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Evaluation of CO Coordination Energies from Spectroscopic Data: On the Use of Vibrational Isotopic Effects

Benoît Tremblay* and Laurent Manceron

Université Pierre et Marie Curie, CNRS, Laboratoire de Dynamique, Interactions et Réactivité, UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris, Cedex 05, France

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For molecules containing a linearly coordinated carbonyl group, relationships linking ^{13}C and ^{18}O isotopic effects on the CO stretching vibration to the force constant of the M−C coordination bond are proposed. These relationships are rationalized by simple considerations involving the mechanical coupling of the CO and M−C oscillators, tested on model triatomic molecules, and generalized to larger systems. Previous theoretical considerations and several examples presented here show that the long-accepted relation between the shift in the stretching frequency of the coordinated CO with respect to that of isolated CO and the coordination strength has no general predictive power. In contrast, the force constant of the coordination bond can be correlated with the coordination binding energy, and a method for empirically estimating this important parameter from spectroscopic observations of the strongly absorbing CO stretching vibrations of molecular systems or adsorbates is proposed.

1. Introduction

The intense infrared signature of the CO molecule makes it a popular probe in the study of many systems. In most vibrational studies of metal carbonyl compounds, conclusions have been based on an analysis of the energies of the carbonyl stretching vibrations because of the relative success of the energy-factored force field approximations in discussing molecular shapes.[1,2] Because of the large body of data on carbonyl stretching vibrations, several workers have tried to link variations in the pseudodiatomic C≡O force constant to changes in the electronic structure or the metal−CO binding energy.[3] Even if some empirical relationships enjoy limited success within a homologous series of compounds involving the same metal, it is obvious that they have no general predictive power, as systems with very different coordination binding energies can also present very similar C–O stretching frequencies. A simple example is provided by a comparison of the monocarbonyls of the neighboring atoms Ni and Cu, which have almost identical C–O stretching frequencies (1995 cm^{-1} for NiCO[4] and 2010 cm^{-1} for CuCO[5]) in spite of very different binding energies[6,7] (41 and 6 kcal/mol, respectively). More generally, recent data on binding energies of MCO triatomics in the gas phase[6–11] and on C–O stretching frequencies[4,5,12–16] enable a more general comparison of model triatomic molecules (Figure 1a) that clearly dispels the old preconception that the C–O frequency decrease reflects the coordination strength, which is in fact due mostly to charge-transfer effects.[17]

In regard to the derivation of better spectroscopic indicators of the coordination strength, the lower-frequency modes,

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* To whom correspondence should be addressed. E-mail: benoit.tremblay@upmc.fr.

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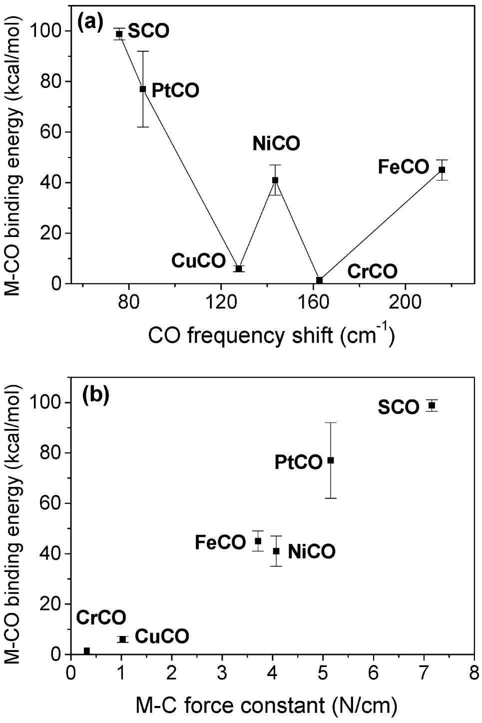

Figure 1. Plots of experimental M−CO binding energies for various transition-metal (M) carbonyls in the gas phase as functions of (a) the shift in the monocarbonyl C−O stretching frequency with respect to that of free diatomic CO and (b) the M−C force constant. Data for the SCO molecule are also given for comparison.

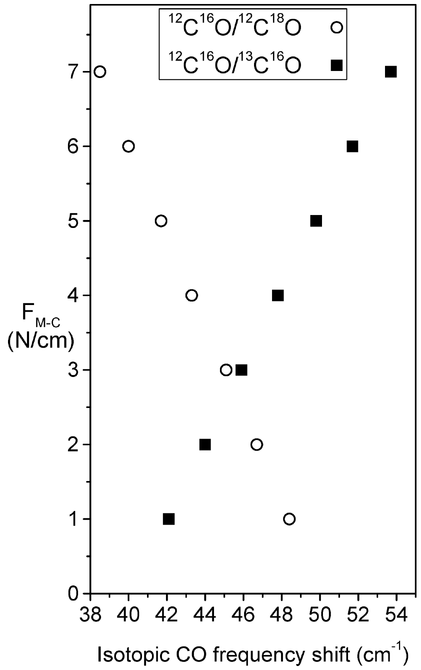

Figure 2. Plot of isotopic shifts in the C–O stretching frequency of a hypothetical monocarbonyl molecule MCO for different values of the M−C force constant F_{MC}: (■) $\nu_{^{12}C^{16}O} - \nu_{^{13}C^{16}O}$; (○) $\nu_{^{12}C^{16}O} - \nu_{^{12}C^{18}O}$.

primarily those involving the metal−ligand stretching and bending coordinates, are more direct markers of the interaction strength but are intrinsically very weak or can be obscured by inorganic solvent or oxide-support adsorption. Thus, they have often been left aside in most studies, except in the comprehensive work of Jones[18] on the coordinatively saturated species $Ni(CO)_4$, $Fe(CO)_5$, and $M(CO)_6$ (M = Cr, Mo, W).

Over the past decade, we have shown that it is possible to obtain complete sets of vibrational data for MCO or M_2CO model molecules isolated in rare-gas matrices and to derive accurate values of M−C force constants, which are much more directly related to the strength of the coordination.[4,5,13,19–22] For several monocarbonyls, these can be directly compared to binding energies obtained in the gas phase, and the results show that the metal−carbon force constant is a reliable indicator of the M−CO binding energy (Figure 1b). Recent gas-phase observations have confirmed that the matrix perturbation is very small. For example, in NiCO, the C−O stretching vibration was observed at 1994.4 cm^{-1} in solid argon,[4] at 2006.6 cm^{-1} in solid neon,[12] and at 2010.7 cm^{-1} in the gas phase.[23]

In these studies of model MCO triatomic molecules, we have noted a direct relationship between isotopic effects on the C–O stretching mode and the M−C coordination force constant. Our goal here is to propose a method for extracting reliable information on the M−CO bond strength on the basis of ^{13}C and ^{18}O isotopic substitution effects on the easily observable carbonyl stretching modes. We will show that these isotopic effects are linked to the mechanical coupling between the M−C and C≡O bonds and, consequently, to the binding energies in MCO molecules and, more generally, in larger systems involving CO coordination.

2. Transition-Metal Monocarbonyl Model Systems

In this section, we examine the existing experimental data on transition-metal monocarbonyls and the effect of varying the force constant of the M−C coordination bond on isotopic effects on the C–O stretching mode. In linear A−B−C triatomic systems, simple mechanical coupling between the A−B and B−C oscillators causes a combination of the two bond coordinates to yield in-phase and out-of-phase normal modes, with an admixture in inverse proportion to the separation of the energies of the two oscillators or to the mass of the central, connecting atom, B. In MCO systems, because of the large difference in the frequencies of the C−O and M−C oscillators, mechanical coupling between the C−O and M−C modes is usually considered to be negligible. In fact, a more detailed examination of the isotopic effects shows that this coupling is still present and may be clearly observable in the so-called C–O stretching modes.[24] For example, the C–O stretching frequency in $Se^{12}C^{18}O$ is larger than that in $Se^{13}C^{16}O$ in spite of the smaller reduced mass for an isolated $^{13}C^{16}O$ oscillator. This indicates the presence

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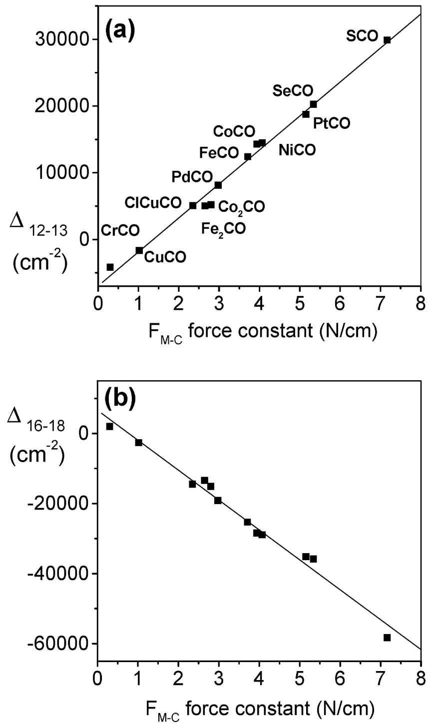

Figure 3. Plots of (a) Δ_{12-13} and (b) Δ_{16-18} as functions of the M−C force constant F_{MC} for several monocarbonyls. The solid lines are linear fits of the data.

of substantial vibrational coupling between the C−O and Se−C oscillators in spite of the differences in their reduced masses and bond strengths. Comparing the difference between the frequencies for isolated $^{13}C^{16}O$ and $^{12}C^{18}O$ oscillators (+3.95 cm^{-1}) with that actually observed for gas-phase $Se^{13}C^{16}O$ and $Se^{12}C^{18}O$ (−9.65 cm^{-1} [15]) indeed provides an alternative, albeit indirect, indication of the metal−ligand bond strength. Figure 2 illustrates this effect for a hypothetical carbonyl MCO by presenting relative isotopic shifts for different values of the M−C force constant, F_{MC}, assuming an atomic mass of 100 u for M, a C−O force constant (F_{CO}) of 16 N/cm, and an interaction constant ($F_{MC,CO}$) of 1 N/cm. It is easy to see that variation of F_{MC} has a direct influence on the isotopic shifts of the C−O stretching frequency.

In order to quantify and discuss the relationship between the molecular force constants and the masses of the atoms, we can use the well-known GF method, where the elements of the **F** matrix are the force constants and the elements of the **G** matrix are expressions connecting reciprocal masses of the atoms and internal coordinates.[25] Solving the system $\|\mathbf{GF} - \lambda\mathbf{E}\| = 0$, where **E** is the unit matrix, $\lambda = 4\pi^2c^2\nu^2$, and c is the speed of light, yields the eigenvalues λ in the harmonic approximation. To simplify the discussion, we will use the simplest possible case, namely, the monocarbonyl MCO. In this case, the stretching and bending modes by symmetry cannot interact, and the description of the M−C and C−O stretching modes requires only three force constants: F_{CO}, F_{MC}, and the interaction constant $F_{MC,CO}$. Thus, the **G** and **F** matrices are given by

$$\mathbf{G} = \begin{bmatrix} a & b \\ b & c \end{bmatrix} \qquad \mathrm{F} = \begin{bmatrix} F_{CO} & F_{MC,CO} \\ F_{MC,CO} & F_{MC} \end{bmatrix}$$

where $a = 1/m_C + 1/m_O$, $b = -1/m_C$, and $c = 1/m_C + 1/m_M$, in which m_C, m_O, and m_M are the atomic masses of the carbon, oxygen, and metal atoms, respectively. To solve $\|\mathbf{GF} - \lambda\mathbf{E}\| = 0$, the first-order approximations that $F_{MC,CO}$ is small in comparison with F_{MC} and F_{MC} is small in comparison with F_{C-O} can be made. We then obtain the following expression for the $^{12}C^{16}O$ isotope:

$$\lambda = aF_{CO} + 2bF_{MC,CO} + \frac{b^2}{a}F_{MC} \qquad (1)$$

Since the force constant values are independent of the atomic masses, for another CO isotope ($^{13}C^{16}O$ or $^{12}C^{18}O$), eq 1 becomes

$$\lambda' = a'F_{CO} + 2b'F_{MC,CO} + \frac{(b')^2}{a'}F_{MC} \qquad (2)$$

Combining eqs 1 and 2 yields a direct linear relationship between the difference in the C–O stretching vibrations of two different isotopologues and the force constant F_{MC}, the slope of which depends only on the masses of the oxygen and carbon atoms:

$$a'\lambda - a\lambda' = 2(a'b - b'a)F_{MC,CO} + \left(\frac{a'b^2}{a} - \frac{a(b')^2}{a'}\right)F_{MC} \qquad (3)$$

For the two most-common couples of CO isotopologues ($^{12}C^{16}O/^{13}C^{16}O$ and $^{12}C^{16}O/^{12}C^{18}O$), the following relations are thus obtained:

$$\left(\frac{1}{m_{^{13}C}} + \frac{1}{m_{^{16}O}}\right)\lambda_{12-16} - \left(\frac{1}{m_{^{12}C}} + \frac{1}{m_{^{16}O}}\right)\lambda_{13-16} = -0.00080F_{MC,CO} + 0.00045F_{MC} \qquad (4)$$

$$\left(\frac{1}{m_{^{12}C}} + \frac{1}{m_{^{18}O}}\right)\lambda_{12-16} - \left(\frac{1}{m_{^{12}C}} + \frac{1}{m_{^{16}O}}\right)\lambda_{12-18} = 0.00116F_{MC,CO} - 0.00068F_{MC} \qquad (5)$$

To make eqs 4 and 5 easier to use, we can reformulate these expressions to use wavenumbers (cm^{-1}) directly. Also, to simplify the notation, we can introduce the symbols Δ_{12-13} and Δ_{16-18}, respectively. For force constants in units of newtons per centimeter, we obtain

$$\Delta_{12-13} = (\nu_{12-16})^2 - 1.046(\nu_{13-16})^2 = -9788F_{MC,CO} + 5495F_{MC} \qquad (6)$$

$$\Delta_{16-18} = (\nu_{12-16})^2 - 1.050(\nu_{12-18})^2 = 14179F_{MC,CO} - 8304F_{MC} \qquad (7)$$

We turn now to a comparison with experimental data. Figure 3 presents isotopic parameters for the isotopic pairs $^{12}C^{16}O/^{13}C^{16}O$ and $^{12}C^{16}O/^{12}C^{18}O$ for several transition-metal monocarbonyls studied in solid-argon matrices[4,5,13,19–22,26] and for two less-reactive linear molecules, SeCO[15] and SCO,[16] studied in the gas phase. The slopes, intercepts, and correlation

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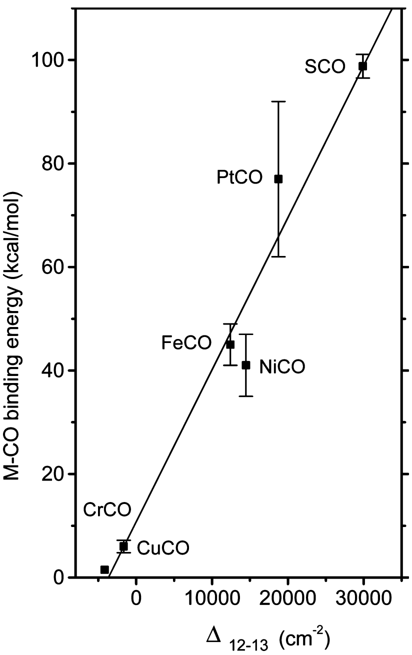

Figure 4. Plot of experimental M−CO binding energies as a function of Δ_{12-13} for the monocarbonyls in Figure 1. The solid line is a linear fit of the data.

coefficients obtained from linear fits of the experimental data for the two considered isotopologue pairs were 5092 and −8537, −6954 and 6595, and 0.995 and 0.992, respectively. Since $F_{MC,CO}$ does not remain constant for different molecules, we now directly use the values obtained from the linear fits of the experimental data to write the final expressions

$$\Delta_{12-13} = -6954 + 5092F_{MC} \tag{8}$$

$$\Delta_{16-18} = 6595 - 8537F_{MC} \tag{9}$$

The empirical relationships 8 and 9 derived from experimental data show good quantitative agreement with the relationships 6 and 7 derived from the harmonic model, lending support to the proposed relationships and showing that they have a general character and should be applicable to all comparable carbonyl systems.

Since the isotopic parameters Δ_{12-13} and Δ_{16-18} are highly correlated with the M−C force constant, it is expected that they should correlate strongly with the M−CO binding energy. This possibility is tested in Figure 4, which is a plot of experimentally measured M−CO binding energies versus experimentally measured Δ_{12-13} values. The high correlation shows that measured values of Δ_{12-13} provide a useful means of estimating M−CO binding energies in cases where this parameter has not been measured directly.

3. General Relevance and Application to Larger CO-Coordinating Systems

It is of interest to extend the above discussion of the relation between the force constant F_{MC} and isotopic effects on the C–O stretching frequencies of monocarbonyl model molecules to other systems of more practical interest. In this section, we examine relevant experimental data on polyatomic $M(CO)_6$ (M = Cr, Mo, W) and $Ni(CO)_4$ molecules[18] and on CO adsorbed on metal-crystal surfaces,[27–44] on oxide surfaces, and in zeolites.[45–52] We have chosen from the literature infrared or Raman studies reporting at least $^{12}C^{16}O/^{13}C^{16}O$ isotopic data and M−C stretching frequencies. In data on CO adsorbed on oxide or zeolite surfaces, the M−C vibration frequencies were essentially deduced from the $\nu_{CO} + \nu_{MC}$ combination mode, neglecting the anharmonicity correction. In fact, when anharmonicity was been measured,[49] it accounted for an energy difference of 2 cm^{-1} (i.e., 0.1%) in the frequencies and a similar percentage in the isotopic shifts, which truly is negligible here. Next, we calculated effective harmonic force constants F_{MC} by treating the M−CO group as a triatomic model molecule. This approach has been shown to be a reasonable assumption for CO adsorbed on metal-crystal surfaces.[32,39]

For $Ni(CO)_4$ and the $M(CO)_6$ molecules, we considered the A_1 and A_{1g} frequency blocks, respectively, for which the values depend only on the three force constants F_{CO}, F_{MC}, and $F_{MC,CO}$, since by symmetry the bending coordinate cannot couple with the stretching ones, as in the case of MCO triatomic molecules. The results are presented in Figure 5. The good correlation between the M−C force constant and the isotopic effects on the C–O stretching frequencies shows that eqs 8 and 9 can be applied to other systems that are more complex and chemically relevant. In cases where strongly bound carbonyl species present marked deviations from linearity, the proposed relationships are no longer strictly valid and should be employed with caution.

However, determining the value of the M−C force constant is not necessarily the main object of all of these

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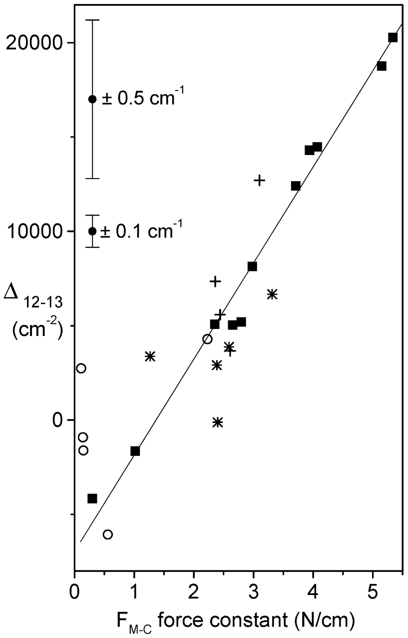

Figure 5. Plots of Δ_{12-13} versus the M−C force constant F_{MC} for (■) monocarbonyls, (+) M(CO)$_6$ (M = Cr, Mo, W) and Ni(CO)$_4$, (○) CO adsorbed on different oxide surfaces or zeolites, and (∗) CO adsorbed on metal-crystal surfaces.

studies. It can help to estimate low-frequency fundamental vibrations that are masked by strong infrared absorption of the support, as in zeolites.[24] Often, the purpose of these investigations using CO molecule is to obtain other physical or chemical parameters. From this point of view, how can eqs 8 and 9 help these studies?

For studies on oxide supports, the use of isotopic C–O stretching data can directly give information about the M−C stretching vibration through the value of the M−C force constant (where in this case, M is a transition-metal or alkali cation). Since two or more monocarbonyls can be characterized by very similar fundamental C–O frequencies but have low-frequency M−C modes that differ significantly, they can be clearly discriminated. The different values for the M−C modes provide information on the specific cation present in the zeolite as well as on the localization of metal carbonyls in the zeolite framework.[45,47,49,50]

For CO adsorbed on metal-crystal surfaces, it is of interest to relate the M−C force constant to the adsorption energy. In the literature, a relationship that links the CO−surface binding energy to the square of the M−C stretching frequency has been proposed.[32] Since in a diatomic model the square of the M−C frequency is proportional to the force constant F_{MC}, this relationship is consistent with that implied in Figure 1 for isolated MCO molecules or, more generally, with a Morse potential model (considering, however, that the anharmonicity remains constant). Such a correlation also implies that the energetic contribution of surface reconstruction effects caused by adsorption is much smaller than the adsorption energies.

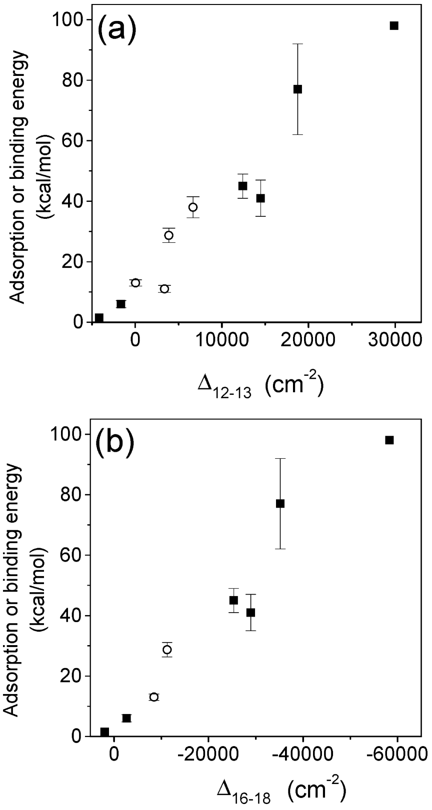

Figure 6. Plots of the binding and adsorption energies, respectively, as functions of (a) Δ_{12-13} and (b) Δ_{16-18} for (■) the monocarbonyls in Figure 4 and (○) CO adsorbed on metal-crystal surfaces in Figure 5.

Figure 6 was obtained for the $^{12}C^{16}O/^{13}C^{16}O$ and $^{12}C^{16}O/^{12}C^{18}O$ isotopic pairs using the spectroscopic data reported in Figure 5 (*) and the binding energies reported in the literature for the same systems[40–44] as well as the monocarbonyl data from Figure 4. We used data with a similar low coverage in order to make a comparison with these results. Also, the experimental values for the binding energy varied from one study to another and depended on the coverage value. When possible, the mean values are given. Finally, this reasonable correlation in turn means that the spectroscopic method can possibly constitute an alternative approach to direct calorimetric measurements for obtaining a first estimate of adsorption energies.

In all of these studies, however, an important limiting factor is the resolution or accuracy of the frequency determination. For this reason, error bars representing the uncertainties in the values of Δ_{12-13} arising from accuracies of 0.1 and 0.5 cm^{-1} in the frequency determination are presented in Figure 5. We can see that the validity of the relationship is strongly dependent on the accuracy of the measurements. Thus, for systems where determination of the frequency to within only 0.5 cm^{-1} is possible, combining the ^{13}C and ^{18}O data is advisable in order to improve the accuracy of the estimates. We can state that the accuracy of the frequency determination should be at least 0.5 cm^{-1} in order to obtain from eqs 8 and 9 an evaluation of the force constant F_{MC} accurate to better than 0.7 N/cm and at least 0.1 cm^{-1} to obtain an accuracy better than 0.2 N/cm.

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