

CHEMICAL PSEUDOEXCITATION OF THE CO LIGAND AND VIBRATIONAL FREQUENCIES OF TRANSITION METAL CARBONYLS*.*.*

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The forward- and back-donations of electrons between the CO ligand and central transition element atom lead to a system of cumulated multiple bonds of the type $X=Y=Z$. From a "vibrational" point of view this fact means a non-separability of vibrational motions of the three MCO nuclei. A coupling of the stretching vibrations $\nu_1(\text{MC})$ and $\nu_3(\text{CO})$ leads to analogous fundamental frequencies as in the case of the isolated stable molecules of $\text{O}=\text{C}=\text{O}$, $\text{S}=\text{C}=\text{O}$, $\text{Se}=\text{C}=\text{O}$, etc. The magnitude of the vibrational coupling between ν_1 and ν_3 is roughly proportional to the fundamental frequency of the degenerated deformation vibration ν_{2ab} of the MCO grouping, i.e., a ratio of the frequencies should be constant. With free molecules of CO_2 , SCO , CS_2 , N_2O and others, the ratio $(\nu_1 + \nu_3)/\nu_{2ab}$ of the fundamental frequencies is equal to 5.5 like with complex anions $[(\text{CO})\text{PtX}_3]^-$ regardless $X = \text{Cl}, \text{Br}$ or I . For other transition metal carbonyls the ratio is within the range of 4.0–6.0. On the other hand, the $\text{H}_3\text{B}-\text{C}\equiv\text{O}$ molecule as a system with the essentially single $\text{B}-\text{C}$ and the triple $\text{C}\equiv\text{O}$ bond is characterized by a markedly different value (9.0). In the latter, the local electronic state of CO is similar to the electronic ground state of the positive ion CO^+ of the free molecule. In the transition metal carbonyls the chemical-pseudoexcitation of the CO ligand leads to its local electronic states which are similar to electronic excited states lying between an excited valence state of the free neutral CO molecule (back-donation is equal to one electron) and an excited valence state of the free negative ion CO^- (back-donation is equal to two electrons).

Stability (thermal or toward chemical reagents²) of coordination compounds had been a well-known empirical fact for more than one century. Until 1916, there had been no rationale for explaining the unusual strength of the coordinative bond between the transition element atom and, e.g., carbonyl group. In 1916, Lewis³ characterized a single chemical bond as a sharing of an electron pair between the bonded atoms. In 1921, Langmuir⁴ described the coordinative bond between Ni atom and carbon monoxide in $\text{Ni}(\text{CO})_4$ as a double bond $\text{Ni}=\text{CO}$, only to point out the unexpected formation of a stable bond between the zerovalent nickel atom and neutral CO molecules. Such a formula with the $\text{Ni}=\text{C}$ double bond implies a shorter internuclear distance and a larger force constant than expected for a single $\text{Ni}-\text{C}$ bond. The experimental evidence of these implications was obtained some years later by electron diffraction⁵ on gaseous $\text{Ni}(\text{CO})_4$ and by the normal coordinate analysis of its vibrational spectra⁶.

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Within the framework of Valence Bond method, a new look at the chemical behavior of transition elements has been formulated⁷: "Atoms of the transition groups are not restricted to the formation of single covalent bonds, but can form multiple covalent bonds with electron-accepting groups by making use of the electrons and orbitals of the shell within the valence shell". Simultaneously, other authors⁸⁻¹⁸ proposed an analogous picture of bonding between the transition element atom and other ligands like nitrosyl, cyano or isonitrile groups, *i.e.*, the coordinative bond was presented as at least a double bond.

Meanwhile, the MO theory came into consideration in coordination chemistry. The first qualitative orbital picture of the coordinative bond was drawn by Dewar¹⁹ for the [(alkene)Ag]⁺ ion. This general model of bonding, the so-called " π -complex theory of metal-olefin complexes"²⁰, was extended by Chatt and Duncanson²¹ to alkene-Pt(II) compounds, especially to Zeise's anion, [(C₂H₄)PtCl₃]⁻. Generally, the coordinative bond between ethene and the transition element atom was described as a double bond, composed of two occupied molecular orbitals differing by their symmetry with respect to the two-fold rotation axis C₂: one bonding MO has the σ symmetry and is occupied by the electron pair the donor of which is C₂H₄ (σ forward-donation bond); the other bonding MO has the π symmetry and is occupied by the electron pair the donor of which is the transition element ion species (π back-donation bond). This model of the π -complexes is very suitable for metal carbonyls. Its application to the grouping MCO was not, however, consistent with experiment, namely with the "characteristic" infrared frequency $\nu(\text{CO})$. In the free CO molecule there are two degenerated unoccupied antibonding π^* orbitals (LUMO) suitable for π back-bonding with a transition element atom or ion. Their population by the electron back-donation must lower the carbon-oxygen bond order and the force constant, *i.e.*, the fundamental stretching frequency must be reduced correspondingly. For instance, with the free CO molecule a promotion of one electron from HOMO (essentially nonbonding $5s\sigma$) to LUMO (π^*) reduces the value of $\omega_e(\text{CO})$ from 2170 cm⁻¹ to 1743-1092 cm⁻¹, in dependence on multiplicity of the final electronic state of the molecule²². On the other hand, the so-called characteristic IR absorption band $\nu(\text{CO})$ is found for most cases of metal carbonyls around 2000 cm⁻¹. On one hand the shift of about 150 cm⁻¹ seemingly proves a small contribution of π back-donation in bonding between CO and the central atom, on the other hand a great stability of metal carbonyls remains unexplained. An incomplete interpretation of the $\nu(\text{CO})$ band leads to a preference of Pauling resonance formula M-C \equiv O with one single and one triple bond.

The aim of this work was to compile experimental vibrational data for some typical metal carbonyls, especially with one CO group, and to compare them with isolated molecules representing systems of cumulated multiple bonds like SCO, SeCO, *etc.*

RESULTS AND DISCUSSION

A great stability of transition metal carbonyls can be easily explained by multiorbital nature of the coordinative bond with a large contribution of π back-bonding. Any electron back-donation from metal atom to the CO ligand means a reduction of the CO bond order but simultaneously a strengthening of the metal-carbon bond. A linear MCO grouping becomes a system of cumulated multiple bonds which, however, reveals some specific vibrational properties.

There exists a great number of stable triatomic molecules which are well under-

stood as systems of cumulated multiple bonds²³. The most studied molecule of this type is carbon dioxide, formally $\text{O}=\text{C}=\text{O}$.

In the electronic ground state of the molecule, both $\text{C}=\text{O}$ bonds are equivalent so that the molecule is linear and has the centre of symmetry. The vibrational motions of nuclei represent a system of coupled identical oscillators with the common carbon atom. Instead of one stretching frequency for both identical $\text{C}=\text{O}$ oscillators, two group frequencies are observed for the in-phase stretching and the out-of-phase stretching modes. The first of them is lower and the other is higher than a single frequency expected for the uncoupled identical oscillators which, however, is not equal to their arithmetical mean (Fig. 1). The stretching force constant of the $\text{C}=\text{O}$ bond calculated from both fundamental frequencies is either²³ $1\,680\text{ N/m}$ ($\nu_1 = 1\,337\text{ cm}^{-1}$) or $1\,420\text{ N/m}$ ($\nu_3 = 2\,349\text{ cm}^{-1}$).

An analogue of CO_2 is carbon disulphide which is also described as the system of two cumulated double bonds, $\text{S}=\text{C}=\text{S}$, although the $\text{C}=\text{S}$ stretching force constant calculated analogously²³ is roughly half of that of CO_2 : either 810 N/m ($\nu_1 = 657\text{ cm}^{-1}$) or 690 N/m ($\nu_3 = 1\,523\text{ cm}^{-1}$). It is clear that there is no simple and universal relationship between the force constant and the bond order which would justify a molecular formula $\text{S}-\text{C}-\text{S}$ with the single bonds, *i.e.*, with the half bond order. Moreover, such an $\text{S}-\text{C}-\text{S}$ molecule would be bent rather than linear which is not in agreement with experiment²³.

Linear molecule of carbonylsulphide has the fundamental stretching frequencies at 859 and $2\,079\text{ cm}^{-1}$ for ν_1 and ν_3 , respectively²³, which do not justify a formula

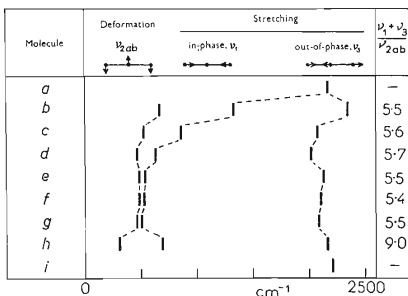


FIG. 1

The fundamental frequencies of $\text{X}=\text{Y}=\text{Z}$ systems with the cumulated multiple bonds (cm^{-1}). a $\text{CO}(\tilde{\text{X}})$, b $\text{O}=\text{C}=\text{O}$, c $\text{S}=\text{C}=\text{O}$, d $\text{Se}=\text{C}=\text{O}$, e $\text{Cl}_3\text{Pt}=\text{C}=\text{O}^{(-)}$, f $\text{Br}_3\text{Pt}=\text{C}=\text{O}^{(-)}$, g $\text{I}_3\text{Pt}=\text{C}=\text{O}^{(-)}$, h $\text{H}_3\text{B}-\text{C}=\text{O}$, i $\text{CO}^{(+)}(\tilde{\text{X}})$

S=C=O or even S=C≡O. Despite the values of the stretching force constants $k_{SC} = 800 \text{ N/m}$ and $k_{CO} = 1420 \text{ N/m}$ the formal description of the molecule is again the system of the cumulated double bonds, S=C=O. Both frequencies ν_1 and ν_3 are assigned to the stretching frequencies of the whole triatomic molecule, to the in-phase and the out-of-phase S=C=O stretching modes²³.

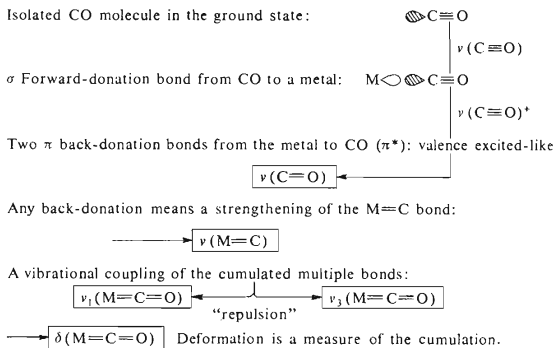
Another analogue is the linear carbonylselenide molecule, Se=C=O. Its fundamental stretching frequencies $\nu_1 = 642 \text{ cm}^{-1}$ and $\nu_3 = 2021 \text{ cm}^{-1}$ cannot be interpreted as the isolated characteristic modes, namely the Se—C stretching (642 cm^{-1}) and the C≡O stretching (2021 cm^{-1}) frequencies, leading to a formula²³ Se—C≡O.

Considering the complex anion $[\text{Cl}_3\text{Pt}(\text{CO})]^-$, we can restrict ourselves in the first approximation to the PtCO grouping with the fundamental frequencies of 485, 539, and 2126 cm^{-1} . Other fundamentals of the Cl_3Pt^- fragment lie below 400 cm^{-1} . One of the low frequency bands at 485 or 539 cm^{-1} and further the 2126 cm^{-1} band are frequently interpreted just as the isolated characteristic stretching frequencies of the uncoupled oscillators, of the single Pt—C and of the triple C≡O bonds²⁴. The inconsistency of this description is obvious from the preceding text and from Fig. 1. Moreover, the interpretation of the 2126 cm^{-1} band as the $\nu(\text{CO})$ fundamental frequency means a very small shift compared to the free CO molecule (about 1%). An unjustified conclusion about negligible π back-bonding between Pt(II) and the CO ligand can be drawn. At this moment the assignment of both low frequency bands at 485 and 539 cm^{-1} has to be clarified, *i.e.*, the fundamental deformation PtCO frequency must be found since both possible assignments were already made^{25,26}. Our solution is based on the following reasons.

The isolated triatomic molecules OCO, SCO, and SeCO have at least the $C_{\infty v}$ point symmetry and thus the two deformation vibrations are degenerated. A single fundamental frequency is observed which is the lowest of the three fundamentals. In the complex anion $[\text{Cl}_3\text{Pt}(\text{CO})]^-$ the local point symmetry $C_{\infty v}$ of the PtCO fragment is not preserved. A lower point symmetry of the complex (C_{2v}) removes the degeneracy of the two deformation vibrations. Two fundamental deformation frequencies can be observed in the form of a more or less separated doublet. It is the case of the IR spectrum of solid salts of $[\text{Cl}_3\text{Pt}(\text{CO})]^-$ where such a doublet at 481 and 489 cm^{-1} was recorded²⁵. Summarising, these deformation frequencies are again the lowest ones of the PtCO fundamentals. The arithmetical mean of the two values was used in Fig. 1 and an analogous assignment of the deformation frequencies of the bromo and iodo analogues²⁶ was made according to chloro complex²⁵.

Thus, the 539 and 2126 cm^{-1} bands of $[\text{Cl}_3\text{Pt}(\text{CO})]^-$ represent the coupled stretching fundamentals of the whole triatomic fragment Pt=C=O, the in-phase mode at 539 cm^{-1} and the out-of-phase mode at 2126 cm^{-1} (Fig. 1). There are some additional facts in support of this statement. An indirect experimental evidence

of this vibrational coupling comes from the isotopical studies of metal carbonyls with ^{13}CO and C^{18}O . "Isotopic shifts for a particular compound are almost the same, irrespective of whether a molecule is substituted with C^{18}O or ^{13}CO , and neither shift is usually equal to the expected theoretical value. Thus, monosubstitution with C^{18}O produces isotope bands with frequencies almost identical to, or even higher than those which arise from ^{13}CO substituted species"²⁷. From these facts, additional conclusions can be drawn.



SCHEME 1

The higher the bond orders in an $\text{X}=\text{Y}=\text{Z}$ grouping, the higher the energy needed for a non-linear distortion of the $\text{X}=\text{Y}=\text{Z}$ system. In other words, the magnitude of the fundamental deformation frequency ν_{2ab} is a measure of the cumulation of the multiple bonds in the PtCO grouping and of the vibrational coupling of both stretching vibrations. And the higher the values of ν_{2ab} , the larger is the separation of the vibrational levels of both stretching modes. At least two counteracting effects are then involved in the final position of the so-called $\nu(\text{CO})$ band: any π back-donation lowers its wavenumber but the vibrational coupling with the so-called $\nu(\text{MC})$ increases it. Thus, the resulting position of the $\nu(\text{CO})$ is determined by a small difference of the two huge effects (*cf.* Scheme 1). Moreover, the fundamental frequencies ν_1 , ν_{2ab} , ν_3 are dependent on bond lengths in the $\text{X}=\text{Y}=\text{Z}$ grouping which are not, however, known for most of the metal carbonyls²⁸.

If the deformation frequency ν_{2ab} really is proportional to the vibrational coupling of ν_1 and ν_3 (*i.e.*, to their separation) then the ratio, say, $(\nu_1 + \nu_3)/\nu_{2ab}$ must be

constant or nearly constant from a chemical point of view. It is obvious from the right hand side of Fig. 1. In other words, changes of effects of masses, of bond lengths and of their force constants practically compensate each other.

In contrary to this is the $\text{H}_3\text{B}-\text{CO}$ molecule with the ratio equal to 9.0. The B—C bond is an essentially single bond, for the contribution of hyperconjugation which is analogous to a back-donating from H_3 to the CO π^* antibonding orbitals²⁹ is negligible on this qualitative level of discussion. The wavenumber of $\nu(\text{CO})$ for the bonded CO lies between the values for free CO and CO^+ molecules. The presentation of the B—C \equiv O skeleton as a system with one single and one triple bond is much closer to reality. For transition metal carbonyls, however, such description is not suitable because the numerical estimates^{30,31} of the MC bond order are within the range 2.5–1.5. It is clear from Fig. 1 and the related discussion that a simple formula like $\text{M}=\text{C}=\text{O}$ with the cumulated double bonds is more relevant to the vibrational properties of the MCO grouping which are the consequences of electron density redistributions between the ligand and the central atom.

Another examples³² of monocarbonyls of transition elements with the general formula $[\text{X}_5\text{M}(\text{CO})]^-$ are presented in Table I. The assignment of both low frequency bands is not obvious in this case since the degeneracy of the deformation vibrations of MCO's is not removed: the point symmetry of the anions remains C_{4v} . No doublet was observed and thus the deformation frequency can be either of the two. For that reason, both possible values of the ratio are quoted in Table I where the

TABLE I

The IR fundamental frequencies of the triatomic MCO grouping in octahedral anions of the type $[\text{X}_5\text{MCO}]^{-n}$ with C_{4v} symmetry (cm^{-1})^a

Anion	ν_1	ν_{2ab}	ν_3	$\nu_1 + \nu_3/\nu_{2ab}$	$\nu_3 + \nu_{2ab}/\nu_1$
$[\text{Cl}_5\text{RuCO}]^{-3}$	545	478	2 022	5.4	4.6
$[\text{Cl}_5\text{OsCO}]^{-2}$	577	522	1 968	4.9	4.3
$[\text{Br}_5\text{OsCO}]^{-2}$	571	528	1 961	4.8	4.4
$[\text{Cl}_5\text{RhCO}]^{-2}$	515	501	2 117	5.3	5.1
$[\text{Br}_5\text{RhCO}]^{-2}$	513	501	2 067	5.1	5.0
$[\text{Cl}_5\text{IrCO}]^{-2}$	509	567	2 060	4.5	—
$[\text{Br}_5\text{IrCO}]^{-2}$	520	560	2 037	4.6	—
$[\text{Cl}_5\text{Ir}(\text{}^{13}\text{CO})]^{-2}$	506	549	2 010	4.6	—
$[\text{Br}_5\text{Ir}(\text{}^{13}\text{CO})]^{-2}$	515	541	1 992	4.6	—

^a Cs-salts, ref.³²; ν_1 : in-phase MCO stretching; ν_{2ab} : degenerated MCO deformation; ν_3 : out-of-phase MCO stretching.

ν_{2ab} , however, was presented according to Denning and Ware²⁵ as the lowest one. In any case, the values of the ratio are within the interval of 4.3–5.4 so that the skeleton formula $M=C=O$ remains more appropriate than $M-C\equiv O$, similarly to Pt(II). With the limitation quoted, it is clear from Table I that a larger downshift of $\nu(CO)$, compared to PtCO in Fig. 1, is always accompanied by an increase in the value of the so-called $\nu(MC)$, *i.e.*, the increasing contribution of π back-donation strengthens the metal-carbonyl bond.

Downshifts of the $\nu(CO)$ frequency accompanied by a simultaneous increase in the $\nu(MC)$ are also evident in the series of tetra- and hexacarbonyl complex ions^{33,34}, summarized in Table II. Since polycarbonyl compounds are concerned in this case, their vibrational frequencies are the group frequencies of the whole molecule and not of a separable MCO fragment. For that reason only the totally symmetric species are comparable and thus the non-totally symmetric deformation frequencies are excluded from such comparison. Thus, usefulness of the frequency ratio $(\nu_1 + \nu_3)/\nu_{2ab}$ is limited for metal polycarbonyls, especially for those with high symmetry T_d or O_h . For metal polycarbonyls with a lower symmetry some numerical treatment of vibrational data should be made to obtain reasonable data, as it is illustrated on the series of phosphine carbonyls of nickel³⁵.

With $(F_3P)_3NiCO$ (symmetry C_{3v}) the fundamental frequencies of NiCO are (in cm^{-1}): $\nu_1 = 449$, $\nu_{2ab} = 430$, $\nu_3 = 2\,079$, their ratio is 5.9. With $(F_3P)_2Ni(CO)_2$ (symmetry C_{2v}) it is necessary to consider a bent planar OCNiCO grouping with 9 normal vibrations: 4 stretching modes, 3 in-plane and 2 out-of-plane deformations.

TABLE II

The fundamental frequencies of the totally symmetric stretching vibrations (A_1) of the metal tetra- and hexacarbonyls (cm^{-1})

Vibration ^a	Ni(CO) ₄	[Co(CO) ₄] ⁻	[Fe(CO) ₄] ⁻²
The so-called $\nu(CO)$	2 128	1 918	1 788
The so-called $\nu(MC)$	380	439	464
Vibration ^b	Mn(CO) ₆ ⁺	Cr(CO) ₆	V(CO) ₆ ⁻
The so-called $\nu(CO)$	2 096	2 000	1 859
The so-called $\nu(MC)$	416	441	460

^a Ref. ³¹; ^b ref. ³⁴.

Around $2\,000\text{ cm}^{-1}$, instead of one stretching frequency for the so-called $\nu(\text{CO})$ the two at $2\,050 (B_1)$ and $2\,096 (A_1)$ cm^{-1} were observed and their arithmetical mean is $2\,073\text{ cm}^{-1}$. Analogously, around 400 cm^{-1} a pair at $429 (A_1)$ and $456 (B_1)$ cm^{-1} was observed for the so-called $\nu(\text{MC})$ frequency, their mean being 442.5 cm^{-1} . Of the three in-plane deformation frequencies only two were observed at $379 (B_1)$ and $467 (B_2)$ cm^{-1} , their average value is 423 cm^{-1} . The ratio $(\nu_1 + \nu_3)/\nu_{2ab}$, using the mean values quoted above, is again 5.9 as for the corresponding monocarbonyl. With $(\text{F}_3\text{P})\text{Ni}(\text{CO})_3$, due to degeneracy usual for C_{3v} symmetry, only couples of frequencies are observed (in cm^{-1}): $2\,111 (A_1)$ and $2\,042 (E)$ for the so-called $\nu(\text{CO})$, $407 (A_1)$ and $439 (E)$ for the so-called $\nu(\text{NiC})$, and 400 and 460 for the deformation modes. The ratio of the mean values is equal to 5.8, close to the cases of mono- and dicarbonyls. In other words, each grouping NiCO is a system of cumulated multiple bonds rather than $\text{Ni}-\text{C}\equiv\text{O}$.

Summarizing, for the vibrational and electronic characterization of the metal-carbonyl bond, it is desirable to publish all the 3 or 4 fundamental frequencies of the MCO grouping, not only the so-called $\nu(\text{CO})$. In this connection, it is noteworthy to comment upon the infrared spectra of CO chemisorbed on oxides, metals, *etc.*³⁶. The low frequency modes of the sorbed CO usually are not measurable because of opacity of the support. The only source of vibrational information about the system is the value of the so-called $\nu(\text{CO})$, eventually its overtones. With regard to the preceding discussion, the significance of the $\nu(\text{CO})$ quantity is reduced to an empirical constant of the whole system. Its interpretation cannot be straightforward because the final position of the $\nu(\text{CO})$ band(s) is a superposition of many counteracting effects. A small shift of $\nu(\text{CO})$ is not an evidence whether the CO molecule is a better σ donor or π acceptor of electrons.

A solution to this unfavourable situation offer the vibrational spectra of metal carbonyls isolated in matrices of noble gases by co-condensation technique. For instance³⁷, the CO-Ar-Ni system was studied and all species $\text{Ni}(\text{CO})_n$ for $n = 1, 2, 3, 4$ were observed. The monocarbonyl of nickel was identified by an infrared band at $1\,996\text{ cm}^{-1}$. Moreover, three low frequency bands were detected at 516, 457, and 435 cm^{-1} and their assignment has been commented: "None of these bands appear to belong to NiCO since the $1\,996\text{ cm}^{-1}$ band assigned to NiCO has appeared strongly in several experiments without observation of the bands at 516, 457, and 435 cm^{-1} . Annealing experiments indicate that the 435 cm^{-1} band belongs to a different molecule than the two bands at 516 and 457 cm^{-1} ... These absorptions may belong to the $\text{Ni}(\text{CO})_2$ and $\text{Ni}(\text{CO})_3$ molecules, but they are too weak to be assigned³⁷. Assuming that the 516 and 457 cm^{-1} bands do belong to NiCO then the ratio $(\nu_1 + \nu_3)/\nu_{2ab}$ is equal to either 5.5 (deformation $\nu_{2ab} = 457\text{ cm}^{-1}$ and $\nu_1 = 516\text{ cm}^{-1}$) or 4.8 for the reversed assignment. The concept of the cumulated double bonds in $\text{Ni}=\text{C}=\text{O}$ is plausible in both cases. Unfortunately, for other CO-Ar-M systems the low frequency bands were not observed at all or with very weak intensities.

Let us consider the local electronic state of the CO ligand in different molecules. In $\text{H}_3\text{B}-\text{CO}$, the $\nu(\text{CO})$ at 2169 cm^{-1} is close to the value of $\omega_e = 2214\text{ cm}^{-1}$ for free CO^+ in the electronic ground state²². In the first approximation the forward-donation of electrons from CO to the H_3B moiety is comparable with the removal of one electron from the essentially non-bonding orbital in the free CO molecule in the electronic ground state. In other words, although the lowering in the electron density on CO due to the coordination represents a fraction of elemental charge it has a similar effect on $\nu(\text{CO})$ as the ionization of the free CO molecule. The coordination in this case can be denoted as a chemical pseudoionization of CO by BH_3 because no back-bonding is possible between these partners.

In the $[\text{X}_3\text{Pt}(\text{CO})]^{(-)}$ anions, an extensive back-bonding between Pt and CO can be deduced from the vibrational coupling of the PtCO stretching frequencies. These back-donations of electrons from the d_{xz} -like and d_{yz} -like Pt orbitals mean an effective increase of electron density in the originally degenerated π^* antibonding MO's of CO molecule. Then, the local electronic state of CO in the complexes should be comparable with an excited valence state of the free neutral CO molecule (back-donation is equal to one electron) or to an excited valence state of the free negative ion CO^- (back-donation is equal to two electrons). The actual electronic changes due to forward- and back-donations are only fractional and are within the extreme limits of the scale of electronic models. It is clear, however, that such redistributions of electron density in the CO ligand must result in a change of the electric dipole moment of CO. The free CO molecule in the electronic and vibrational ground state has a small electric dipole moment³⁸ of 0.122 D whereas for, e.g., CO chemisorbed on tungsten a value of 0.72 D was determined³⁹.

Till this point, only the linear grouping MCO was considered. If the CO ligand is not on a more-than two-fold axis of symmetry, the MCO grouping can be bent³⁰ at an angle of $165-179^\circ$. In such cases also the $3s$ Rydberg orbital of CO with σ symmetry can be taken into account for back-bonding with transition element atom through the d_{xz-yz} -like and d_{z^2} -like orbitals. Then, an extensive orbital mixing in the coordinative bond is possible. If the $\sigma-\pi$ separability of orbitals is yet plausible, we believe the synergic effect³⁴ of forward- and back-donations of different symmetries plays its role mainly during formation of the complex.

An analogous picture of bonding can be formulated also for coordinated or chemisorbed N_2 molecule which is isoelectronic with CO. The free N_2 molecule in the electronic ground state has the centre of symmetry and no electric dipole moment. Although at low pressures no absorption of infrared radiation is detected, after low temperature chemisorption on Ni an IR absorption near 2000 cm^{-1} has been observed⁴⁰. The band is so intense that the chemisorbed N_2 represents an IR absorber even stronger than ketones, siloxanes, or H-bonded species. Thus, a very strong polarization of N_2 in the coordinated $\text{M}=\text{N}=\text{N}$ species should be considered, together with an effect of the electric field of the metallic surface. The low wave-

number bands of the $M=N=N$ have not been detectable again as with the chemisorbed CO.

We believe that the concept of cumulated multiple bonds proposed here is useful not only for other diatomic ligands like CS, $-\text{CN}$, NO, NS, $-\text{NC}$, but also for triatomic species NCO, NCS, N_3 , etc. In such cases the coordinative bond with a transition element atom in $M=X=Y=Z$ should be compared, as to its vibrational properties, with a fouratomic species with cumulated multiple bonds like in, e.g., butatriene with the $\text{C}=\text{C}=\text{C}=\text{C}$ skeleton⁴¹.

As a concluding remark the results of another experimental method, ESCA, can be summarized. The X-ray photoelectron spectra of metal carbonyls show that the coordination of CO to a transition element atom influences the mutual positions of all electronic levels of CO, including the lowest $1s$ levels of oxygen and carbon⁴². This experimental fact is also included in the vibrational frequencies of that compound. Nevertheless, the overall electronic change of CO after coordination is such that the observed vibrational frequencies of the MCO grouping are comparable to those of an isolated triatomic molecule forming a system of cumulated multiple bonds.

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Translated by the author.

Notes added in proof: The low frequency vibrational modes of CO chemisorbed on alumina supported Fe were detected by inelastic electron tunneling spectroscopy⁴³. The bands at 436 and 519 cm^{-1} were assigned to the deformation and the 569 cm^{-1} band to the in-phase stretching vibrations of the surface Fe=C=O grouping. The system CO on Ni/Al₂O₃ was studied by the same spectroscopic method⁴⁴. The electronic structure of the NiCO fragment was treated quantum-mechanically⁴⁵⁻⁷; it was suggested⁴⁷ that the most adequate description of the NiCO system is provided by strong semipolar bonds. The system CO on Pt(111) surface was investigated by electron energy loss spectroscopy⁴⁸ which revealed the pairs of bands at 2 100 and 465 cm^{-1} and for higher coverages at 1 870 and 384 cm^{-1} .