

Why Do Cationic Carbon Monoxide Complexes Have High C–O Stretching Force Constants and Short C–O Bonds? Electrostatic Effects, Not σ -Bonding

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Abstract: A significant increase in the C–O stretching force constant (F_{CO}) and a decrease in C–O bond length (r_{CO}) result upon coordination of carbon monoxide to various cationic species. We report a study designed to elucidate the factors responsible for this effect. In particular, we distinguish between an explanation based on electrostatic effects and one based on withdrawal of electron density from the 5σ orbital of CO, an orbital generally considered to have some antibonding character. Ab initio electronic structure calculations on CO in the presence of a positive point charge (located on the carbon side of the bond axis) reveal that a simple Coulombic field increases the C–O stretching force constant and decreases the bond length. Coordination of CO to a simple cationic Lewis acid such as H^+ or CH_3^+ is calculated to increase F_{CO} (and decrease r_{CO}) to extents slightly less than those engendered by a point charge at the same distance from the carbonyl carbon. These results indicate that electron donation from the 5σ orbital has no intrinsic positive effect on the magnitude of F_{CO} . Calculations were also conducted on several symmetrical, neutral, and cationic transition metal complexes, including some examples of the recently discovered homoleptic noble-metal carbonyls. It is found that F_{CO} values can be quantitatively interpreted using a model which invokes only the effects of M–CO π -back-bonding and an electrostatic parameter. There is no correlation between the extent of σ -bonding (as measured by the depopulation of the CO σ orbitals) and F_{CO} . Calculations on trigonal bipyramidal d^8 metal pentacarbonyls permit a comparison between inequivalent ligands (axial and equatorial) which, being coordinated to the same metal center, must experience approximately the same electrostatic field. In the case of $Ru(CO)_5$, π -back-bonding to the axial and equatorial carbonyls is of virtually equal magnitude, while σ -donation is much greater from the axial ligands than from the equatorial ligands. Nevertheless, the F_{CO} and r_{CO} values of the two ligand sets are essentially equal, confirming that the magnitude of σ -donation does not affect these parameters.

The nature of bonding between transition metals and carbon monoxide is one of the most fundamental aspects of organo-transition metal chemistry. Virtually any discussion of such bonding involves the C–O stretching frequencies (ν_{CO}) of metal carbonyls, which are believed to be determined by the relative magnitudes of M–CO π -back-bonding and C→M σ -bonding. Whereas π -back-bonding clearly induces a decrease in ν_{CO} , C→M σ -bonding tends to receive less attention but is generally believed to increase ν_{CO} .¹ The magnitude of the π -back-bonding effect is widely accepted as much greater than that of σ -bonding, in accord with the observation that ν_{CO} values of most metal carbonyls are significantly lower than that of free CO.

However, the relative contributions of the π and σ components have been the subject of surprisingly little quantitative discussion. A detailed study was conducted by Hall and Fenske² for first-row d^6 metal carbonyl halides in which calculated orbital populations were compared with experimental vibrational frequency data. An equation was derived for the CO stretch force constant, k_{CO} ,³ which can be rearranged as eq 1:

$$k_{CO} \text{ (mdyn/\AA)} = 16.805 + 9.504\sigma_M - 11.729\pi_M \quad (1)$$

For a given complex, π_M is the total occupancy of the CO $2\pi^*$ orbitals and σ_M is the reduction in occupancy of the 5σ orbital. Using calculated σ_M and π_M values, eq 1 provided an excellent fit to the experimental force constants. Although the magnitude of the coefficients of eq 1 suggest that the respective contributions of the two components are of comparable magnitude, it would seem unwise to attribute much physical significance to such an interpretation. Note, for example, that the force constant of free CO, 18.56 mdyn/\AA, is much greater than the value of 16.805 mdyn/\AA which would be implied by a simple interpretation of eq 1 in the limit $\sigma_M = \pi_M = 0$. Conversely, the force constant of free CO^+ , 19.26 mdyn/\AA, is much smaller than the value of 26.31 mdyn/\AA naively derived on the basis of eq 1 ($\sigma_M = 1$; $\pi_M = 0$).

In recent years, a new and very intriguing class of late-metal complexes has been discovered: homoleptic noble metal carbonyl cations.^{4,5} M–CO bonding in these complexes is believed to involve little or even negligible M–CO π -back-bonding and, accordingly, the complexes have been termed “non-classical”. Carbonyl frequencies in these complexes are found to be *greater* than that of free CO (2143 cm^{-1}), in many cases by more than 100 cm^{-1} .^{4–7} This has been attributed to

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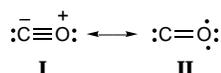
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the effect of C→M σ -bonding,⁴ an interpretation which implies that the influence of C→M σ -donation on ν_{CO} is quite strong, particularly since the bonding in the nonclassical complexes overall is fairly weak. Additionally, theoretical calculations indicate that covalent C→M σ -bonding is responsible for only a fraction of the small binding energies in these complexes^{8,9} (although J_{MC} values may suggest otherwise¹⁰); if so, this would further imply that even a very small degree of covalent C→M σ -bonding can effect a substantial increase in ν_{CO} .

The 5 σ orbital of CO is assumed to possess some C–O antibonding character.^{1,11} Hence, C→M σ -bonding should engender removal of electron density from this orbital and, accordingly, raise ν_{CO} . However, neutral carbonyl complexes in which M–CO π -bonding is believed to be weak and σ -bonding dominates (e.g., H₃B–CO) do not display very high ν_{CO} values. Indeed, many formally d⁰ neutral metal carbonyls have recently been discovered and all are found to possess ν_{CO} values less than that of free CO (however, it is proposed that in spite of the formal d⁰ electron configuration, the CO π^* orbitals are significantly populated in all such complexes¹²). Furthermore, even the gas phase CO⁺ cation has a ν_{CO} value of only 2184 cm⁻¹,¹³ much less than the average ν_{CO} value observed in many of the nonclassical carbonyl cations. Since it is implausible that more than one unit of charge is “removed” from the CO ligands in the metal carbonyl cations (indeed, previous calculations⁸ have suggested that net removal of charge from CO is quite small), the standard explanation (C→M σ -donation) for their high ν_{CO} values would appear problematic.

The bonding orbitals of free CO possess more oxygen than carbon character; i.e., they are polarized toward oxygen. Placing the molecule in an electrostatic field with C facing the positive pole, or placing a positive charge near C, would be expected to oppose this polarization, thus increasing the covalency of the molecule and the value of the stretching force constant.¹⁴ Alternatively, the same idea can be easily illustrated in terms of valence bond structures: a positive charge near the C-terminus should preferentially stabilize resonance form I.



Such an electrostatic effect on ν_{CO} of free CO was calculated by Hush and Williams as early as 1974 using semiempirical MO theory.¹⁵ Since then, other theoretical studies have concluded that the stretching frequency of free CO,^{16–18} as well

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(14) Note in this context that the (anharmonic) stretching force constant of N₂—the symmetrical analog of CO—is 22.39 mdyne/Å, and the bond distance is 1.0977 Å, vs 18.556 mdyne/Å and 1.1283 Å, respectively, for CO: Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*. Vol. IV. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

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as surface-bound CO,^{17,18} is increased by an electric field.¹⁹ Electrostatic effects certainly could contribute to the high ν_{CO} values of the nonclassical carbonyl cations,²⁰ an explanation previously suggested by Strauss¹⁰ though not discussed in detail. Herein we report calculations on organic carbonyls and homoleptic metal carbonyls, cationic and neutral, which demonstrate that not only do electrostatic effects indeed contribute to the observed high ν_{CO} values of the nonclassical carbonyl cations, but also that electrostatic effects may be the *only* major factors. We suggest that the degree of C→M σ -bonding plays no major role in raising the ν_{CO} values of these systems or, by extension, any other transition metal carbonyls.

Computational Details

Ab initio electronic structure calculations were carried out using methods implemented in the Gaussian 94 series of programs.²¹ For all transition metals, the effective core potentials and corresponding basis sets generated by Hay and Wadt were used.²² Small core type potentials, which liberate the penultimate electron shell along with the valence electrons for explicit treatment via basis functions, were employed, and the basis sets were of split valence quality (“LANL2DZ” model). In metal–carbonyl complexes, the carbonyls were described by the all-electron 6-31G* basis sets,²³ whereas we used the larger 6-311G* basis sets²⁴ for first and second row elements in calculations where transition metals were not included. All calculations were carried out including electron correlation at the level of Møller–Plesset second-order perturbation theory (MP2).²⁵ Systematic studies on complexes identical with or similar to the ones under study here^{8,26,27} have shown that this computational model generally predicts geometries and vibrational frequencies of most closed shell transition metal complexes in good agreement with experiment; some notable exceptions do, however, occur (e.g., Fe(CO)₅; see below).^{8,26,27}

Stationary points on the potential energy surfaces were located by optimizing all geometrical parameters within appropriate overall molecular point group constraints using analytical energy gradient methods.²⁸ Harmonic vibrational frequencies on non-metal-containing species were computed using analytical second derivatives. For metal-

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containing systems, our analysis relies on the use of internal harmonic carbonyl force constants as defined below. Molecular charge distributions were partitioned using the techniques developed by Weinhold et al. (NBO Analysis).²⁹

The Coulombic field effects of a unit positive point charge were simulated through the use of a pseudo-hydrogen ion (denoted H⁺) possessing a single, very diffuse (exponent 0.001 bohr⁻²) s-type orbital. In calculations on molecular cations, this limited basis set effectively eliminates covalent interactions between H⁺ and the remainder of the cation and prevents electrons from occupying the orbital on H⁺. Similarly, a He²⁺ ion carrying the same single s-type orbital simulated a positive point charge of two units (He²⁺), etc.

Internal harmonic force constants for carbonyl stretching, F_{CO} , were obtained from the energy changes resulting from extension of a single C–O bond length by 0.01 Å relative to the energy minimized geometries in, respectively, the carbonyl complex (ΔE_{MCO}) and free CO ($\Delta E_{free-CO}$), i.e.,

$$F_{CO} = (\Delta E_{MCO} / \Delta E_{free-CO}) F_{free-CO} \quad (2)$$

For the non-metal-containing systems, $F_{free-CO}$ is the force constant calculated for free CO at the MP2/6-311G* level, 18.43 mdyn/Å. For metal-containing systems, in which 6-31G* basis sets were used for the carbonyl ligands, F_{CO} values were scaled by the experimental value for free CO, $F_{free-CO} = 18.56$ mdyn/Å, rather than the value calculated at the MP2/6-31G* level (18.14 mdyn/Å). This facilitates comparison with experimentally obtained values. It was ascertained that the magnitude of the carbonyl bond length displacement was well within the parabolic range of the potential energy curve.

Results and Discussion

While “ ν_{CO} ” values, either observed or calculated, typically are approximated to force constants, F_{CO} , according to the harmonic oscillator expression, eq 3, it is important to keep in mind some limitations of this approach.

$$\nu_{CO} = (2\pi)^{-1} (F_{CO} / \mu_{CO})^{1/2} \quad (3)$$

When CO is bound to a light atom, as in HCO⁺, mixing of the vibrational coordinates may be strong and eq 3 is no longer useful as an interpretational tool. For example, the experimental “ ν_{CO} ” value⁴ of HCO⁺ is 2184 cm⁻¹ (as compared with 2143 cm⁻¹ for free CO); however, this normal mode is the C–O stretch substantially mixed with the C–H stretch coordinate. Ab initio electronic structure calculations (MP2/6-311G*) afford “ ν_{CO} ” values of 2142 cm⁻¹ for HCO⁺ and 2136 cm⁻¹ for CO, respectively. The effect of ν_{HC} mixing can be reduced, for comparative purposes, by conducting the normal mode calculation assuming a very large mass for H (e.g., $m_H = 500$ au gives $\nu_{CO} = 2369$ cm⁻¹); more generally, the calculated effect of mixing between the C–O and M–C stretching coordinates (M = any atom coordinated to CO) can be similarly reduced. However, adduct formation will always influence ν_{CO} values (experimental or calculated), even in the limit of M having infinite mass. For example, as noted by Hush and Williams,¹⁵ consider M–CO where $m_M = \infty$, $F_{MC} = 1.856$ mdyn/Å (i.e., 10% the value in free CO and corresponding to $\nu_{MC} = 330$ cm⁻¹). If $F_{CO} = 18.56$ mdyn/Å, unchanged from that of free CO, then the molecular ν_{CO} value will be 2179 cm⁻¹. If F_{MC} is twice as large (3.71 mdyn/Å, corresponding to $\nu_{MC} = 459$ cm⁻¹), then ν_{CO} will be increased further to 2215 cm⁻¹. Indeed, a reasonably thorough analysis of observed ν_{CO} values requires a complete set of vibrational spectral data for several isoto-

Table 1. Computed Data for MCO Species with Full (6-311G*) and Limited (Indicated by Asterisk) Basis Sets

MCO	r_{MC} (Å)	F_{elec}^a (au)	$r_{CO}(\text{calc})$ (Å)	F_{CO}^b (mdyn/Å)	ΔF^c (mdyn/Å)	ν_{CO}^d (cm ⁻¹)
CO			1.139	18.43	0.00	2136
HCO ⁺	1.094	0.102	1.120	20.42	1.99	2248
H*CO ⁺	1.000	0.115	1.117	20.97	2.54	2278
H*CO ⁺	1.094	0.102	1.119	20.76	2.33	2267
H*CO ⁺	1.126	0.099	1.119	20.83	2.40	2270
H*CO ⁺	1.434	0.070	1.123	20.16	1.73	2234
H*CO ⁺	1.800	0.050	1.127	19.73	1.30	2210
H*CO ⁺	1.900	0.046	1.128	19.63	1.20	2204
H*CO ⁺	2.000	0.043	1.128	19.53	1.10	2198
H*CO ⁺	2.100	0.040	1.129	19.43	1.01	2193
H*CO ⁺	2.200	0.037	1.130	19.36	0.93	2189
H*CO ⁺	2.300	0.034	1.130	19.29	0.86	2185
H*CO ⁺	2.500	0.030	1.132	19.16	0.73	2178
H*CO ⁺	3.000	0.022	1.134	18.94	0.51	2165
H*CO ⁺	3.060	0.021	1.134	18.92	0.49	2164
H*CO ⁺	3.440	0.018	1.135	18.82	0.39	2158
H*CO ⁺	4.732	0.010	1.137	18.64	0.21	2148
He*CO ²⁺	3.060	0.043	1.131	19.49	1.06	2196
Li*CO ³⁺	3.060	0.064	1.121	19.85	1.42	2216
Li*CO ³⁺	3.540	0.050	1.123	19.76	1.33	2211
Be*CO ⁴⁺	5.550	0.030	1.126	19.51	1.08	2197
Be*CO ⁴⁺	4.732	0.040	1.125	19.61	1.18	2203
Be*CO ⁴⁺	4.173	0.050	1.123	19.66	1.23	2206
Be*CO ⁴⁺	3.761	0.060	1.122	19.69	1.26	2207
Be*CO ⁴⁺	3.440	0.070	1.122	19.66	1.23	2206
Be*CO ⁴⁺	3.060	0.085	1.121	19.52	1.09	2198
Be*CO ⁴⁺	2.787	0.100	1.121	19.22	0.79	2181
MeCO ⁺	1.434	0.070	1.127	19.60	1.17	2202
MeCO ⁺	1.550	0.063	1.126	19.78	1.35	2212
H ₃ BCO	1.551		1.138	18.53	0.098	2141

^a $F_{elec} = q/r_{cent}^2$, where r_{cent} is the distance between M and the center of the CO molecule. ^b F_{CO} calculated according to eq 2. ^c F_{CO} minus the value calculated for free CO, 18.43 mdyn/Å. ^d Hypothetical frequency (provided only for purposes of qualitative comparisons with ν_{CO} values of actual molecules) calculated from F_{CO} ,^b assuming the relationship expressed in eq 3.

omers of the complexes under study.^{30,31} For example, in a study of the relatively simple molecule borane carbonyl, Jones et al. analyzed up to 21 observed vibrational bands in each of 10 different isotopomers of H₃B–CO.³² Computationally, however, a useful and simple approach toward an understanding of the factors which influence ν_{CO} is possible: total energies can be calculated at the equilibrium and one or more discrete nonequilibrium C–O distances while the M–C distances are held fixed. In principle, this approach yields “true” internal F_{CO} values.^{3,31} While these are expected to differ from experiment-based k_{CO} values, it is expected that any significant trends in k_{CO} and F_{CO} values would closely parallel each other.^{3,33}

Non-Metal-Containing Systems: Cationic CO-Adducts and CO in an Electric Field. Table 1 gives the calculated F_{CO} values and metric parameters for [M*CO]ⁿ⁺, where M* is a simulated point charge (H⁺, He²⁺, Li³⁺, Be⁴⁺; see Computational Details) and r_{M^*C} is fixed at various distances ($\angle M^*-C-O = 180^\circ$). The effects of M* on F_{CO} , and hence ν_{CO} , are seen to be substantial. For example, in H*CO⁺ at $r_{H^*C} = 1.80$ Å, the electric field induces a change in F_{CO} of approximately 1.3 mdyn/Å relative to free CO, a change which translates into a vibrational frequency increase of more than 70 cm⁻¹. At M*–C distances above ca. 1.80 Å, a range which

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includes all M–C distances found in transition metal carbonyls, the effect of M* on the magnitude of F_{CO} is found to correlate well with the electric field strength exerted by the positive point charge at the center of the C–O bond (F_{elec} , eq 4).

$$F_{\text{elec}} = q/r_{\text{cent}}^2 \quad (4)$$

r_{cent} is the distance between M and the center of the CO bond. Thus, for the species H^*CO^+ an increase in $r_{\text{H}^*\text{C}}$ of 0.1 Å produces a decrease in F_{elec} of approximately 0.003 au, a relative change in F_{CO} of approximately 0.08 mdyne/Å, and a change in ν_{CO} of approximately 5 cm^{-1} . This observation supports the notion that the essential role of M* is to exert a simple Coulombic field. However, for a given value of F_{elec} , charges situated at distances less than ca. 1.80 Å from C exert a proportionally greater effect on F_{CO} than expected on the basis of eq 4, presumably because the field strength is no longer approximately uniform across the entire carbonyl. For example, the Coulombic field strength at the center of the C–O bond due to Be^{*4+} at a distance of 2.79 Å from C should be the same as that of H^{*+} at 1.11 Å ($F_{\text{elec}} = 0.10$ au); yet, the effect on F_{CO} of the H^{*+} is much greater ($\Delta F_{\text{CO}} = 2.33$ mdyne/Å vs 0.79 mdyne/Å due to Be^{*4+}). For all M^*CO^{n+} species, the point-charge induced decrease in r_{CO} (relative to that of free CO) is small (~ 0.01 – 0.02 Å) and generally correlates well with the magnitude of F_{elec} .

MP2/6-311G* level calculations on HCO^+ yield equilibrium H–C and C–O bond distances of 1.094 and 1.120 Å, respectively, in good agreement with experimental values (1.097 and 1.105 Å).^{34,35} When r_{CO} is varied with r_{HC} held fixed at 1.094 Å, the value obtained for F_{CO} in HCO^+ is 20.42 mdyne/Å, 1.99 mdyne/Å greater than F_{CO} computed for free CO (18.43 mdyne/Å). For H^*CO^+ , the optimized C–H* and C–O distances are calculated to be 1.126 Å and 1.119 Å, and F_{CO} is calculated to be 20.83 mdyne/Å. A more relevant comparison with the HCO^+ molecule is provided by fixing $r_{\text{H}^*\text{C}}$ at 1.094 Å, the optimized value of r_{HC} in HCO^+ . For this configuration of H^*CO^+ , F_{CO} is calculated to be 20.76 mdyne/Å and r_{CO} optimizes to 1.119 Å. Thus, at either $r_{\text{H}^*\text{C}}$ distance, the presence of the +1 point charge is calculated to increase F_{CO} by more than 2 mdyne/Å with respect to the value in free CO (see Table 1); however, the differences in F_{CO} between H^*CO^+ and HCO^+ are found to be small (0.3–0.4 mdyne/Å). Therefore, in so far as one can abstract the contribution to F_{CO} made by covalent (purely σ) bonding of H^+ to CO, it is calculated to be quite small and actually *diminishing* the magnitude of F_{CO} .

The acetyl cation (H_3CCO^+) may be viewed as CO coordinated to a nearly pure σ -acceptor cation, CH_3^+ . Our calculations on H_3CCO^+ yield equilibrium H_3C –CO and C–O bond distances of 1.439 Å and 1.127 Å, in good agreement with the experimental value for this (1.435 Å and 1.099 Å, respectively)^{34,36} and related acylium cations.^{10,34,37} The value of F_{CO} is found to be 19.61 mdyne/Å, 1.2 mdyne/Å larger than its value

(34) The bond distance in free CO is calculated as 1.1387 Å (MP2/6-311G*) and 1.1512 Å (MP2/6-31G*) as compared with an experimental value of 1.1282 Å (ref 13). For HCO^+ , calculated (MP2/6-311G*) and experimental C–O bond lengths are 1.1201 Å and 1.1047 Å, respectively (ref 35). These fairly small discrepancies are typical of those found in much of this work; i.e., calculated C–O distances are about 0.01–0.02 Å greater than the apparently highest quality experimental values.

(35) The experimental H–C and C–O bond lengths in HCO^+ are reported to be 1.097 26 and 1.104 74 Å, respectively: Woods, R. C. Private communication in: Berry, R. J.; Harmony, M. D. *J. Mol. Spectrosc.* **1988**, *128*, 176–194.

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in free CO. By comparison, H^*CO^+ has an F_{CO} value of 20.15 mdyne/Å when $r_{\text{H}^*\text{C}}$ is held fixed at 1.44 Å. Thus, in this case, as in the above comparison of H^*CO with HCO^+ , “turning on” σ -bonding apparently has a slightly *diminishing* effect on the value of F_{CO} .

Our calculated effects of a point charge on F_{CO} agree well with results from early semiempirical electronic structure calculations (CNDO/2) by Hush and Williams.¹⁵ While values for F_{CO} were only reported for axial uniform fields in strength increments of 0.1 au, an approximately parabolic curve was obtained from which it can be estimated that a field strength of 0.05 au would result in an increase in F_{CO} of ca. 1.35 mdyne/Å. This compares favorably with the value of 1.30 mdyne/Å obtained for H^*CO^+ when r_{CH^*} is fixed at 1.80 Å, the H*–C distance which produces a Coulombic field strength (F_{elec}) of 0.05 au at the center of the CO bond. The effect of a point charge would presumably better approximate that of a uniform axial field at greater distances from CO. Charges of +3 and +4 held at 3.54 Å and 4.17 Å from C, respectively, should each result in an effective electrostatic field of 0.05 au at the CO bond center. Indeed, the species $\text{Li}^*\text{CO}^{3+}$ ($r_{\text{CLi}^*} = 3.54$ Å) has an F_{CO} value of 19.76 mdyne/Å, i.e., 1.33 mdyne/Å greater than that calculated for free CO; the calculated F_{CO} value of $\text{Be}^*\text{CO}^{4+}$ ($r_{\text{CBe}^*} = 4.17$ Å) is 1.23 mdyne/Å greater than that of free CO.

The vibrational frequency of free CO in a weak electric field has been previously calculated, at the *ab initio* Hartree–Fock level only, in the context of electric field effects on chemisorbed CO.^{17,18} These studies predicted an increase of ca. 34 cm^{-1} in a uniform field of +0.01 au, as compared with our calculated shift of 12 cm^{-1} for H^*CO^+ when $r_{\text{H}^*\text{C}} = 4.73$ Å, $F_{\text{elec}} = +0.01$ au. In another study, Gagarin and Chuvylkin¹⁶ used a model potential for field-free CO and calculated that a unipositive point charge 2.5 Å from the center of CO (ca. 1.94 Å from C) produced an increase in ν_{CO} of 77 cm^{-1} ; at a distance of 4.0 Å (3.44 Å from C) the increase was calculated to be 25 cm^{-1} . These values are in excellent agreement with our own calculated shifts for H^*CO^+ : 66 cm^{-1} and 23 cm^{-1} , respectively (Table 1).

Hush and Williams¹⁵ also calculated that an axial electric field strength of +0.1 au results in an increase in F_{CO} of 1.80 mdyne/Å ($\Delta\nu_{\text{CO}} = 102$ cm^{-1}). This effect was calculated to be approximately a maximum; further increase of the field resulted in a calculated decrease of F_{CO} . Our calculations also predict a maximum F_{CO} value, though at a lower electric field strength. When the distance between CO and a Be^{*4+} point charge is varied, F_{CO} is calculated to be at a maximum value of 19.69 mdyne/Å (1.26 mdyne/Å greater than that for free CO) at a distance of 3.76 Å (corresponding to $F_{\text{elec}} = +0.06$ au; see Table 1). Likewise, when a point charge held at 3.06 Å from C is increased in magnitude from +1 to +4 au, in unit increments, a maximum F_{CO} value of 19.85 mdyne/Å (1.42 mdyne/Å greater than that of free CO) is found at $q = +3$ au (Li^{*3+} ; $F_{\text{elec}} = 0.064$ au). The appearance of a maximum is presumably due to a reversal of orbital polarization at very high electric field strengths. Our results indicate that the C–O bond becomes most covalent (“N₂-like”) at a field strength of ca. 0.06 au. A snapshot of the changes in the CO electron distribution in the presence of a Coulombic field from a unit positive charge may be found in a paper by Bauschlicher and Barnes on the dissociation energies and bonding in NiCO^+ and TiCO^+ . There is a clear net movement of charge in the π -space from O to C

(diminished C^+-O^- polarization) and a buildup of σ -charge between C and the positive charge.³⁸

The above calculations (in conjunction with the experimental data) on these simple metal-free systems are all consistent with the proposal that σ -bonding has no significant increasing effect on F_{CO} . Instead, the high F_{CO} values found in the cationic complexes HCO^+ and H_3C-CO^+ can be attributed primarily to electrostatic effects.

Borane Carbonyl: A Neutral CO Adduct. H_3B-CO is frequently offered as an example of a neutral Lewis acid/CO complex in which π -back-bonding is presumed to play only a minor role. Unfortunately, it is not clear that the actual magnitude of hyperconjugative π -back-bonding can be neglected, even as a rough but useful approximation.^{32,39,40} Nevertheless, we are aware of no neutral carbonyl complexes which better approximate a purely σ -bonding model; thus, with the above caveat in mind, we offer the following observations.

H_3B-CO has a " ν_{CO} " value only slightly greater than that of free CO: ca. 2167 cm^{-1} versus 2143 cm^{-1} ,^{13,32,41} which, according to eq 3, corresponds to $F_{CO} = 18.93$ mdyne/Å, only 0.38 mdyne/Å greater than that of free CO. However, even this small difference is probably somewhat misleading as it is influenced not only by the "true" CO stretching force constant, but also (*inter alia*) by the B-C stretching force constant, which is fairly large ($\nu_{BC} = 691$ cm^{-1} ,^{32,41} corresponding to $F_{BC} = 2.85$ mdyne/Å³²). Accordingly, an extremely thorough force field analysis by Jones et al. leads to the conclusion that F_{CO} increases by only 0.22 ± 0.13 mdyne/Å upon coordination to BH_3 .³²

Vibrational frequency calculations on H_3B-CO afford ν_{CO} and ν_{BC} values of 2175 cm^{-1} and 707 cm^{-1} , respectively, in excellent agreement with experimental values. Single-point energy calculations with a "stretched" C-O bond imply that F_{CO} is very slightly greater for H_3B-CO (0.10 mdyne/Å) than for free CO. Finally, we note that the MP2/6-311G* calculated C-O bond length in H_3B-CO , 1.1380 Å, is essentially identical with that calculated for free CO, 1.1387 Å. In short, experiment and theory both indicate that complexation to BH_3 has a negligible effect on the C-O stretching force constant.

Transition Metal Carbonyls: Intermolecular Comparisons. Calculated structural data and atomic charges (MP2 level) of several neutral and cationic metal carbonyls, both classical and nonclassical, are shown in Table 2. Where comparisons are appropriate, the calculated geometries are in excellent agreement with recently published data by Frenking^{8,42} and Thiel.²⁷ The validity of Frenking's calculations on noble metal carbonyl cations⁸ has recently received support from experimental bond energy data by Armentrout.⁴³

Increasing net charge on a metal center is expected to lead to increased M-CO σ -bonding and decreased π -bonding, all other factors being equal.^{44,45} Thus, comparisons within an isoelectronic series cannot easily distinguish between electrostatic and covalent effects on F_{CO} . In particular, assuming significant effects from π -bonding,^{44,45} it is difficult to ascertain the importance of σ -bonding and electrostatics by varying only

Table 2. Calculated and Experimental Bond Distances and Calculated Atomic Charges

	r_{M-C}		r_{C-O}		q_{CO}	q_C	q_O	ref
	calc	exp ^a	calc	exp ^a				
CO			1.151	1.128	0	0.45	-0.45	b
Ni(CO) ₄	1.811	1.838(2)	1.161	1.141(2)	-0.17	0.19	-0.36	c
		1.817(3)		1.127(4)				d
Pd(CO) ₄	2.029		1.157		-0.04	0.35	-0.39	
Pt(CO) ₄	1.970	1.92(2)	1.160	1.14(2)	-0.15	0.21	-0.36	e
Cr(CO) ₆	1.854	1.91(1)	1.167	1.15(1)	0.23	0.59	-0.36	f
Mo(CO) ₆	2.054	2.07(1)	1.165	1.15(1)	0.16	0.52	-0.36	g
W(CO) ₆	2.053	2.06(1)	1.166	1.14(1)	0.11	0.46	-0.36	h
Mn(CO) ₆ ⁺	1.794		1.157		0.38	0.64	-0.26	
Re(CO) ₆ ⁺	2.019	2.01(4)	1.155	1.13(3)	0.27	0.53	-0.26	i
[Ag(CO) ₂] ⁺	2.241	2.13(11)	1.143	1.08(6)	0.11	0.37	-0.26	j
[Ag(CO)] ⁺	2.358	2.10(1)	1.143	1.077(16)	0.04	0.31	-0.27	j
[Au(CO) ₂] ⁺	2.017	2.05	1.142	1.11	0.21	0.42	-0.21	k

^a In some cases where more than one reliable experimental value is available (including crystallographically inequivalent carbonyls in a single structure), intermediate values are chosen; error limits, given in parentheses, are estimates. ^b Reference 13. ^c Reference 51. ^d Reference 52. ^e Values are those of $Pt(PPh_2Et)_2(CO)_2$; ref 53. ^f Reference 54. ^g Reference 55. ^h Reference 56. ⁱ Reference 57. ^j Reference 10. ^k Reference 5.

the charge on the metal center. However, by comparing a wide range of complexes we find that the magnitude of F_{CO} does not correlate with CO π^* - and σ -orbital populations; rather, it correlates with π^* -orbital populations and electrostatic effects.

Both increased M-CO σ -bonding and decreased π -bonding are expected to lead to increased charge on the CO ligand and especially on the C atom. Comparisons between species which are not isoelectronic reveal that net charges on the CO ligands (q_{CO}) of cationic complexes are *not* necessarily much greater than on the CO ligands of neutrals. In particular, the ligands of the silver carbonyls possess less positive charge than those of the neutral hexacarbonyls. Furthermore, and perhaps more surprisingly, the charges on the C atoms (q_C) of the silver carbonyls are significantly less than those on the hexacarbonyls. Even comparisons between cations and the respective "isoelectronic" neutrals reveal only small differences in q_C . For example, a comparison of $Re(CO)_6^+$ with $Mo(CO)_6$ reveals that, although the carbonyls engage in more σ -bonding (0.04 e) and less π -back-bonding (0.06 e) in $Re(CO)_6^+$ than in $Mo(CO)_6$, the charges on the carbon atoms of the two complexes are essentially equal (within 0.01 e). By contrast, charges on the O atoms (q_O) of the cations are systematically greater than those on the O atoms of the neutrals by ca. 0.10 e, and within each group (neutral or cationic) the differences between q_O values are strikingly small. Clearly, these charge distributions cannot be explained solely in terms of covalent bonding effects, but must instead be attributed to polarization by the substantial net charge situated at the center of the cationic complexes.³⁸

The calculated F_{CO} values (Table 3) generally compare well with experiment-based k_{CO} values (obtained, for example, using the Cotton-Kraihanzel approximation³³). Computational self-consistency is indicated by a good correlation obtained between calculated F_{CO} values and C-O bond distances (see Figure 1); this correlation implies that most of the discussion herein about (increased) F_{CO} values could be applied as well to (decreased) r_{CO} bond lengths. For purposes of qualitative comparison only, we have converted the calculated F_{CO} values to hypothetical ν_{CO} values (Table 3) using eq 3. Also in Table 3 are net π - and σ -electron populations on the CO ligands, relative to free CO. Inspection of the data immediately suggests that increased σ -donation does not necessarily result in an increased F_{CO} value. For example, $Cr(CO)_6$ and $Pt(CO)_4$ are found to have approximately equal degrees of π -bonding while the extent of

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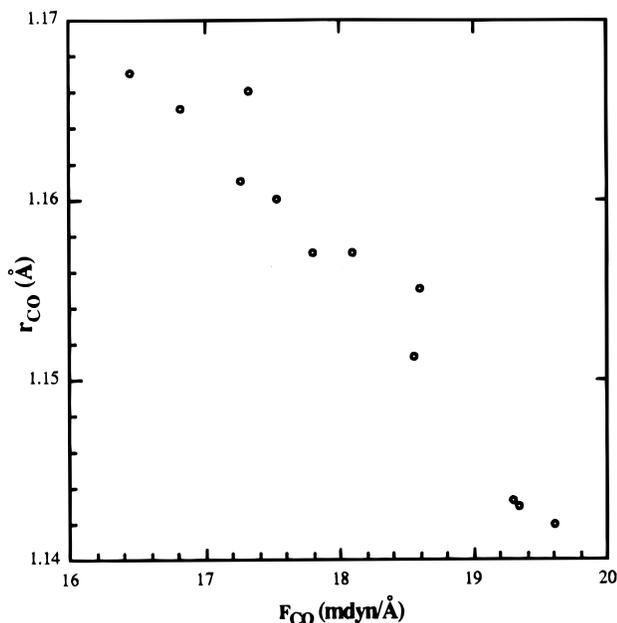
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Table 3. Transition Metal Carbonyl Data: F_{CO} Values Calculated According to Eq 2, Electrostatic Parameter (C^a), Calculated Net Populations Relative to Free CO (π_{M} and σ_{M}), F_{CO} Values Calculated According to Eq 6, and Experimental k_{CO} Values

complex	F_{CO} (eq 2)	C^a	π_{M}	σ_{M}	F_{CO} (eq 6)	Δ^b	$k_{\text{CO}(\text{exp})}$
CO	18.56	0.0	0.000	0.000	18.56	0.00	18.56 ^c
Ni(CO) ₄	17.28	0.0	0.422	0.235	16.91	-0.37	17.23 ^d
Pd(CO) ₄	17.81	0.0	0.258	0.220	17.55	-0.26	17.55 ^d
Pt(CO) ₄	17.53	0.0	0.396	0.233	17.01	-0.52	17.28 ^d
Cr(CO) ₆	16.45	0.0	0.386	0.605	17.05	0.60	17.02 ^e
Mo(CO) ₆	16.82	0.0	0.324	0.469	17.29	0.47	16.52 ^f
W(CO) ₆	17.33	0.0	0.370	0.429	17.11	-0.22	16.95 ^e
Mn(CO) ₆ ⁺	18.10	1.304	0.298	0.662	18.70	0.60	
Re(CO) ₆ ⁺	18.61	1.098	0.262	0.511	18.63	0.02	18.67 ^e
[Ag(CO) ₂] ⁺	19.34	0.900	0.102	0.152	19.06	-0.28	19.50 ^g
[Ag(CO)] ⁺	19.30	0.821	0.026	0.081	19.28	-0.03	19.62 ^h
[Au(CO) ₂] ⁺	19.61	1.083	0.087	0.306	19.30	-0.31	20.1 ⁱ

^a Change in F_{CO} calculated for free CO induced by placement of a unipositive point charge (H^{*+} ; see Table 1) at a distance equal to the M-C bond length (see text). ^b F_{CO} (eq 2) - F_{CO} (eq 6). ^c Reference 13. ^d Reference 58. ^e Reference 59. ^f Reference 33. ^g Reference 60. ^h Reference 10. ⁱ Reference 5.

**Figure 1.** Plot of calculated C-O bond distance (r_{CO}) versus calculated internal harmonic force constant (F_{CO}) values for transition metal carbonyls (data in Tables 2 and 3).

σ -bonding is much greater for $\text{Cr}(\text{CO})_6$. Yet F_{CO} (both experimental and calculated) is significantly less for the chromium complex.

Following Hall and Fenske,² we consider a model in which F_{CO} is assumed to be linearly dependent on the extent of π - and σ -bonding; i.e., F_{CO} varies linearly with the amount of charge transferred. However, in an attempt to derive an equation more amenable to physical interpretation, we fix the intercept ($\sigma_{\text{M}} = \pi_{\text{M}} = 0$) at the experimental value of F_{CO} in free CO (eq 5).

$$F_{\text{CO}} = 18.555 \text{ mdyn/Å} + \alpha(\sigma_{\text{M}}) - \beta(\pi_{\text{M}}) \quad (5)$$

σ_{M} and π_{M} are the net charge transfers resulting from σ - and π -bonding, respectively, for each CO ligand in a given complex.

No satisfactory fit to eq 5 can be found with the calculated values of F_{CO} , σ_{M} , and π_{M} . In particular, best-fit values of α and β ($\alpha = 1.2$, $\beta = 4.4$, $\sum(\Delta^2/n) = 0.50$) predict values of

F_{CO} which are much too low for the cations, particularly for the nonclassical cations. This is consistent with the qualitative observation that the F_{CO} values of the cations are significantly greater than those of the isoelectronic neutrals although there is no substantial difference between the σ_{M} and π_{M} values of the two groups (cf. $\text{Re}(\text{CO})_6^+$ and $\text{Mo}(\text{CO})_6$, for example, in Table 3). Note also that the optimal value of α (1.2 mdyn/Å per electron) is not significantly positive.

The differences in F_{CO} values between the cationic and neutral metal carbonyls are of the order 1–2 mdyn/Å. Given the above calculations on CO in the presence of a point charge (Table 1), this is the order of magnitude expected on the basis of electrostatic effects if the charge on the metals in the cationic complexes is assumed to be approximately 1 au greater than in the analogous neutrals. Such an assumption leads us to consider the following extension of eq 5:

$$F_{\text{CO}} = 18.555 \text{ mdyn/Å} + C + \alpha(\sigma_{\text{M}}) - \beta(\pi_{\text{M}}) \quad (6)$$

For a given complex, C is the change in F_{CO} induced by placement of a unipositive point charge (H^{*+} ; see Table 1) at a distance equal to the M-C bond length, i.e., an electrostatic effect. Appropriate values of C are given in Table 3.

If the effect of σ -bonding is disregarded ($\alpha = 0$), eq 6 has only a single independent variable, as compared with the two-variable equation 5. Nevertheless, eq 6 ($\alpha = 0$) yields a much better fit than can be obtained for eq 5 (without holding $\alpha = 0$). Assuming $\alpha = 0$, a best fit ($\sum\Delta^2/n = 0.15$) for eq 6 is found with $\beta = 3.9$ mdyn/Å per electron.

Further evidence against a significant positive contribution to F_{CO} due to σ -bonding comes from the result that if α is not held at zero, a best fit for eq 6 is found with a substantially negative α value ($\alpha = -1.4$, $\beta = 2.2$, $\sum(\Delta^2/n) = 0.086$). It was found above that σ -bonding for metal-free monocarbonyls seems to have no significant effect on F_{CO} (neither positive nor negative). The negative value obtained for α may imply that σ -bonding by neighboring CO ligands in a polycarbonyl contributes to a buildup of negative charge on the metal which leads to a decrease in F_{CO} .

Metal Pentacarbonyls: Intramolecular Comparisons. Electrostatic effects, in addition to directly influencing the intraligand bonding in CO by polarization of the molecule, will obviously also influence the covalent metal-CO interactions. Indeed, as illustrated by Bauschlicher and Barnes,³⁸ the presence of the positive charge on the metal polarizes the σ -density toward the metal, hence presumably facilitating increased M-CO σ -bonding. Conversely, as suggested in the above discussion of σ -bonding effects, increased covalent metal-carbonyl bonding will affect the magnitude of the electrostatic forces experienced by the ligands. Thus, in spite of the reasonable quantitative success of the above model, it is clear that electrostatic and covalent effects are not fully separable and modest deviations from eq 6 are unsurprising. A particularly crude assumption implicit in the model expressed as eq 6 is that the electrostatic effect on F_{CO} is equal to that which would be exerted by a monopole with charge equal to the overall charge of the complex. In order to circumvent these problems, we have examined neutral d⁸ pentacarbonyls, $\text{M}(\text{CO})_5$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$). These complexes are unique in that they contain two sets of inequivalent carbonyls, yet all the carbonyls in a given complex must experience a nearly identical electrostatic field since the charge distribution can have no net dipole moment.

Optimization of the $\text{M}(\text{CO})_5$ complexes yields geometries in strikingly good agreement with experimental studies (gas-phase

Table 4. Metal Pentacarbonyl Data: Calculated F_{CO} Values, Calculated Net Populations (Relative to Free CO), and F_{CO} Values Calculated According to Eq 2

	r_{M-C}		r_{C-O}		F_{CO}	π	σ	ref
	calc	exp ^a	calc	exp ^a				
Fe(CO) ₅ (ax)	1.692	1.8068	1.174	1.1520	16.35	0.555	0.799	<i>b</i>
		1.811(2)		1.117(2)				<i>c</i>
Fe(CO) ₅ (eq)	1.764	1.8273	1.166	1.1520	17.48	0.414	0.510	<i>b</i>
		1.803(3)		1.133(6)				<i>c</i>
Ru(CO) ₅ (ax)	1.949	1.941(13)	1.161	1.13	16.91	0.374	0.524	<i>d</i>
Ru(CO) ₅ (eq)	1.946	1.961(9)	1.166	1.13	16.98	0.378	0.396	<i>d</i>
Os(CO) ₅ (ax)	1.954	1.982(20)	1.163	1.13	17.77	0.403	0.519	<i>e</i>
Os(CO) ₅ (eq)	1.931	1.937(19)	1.169	1.13	17.03	0.464	0.421	<i>e</i>

^a In some cases where more than one reliable experimental value is available (including crystallographically inequivalent carbonyls in a single structure), intermediate values are chosen; error limits, given in parentheses, are estimates. ^b Electron diffraction; ref 61. ^c X-ray diffraction; ref 52. ^d Electron diffraction; ref 46. ^e Electron diffraction; ref 47.

electron diffraction) for M = Ru⁴⁶ and Os⁴⁷ but much poorer for M = Fe,⁴⁸ as has recently been reported by Frenking.⁴² Metric parameters, calculated F_{CO} values, and values of σ_M and π_M are given in Table 4. The axial ligands of each pentacarbonyl are found to engage in significantly more σ -donation to the metal center than do their equatorial partners. This can presumably be attributed to the axial ligands donating into a formally empty d_{z^2} orbital. The relative magnitudes of axial and equatorial π -back-bonding are not constant within the series. Thus, the axial carbonyls of Fe(CO)₅ accept more π -electron density than do the equatorial carbonyls, while the situation is reversed for Os(CO)₅. Ru(CO)₅ is an intermediate case. Fortuitously, the magnitude of π -back-bonding is essentially equal for the axial and equatorial carbonyls of Ru(CO)₅; notably, the Ru—C distances are also virtually identical. Since the different ligands presumably experience essentially the same electrostatic field, this leaves only one variable in terms of the above model. That variable, the magnitude of C→M σ -bonding, is calculated to differ significantly between the axial and equatorial carbonyls; indeed, the difference, 0.13 e per ligand, is comparable to the total σ -donation calculated for the silver carbonyls. Yet, in spite of this significant difference, it is found that F_{CO} is essentially identical for the axial and equatorial carbonyls of Ru(CO)₅. This observation is, of course, strongly supportive of the idea that the extent of σ -bonding does not significantly influence the magnitude of F_{CO} .

Given that the degree of M—CO σ -bonding does not influence F_{CO} , the remaining pentacarbonyls, Fe(CO)₅ and Os(CO)₅, should in principle afford an opportunity to “directly” quantify the effects of π -bonding without the complications introduced by uncertainty in the magnitude of the charge on the metal center. For example, the difference in π -back-donation between the axial and equatorial ligands in Os(CO)₅ is 0.06 e favoring the equatorial positions, and it is accompanied by a difference in F_{CO} of 0.72 mdyne/Å. This corresponds to a β value of 11.9 mdyne/Å per electron (eq 6). Fe(CO)₅, in which the axial carbonyls each accept 0.14 more electrons than do the equatorials, gives a somewhat lower value of β , 8.0 mdyne/Å per electron. We are reluctant to put too much weight on this calculation since the computed Fe—C(axial) bond distance is quite short and the C—O bond distance is anomalously long,

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but, in any event, calculations on both Fe(CO)₅ and Os(CO)₅ imply values of β significantly greater than that determined on the basis of the intermolecular data comparisons (~ 4 mdyne/Å per electron). β values implied by consideration of CO, NO⁺, or N₂ are in the range from 7 to 9 mdyne/Å per electron. For example, (a) one-electron reduction of isoelectronic N₂ (to the ²Π_g state)¹³ lowers its stretching force constant by 6.7 mdyne/Å, (b) one-electron reduction of NO⁺ (to the ²Π_r state)¹³ lowers its stretching force constant by 8.7 mdyne/Å, and (c) F_{CO} of the lowest excited state of CO (³Π_r; $5\sigma \rightarrow 2\pi^*$) is 6.7 mdyne/Å less than that of the ground state.¹³ The estimates of β obtained from simple diatomics thus seem to be in somewhat better agreement with the values implied by the intramolecular comparisons of metal carbonyls, as compared with the intermolecular comparisons.

The relatively small value of β obtained from the intermolecular comparisons (~ 4 mdyne/Å per electron) may result from an indirect neighboring-ligand effect operative in the polycarbonyls, analogous to the effect suggested above in the context of σ -bonding. Specifically, greater π -back-bonding will result in increased charge on the metal; the resulting increase in electrostatic field strength will contribute to an increase in F_{CO} , in opposition to the direct result of increased back-bonding. In the case of pentacarbonyls, where the comparison is intramolecular, this will not be a factor.

The CO Cation and the Nature of the 5 σ Orbital. Having rationalized the computed F_{CO} values of a wide range of species in terms of π -bonding and electrostatic effects, we are aware of only limited experimental evidence in support of the notion that the 5 σ orbital of CO possesses antibonding nature. The moderate increase in F_{CO} upon ionization of CO, 0.71 mdyne/Å, is generally offered as the primary evidence of the antibonding character of the 5 σ orbital.^{1c,11} However, this increase is also entirely consistent with an electrostatics-based interpretation: removal of a 5 σ electron results in partial localization of positive charge on C which, like an electric field, should polarize the remaining electrons and thereby increase covalency. Klemperer has noted⁴⁹ that the Rydberg B¹Σ⁺ state also has a 5 σ^1 configuration, yet its stretching force constant ($\nu_{CO} = 2082$ cm⁻¹; $F_{CO} = 17.51$ mdyne/Å) is actually less than that of the ground state; this observation lends further support to the electrostatics-based interpretation. We recognize the difficulty in “proving” whether or not the 5 σ orbital is “antibonding”; in the absence of any strong evidence we believe it should be so regarded only with caution. In particular, we question if the “antibonding” label can be specified with sufficient precision to be useful in the context of detailed interpretation of small changes in force constants.

Conclusions

Calculations with electron correlated wave functions on simple model systems, including Lewis acid/CO adducts and free CO in the presence of a point charge, indicate that OC→M σ -bonding makes no positive contribution to the values of the internal harmonic carbonyl force constants (F_{CO}). Calculations on several neutral and cationic transition metal complexes lead to the same conclusion, and it is found that F_{CO} values can be quantitatively interpreted using a model which involves only the effects of π -bonding and electrostatics. Intramolecular comparisons between axial and equatorial carbonyls of d⁸ pentacarbonyl complexes also indicate that the magnitude of σ -bonding has a negligible effect on F_{CO} .

An electric-field induced increase in F_{CO} (and decrease in C—O bond distance) can be qualitatively explained in a

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straightforward fashion: the field diminishes the polarization of the bonding orbitals in free CO, thereby increasing covalency (and making the molecule more "N₂-like").^{14,15,38,50}

We propose that the CO 5σ orbital should be regarded as

(50) It has been suggested that the increase in ν_{CO} upon coordination to BH₃ is due to rehybridization of the CO 4σ and 5σ orbitals. This effect may be operative (to an even larger extent) in the case of the electric field; this is consistent with our view of the molecule as becoming more "N₂-like". We believe that diminished polarization of the π-orbitals should be considered as well. Changes in orbital polarization may often be interpreted as rehybridization (and vice versa). See: Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 567–570 and ref 5.

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essentially nonbonding and that there is presently no reason to invoke a significant positive contribution by OC→M σ-bonding in the interpretation of ν_{CO} or F_{CO} values of carbonyl complexes. Instead, electrostatic effects must be considered when analyzing vibrational and structural data for metal carbonyls and also, presumably, when considering complexes of related ligands.

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