0.977496	0.977088	0.953869
$R - R_v$	2.13×10^{-4}	-12.33×10^{-4}	-8.68×10^{-4}
$R_{v(\text{calcd})}$	0.977425	0.977032	
$R - R_{v(\text{calcd})}$	2.84×10^{-4}	-11.77×10^{-4}	

For *fully* substituted species, Bor[26] has shown that the values of "effective atomic masses" determined for one carbonyl predict the isotopic shifts for other carbonyls better than the "absolute" mass values.

B. Partially Substituted Carbonyls. We now consider the analysis of the IR "carbonyl" bands of $Cr(^{12}C^{16}O)_n(^xC^yO)_{6-n}$ (x,y = 13,16; 12,18; 13,18; n = 0–6). It is only in matrix experiments that accurate data for all the substituted hexacarbonyls are available. The experimental data are collected in Table IV available as additional material.

Since we do not know the anharmonicites for all the various modes of these molecules, we have to attempt to fit the anharmonic frequencies.

The data can be analyzed using an energy-factored force field in two ways. (1) The octahedral species has 3 energy-factored force constants and the computer program is written to adjust these 3 force constants to produce the best fit of observed IR bands. This calculation assumes "absolute" mass values for the isotopic species—i.e., "fixed" reduced mass ratios, i.e., the R values in ref 20. The results are shown in Table IV (fixed R columns) and summarized in Table VA.

The best fit is obtained with $Cr(^{12}C^{16}O)_n(^{13}C^{16}O)_{6-n}$. On complete isotopic substitution the "crude" approximation worked best for $Cr(^{12}C^{16}O)_6 \rightarrow Cr(^{13}C^{16}O)_6$ shifts; although there is mixing of vibrations in the partially substituted species it appears that the anharmonic and MC/CO coupling tend to cancel mostly in the $^{13}C^{16}O$ substitution. Also in light of Table III we can generally expect the crude approximation to work best with $^{13}C^{16}O$ substitution and this is therefore to be generally preferred when performing mixed isotope experiments.

(2) In Section 5 we mentioned the "variable reduced mass ratio" ($\mu_{CO'}/\mu_{CO}$). As Bor hinted in one of his early papers it is possible to introduce this as an extra variable in the computer program. This extra variable has the effect of modifying the energy-factored force constants with isotope. The complete data are shown in Table IV (R_v variable column) and summarized in Table VB. The errors are reduced; with $^{12}C^{16}O/^{13}C^{18}O$ the standard deviation is less than the expected experimental error!

Since the standard deviation for $^{13}C^{16}O$ substitution is very similar whether R is fixed (Table VA) or "floats" (R_v) (Table VB) the "fixed" and "floating" values of R should be similar; the values of $R - R_v$ in Table VB confirm this.

Is there any way to predict the R_v values? The IR bands of partially substituted species derive from the a_{1g}, e_g, and t_{1u} modes of the parent. We might expect the variable R value (R_v) to reflect the R_{eff} values of the parent molecules. In fact, given the appropriate degeneracies we might expect

$$R'_v(\text{calcd}) = {}^1/_6\,[R'_{\text{eff}}(a_{1g}) + 2R'_{\text{eff}}(e_g) + 3R'_{\text{eff}}(t_{1u})] \tag{11}$$

Using the solution data[9] for the frequencies of $Cr(^{13}C^{16}O)_6$ and $Cr(^{12}C^{18}O)_6$ we obtain R_v(calcd) (Table V). The agreement with the R_v that gives the best fit (in the matrix) is very striking.

These calculations thus show how and under what conditions the "fortuitous cancellation of terms" applies and gives an indication of the "analytic expression" for the good fit.

C. Dinitrogen Complexes of Transition Metals. Many metal/dinitrogen and metal/dinitrogen/carbonyl complexes of transition metals have been synthesized in low-temperature matrices.[27] Invariably the vibrational spectroscopic data have been analyzed assuming energy factoring of the high-frequency N–N stretching vibrations.

It is interesting to compare N–N and C–O vibrations using the methods discussed so far. The most important difference is that in the equation corresponding to eq 3

$$K_{NN} = F_{NN} - 2xF_{MN,NN} + x^2F_{MN} \tag{12}$$

$x = 0.5$ for $^{14}N^{14}N$ *and* $^{15}N^{15}N$. Thus if this equation is a good approximation, the $^{14}N^{14}N \rightarrow {}^{15}N^{15}N$ shifts will deviate from that predicted from absolute R values only because of anharmonicity. Conversely, if accurate data are available for isotopic shifts then it is easy to show that anharmonicity constants can be derived. Unfortunately, in practice, experimental errors for $\bar{\nu}_{14/14} - \bar{\nu}_{15/15}$ of ± 0.6 cm^{-1} lead to enormous errors (± 40 cm^{-1}) in the anharmonicity constants. However, very accurate measurements of isotopic shifts of nitrogen compounds would be very valuable.

These remarks are of course also applicable to binary metal dioxygen complexes, with end-bonded O_2 groups.

D. Cyanide Complexes. The GQVFF method has been applied to several metal cyanides[28-30] and the completely substituted isotopic species.

We have applied the eq 9 corrections to these molecules (Table VI, available as additional material). The overall agreement is very good, with a root mean square error of 0.42 cm^{-1} over 34 frequencies. The anharmonic energy factored force field again gives a poor fit (root mean square error of 2.3 cm^{-1}) but gives a better agreement for the $^{12}C^{14}N \rightarrow {}^{13}C^{14}N$ shifts because of the cancellation of anharmonicity and force field corrections. This is analogous to the $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$ shifts in the metal carbonyls.

Conclusion

This work demonstrates under what conditions the energy-factored force field is applicable to metal carbonyls and related species. Further, it is shown that the errors in the approximations can be accounted for by a combination of anharmonicity and MC–CO coupling and that analysis of metal carbonyls with isotopic enrichment is best done with ($^{13}C^{16}O$) ennrichment.

Experimental Section

The isotopic enrichment, matrix isolation and wavenumber measurements were performed using exactly the same methods as Perutz and Turner.[3] All experiments were carried out at 20 K and used CH_4 (BOC Grade X) as the matrix material, $^{12}C^{18}O$ (60% ^{18}O) and $^{13}C^{18}O$ (90% ^{13}C, 95% ^{18}O) BOC Prochem. All calculations were carried out using the Hewlett Packard 2000E computer of the University of Newcastle Computing Laboratory. The wavenumbers of all the IR bands observed for $Cr(^{12}C^{16}O)_n(^xC^yO)_{6-n}$, statistically enriched with $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ in a CH_4 matrix, are listed in Table IV, available as additional material.

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Appendix

For every carbonyl molecule, if the "carbonyl" stretching modes transform as $\Gamma_{\text{vib,CO}}$ then the "MC stretching" modes transform under the same set of representations. One interesting observation found in the rather small number of GQVFF analyses of transition-metal carbonyl to date is that whereas both the MC and CO stretching internal coordinates both contribute to the normal mode loosely described as "CO stretching" the CO stretching internal coordinate does not contribute to the normal mode described as "MC stretching". In addition to these stretching modes, bending and deformation modes will also occur and these possess two important properties. Firstly, they are a long way removed in energy from the predominantly CO stretching modes. Secondly from local symmetry considerations there may be no interaction force constant connecting a CO stretching internal coordinate with the MCO bending coordinate containing that CO group. Thus, coupling between CO stretching and the bending and deformation coordinates is expected to be long range and indeed is found to be very small.

Consider a binary carbonyl and the vibrations contained in one particular symmetry species. We have three symmetry coordinates contained in this representation, CO stretching (R), MC stretching (r), and some bending (δ) coordinate. Only for some irreducible representations will there be a bending mode of this symmetry. The symmetry coordinates are linked to the normal coordinates Q by the eigenvectors of the Wilson GF matrix via the expressions

$$\begin{aligned} S_1(\delta) &= L_{11}Q_1 + L_{12}Q_2 + L_{13}Q_3 \\ S_2(r) &= L_{21}Q_1 + L_{22}Q_2 + L_{23}Q_3 \\ S_3(R) &= L_{31}Q_1 + L_{32}Q_2 + L_{33}Q_3 \end{aligned} \tag{A1}$$

where Q_3 is the normal coordinate representing the "CO stretch" and Q_1 and Q_2 represent the two lower frequency vibrations. The eigenvectors L are related to the G matrix by the simple eq $\sim L\tilde{L} = G$ and the identification of the relevant elements of $\sim L\tilde{L}$ leads to the following expression for the ratio of G_{23} (G matrix element linking CO and MC stretching internal coordinates) to G_{33} (diagonal G matrix element for CO stretching internal coordinate).

$$\frac{G_{23}}{G_{33}} = -\frac{\mu_C}{\mu_C + \mu_O} = \frac{L_{21}L_{31} + L_{22}L_{32} + L_{23}L_{33}}{L_{31}^2 + L_{32}^2 + L_{33}^2} \tag{A2}$$

Approximation 1: From our discussion above, since $S_3(R)$ only contributes to Q_3, $L_{31} = L_{32} = 0$ and

$$-\frac{\mu_C}{\mu_C + \mu_O} = -x(\text{eq } 4) = \frac{L_{23}}{L_{33}} \tag{A3}$$

Now the vibrational frequencies are determined using the expression $GFL = \lambda EL$ and thus the "CO stretching" frequency is given by

$$(GF)_{31}L_{13} + (GF)_{32}L_{23} + (GF)_{33}L_{33} = L_{33}\lambda_{CO} \tag{A4}$$

Approximation 2: The only internal coordinates contributing to Q_3 ("CO stretch") are R and r, i.e., $L_{13} = 0$. Hence from (A4)

$$\lambda_{CO} = (GF)_{33} + (GF)_{32}\frac{L_{23}}{L_{33}} \tag{A5}$$

Use of eq 1 and substitution of the relevant G matrix elements give

$$\lambda_{CO} = \mu_{CO}[F_{CO}(\Gamma) - 2xF_{MC,CO}(\Gamma) + x^2F_{MC}(\Gamma)]$$

where the $F(\Gamma)$ are the relevant combinations of force constants (f) leading to a symmetry force constant. This equation is identical with (3).

Registry No. $Cr(^{13}CO)_6$, 25941-09-7; $Cr(C^{18}O)_6$, 25875-16-5; $Cr(^{13}C^{18}O)_6$, 65392-05-4; $Mo(^{13}CO)_6$, 25941-10-0; $Mo(C^{18}O)_6$, 25875-17-6; $W(^{13}CO)_6$, 25941-11-1; $W(C^{18}O)_6$, 25941-12-2; $Ni(^{13}CO)_4$, 17594-06-8; $Ni(C^{18}O)_4$, 17099-52-4; $Fe(^{13}CO)_5$, 16997-09-4; $Fe(C^{18}O)_5$, 37766-06-6; $Co(^{13}CO)_3{}^{14}N^{16}O$, 17594-03-5; $Co(^{13}CO)_3{}^{15}N^{18}O$, 41582-03-0; $Co(C^{18}O)_3{}^{14}N^{16}O$, 41582-01-8; $Co(C^{18}O)_3{}^{15}N^{18}O$, 41582-02-9; $Cr(^{12}C^{16}O)_6$, 13007-92-6; $Cr(^{12}C^{16}O)_5(^{13}C^{16}O)$, 53109-01-6; $Cr(^{12}C^{16}O)_5(^{12}C^{18}O)$, 65392-04-3; $Cr(^{12}C^{16}O)_5(^{13}C^{18}O)$, 65392-03-2; *cis*-$Cr(^{12}C^{16}O)_4(^{13}C^{16}O)_2$, 53109-00-5; *cis*-$Cr(^{12}C^{16}O)_4(^{12}C^{18}O)_2$, 65437-10-7; *cis*-$Cr(^{12}C^{16}O)_4(^{13}C^{18}O)_2$, 65437-09-4; *trans*-$Cr(^{12}C^{16}O)_4(^{13}C^{16}O)_2$, 53108-99-9; *trans*-$Cr(^{12}C^{16}O)_4(^{12}C^{18}O)_2$, 65378-94-1; *trans*-$Cr(^{12}C^{16}O)_4(^{13}C^{18}O)_2$, 65378-93-0; *fac*-$Cr(^{12}C^{16}O)_3(^{13}C^{16}O)_3$, 53108-98-8; *fac*-$Cr(^{12}C^{16}O)_3(^{12}C^{18}O)_3$, 65391-67-5; *fac*-$Cr(^{12}C^{16}O)_3(^{13}C^{18}O)_3$, 65378-92-9; *mer*-$Cr(^{12}C^{16}O)_3(^{13}C^{16}O)_3$, 53109-02-7; *mer*-$Cr(^{12}C^{16}O)_3(^{12}C^{18}O)_3$, 65378-91-8; *mer*-$Cr(^{12}C^{16}O)_3(^{13}C^{18}O)_3$, 65378-90-7; *cis*-$Cr(^{12}C^{16}O)_2(^{13}C^{16}O)_4$, 53109-11-8; *cis*-$Cr(^{12}C^{16}O)_2(^{12}C^{18}O)_4$, 65437-66-3; *cis*-$Cr(^{12}C^{16}O)_2(^{13}C^{18}O)_4$, 65378-89-4; *trans*-$Cr(^{12}C^{16}O)_2(^{13}C^{16}O)_4$, 53042-53-8; *trans*-$Cr(^{12}C^{16}O)_2(^{12}C^{18}O)_4$, 65378-88-3; *trans*-$Cr(^{12}C^{16}O)_2(^{13}C^{18}O)_4$, 65391-68-6; $Cr(^{12}C^{16}O)(^{13}C^{16}O)_5$, 53109-12-9; $Cr(^{12}C^{16}O)(^{12}C^{18}O)_5$, 58167-58-1; $Cr(^{12}C^{16}O)(^{13}C^{18}O)_5$, 65378-99-6; $Co(^{13}CN)_6{}^{3-}$, 32648-15-0; $Co(C^{15}N)_6{}^{3-}$, 32648-16-1; $Ni(^{13}CN)_4{}^{2-}$, 52540-56-4; $Ni(C^{15}N)_4{}^{2-}$, 52540-55-3; $Pd(^{13}CN)_4{}^{2-}$, 52540-58-6; $Pd(C^{15}N)_4{}^{2-}$, 52540-57-5; $Pt(^{13}CN)_4{}^{2-}$, 52540-60-0; $Pt(C^{15}N)_4{}^{2-}$, 52540-59-7; $Au(^{13}CN)_2{}^{-}$, 65378-98-5; $Au(C^{15}N)_2{}^{-}$, 65378-97-4; $Fe(^{13}CN)_6{}^{3-}$, 65378-96-3; $Fe(C^{15}N)_6{}^{3-}$, 65378-95-2.

Supplementary Material Available: Table III, which lists experimental frequencies for $M(^xC^yO)_6$ (M = Cr, Mo, W; x, y = 13, 16; 12, 18; 13, 18), $Ni(^xC^yO)_4$ (x, y = 13, 16; 12, 18), $Fe(^xC^yO)_5$ (x, y = 13, 16; 12, 18), and $Co(^xC^yO)_3{}^zN^pO$ (x, y, z, p = 13, 16, 14, 16; 13, 16, 15, 18; 12, 18, 14, 16; 12, 18, 15, 18) and the calculated frequencies by the method of eq 9; Table IV, which gives experimental frequencies for $Cr(^{12}C^{16}O)_n(^xC^yO)_{6-n}$ (n = 0–6; x, y = 13, 16; 12, 18; 13, 18) and the calculated values using both fixed and floating R values and employing the energy factored force field; Table VI, which gives experimental frequencies for $^{13}C^{14}N$ and $^{12}C^{15}N$ complexes of Co, Ni, Pd, Pt, Au, and Fe and the calculated values by method of eq 9 (13 pages). Ordering information is given on any current masthead page.

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Thermodynamics of Chelation

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The enthalpy and entropy of solution of various species in chelation reactions, obtained from the literature or estimated by standard procedures, are compiled. These are used in Born–Haber-type cycles to calculate enthalpy and entropy of gas-phase reactions. A basic postulate is that the entropy change in the gas phase for $Cd(MeNH_2)_4{}^{2+} \rightarrow Cd(en)_2{}^{2+}$ (where en = 1,2-ethanediamine) is essentially the same as for $CEt_4 \rightarrow$ spiro[4.4]nonane. The analyses show that the enthalpy of solution of ligands generally is not ideal, and this affects the equilibrium as much as or more than the increase in the theoretical ideal translational entropy, 16 eu for two rings. The Cd–N bond strength is in general not the same in the monodentate and chelate structures; this holds especially for the ligands above. The entropies of solution of all species contribute to the $\Delta G°$ of reaction and are generally not ideal. In particular, the $\Delta S°$ of solution of the coordinated ionic species containing hydrocarbon groups (such as $Cd(MeNH_2)_4{}^{2+}$) are more negative, by as much as 34 eu, than $Cd(NH_3)_4{}^{2+}$. Some reactions have $\Delta H° \simeq 0$ and $\Delta S°$ near the calculated value. This is due to the confluence of several large and opposing enthalpy and entropy changes.

It is well known that many chemical processes differ considerably when carried out in the gas phase, as compared to aqueous solution. An example of this is the proton affinity of amines and ammonia.[1] So far the process of chelation has