# Defining the Stoicheiometry of a Subcarbonylmetal Guest using Mixed Vibrational Isotope Labelling Techniques

**Geoffrey A. Ozin, Saim Özkar, and Douglas F. McIntosh**
*Lash Miller Chemical Laboratory, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 1A1*

The tricarbonyl stoicheiometry, structure, and anchoring site geometry of $M(CO)_3$–$M^*{}_{56}Y$ which are cleanly generated *via* the mild vacuum thermal decarbonylation of $M(CO)_6$–$M^*{}_{56}Y$ (where M = Cr, Mo, or W; M* = Li, Na, K, Rb, or Cs; Y = dehydrated zeolite Y), have been unequivocally established for the first time from analysis of their $M(^{12}CO)_n(^{13}CO)_{3-n}$–$M^*{}_{56}Y$ vibrational isotope patterns.

Intrazeolite metal carbonyls (IMCs) have been traditionally utilized as precursors to encapsulated subcarbonylmetal and metal cluster guests of interest in size/shape selective catalysis.[1] Recently we have instead exploited IMCs for the phototopotactic growth and stabilization of intrazeolite semiconductor quantum dots (QDs) and quantum supralattices (QSs) exemplified by tungsten(VI) oxide *via* reactions of the type in equation (1), where M* = Li, Na, K, Rb, or Cs and $0 < n \leqslant 32$.[2] The successful fabrication of organized assemblies of semiconductor QDs and QSs of this kind necessitates precise knowledge of the location, distribution, stoicheiometry, structure, and support-interactions of the guest precursor and reactive intermediates in the zeolite host lattice which are involved in the pathway to the immobilized QDs and QSs.

$$n\{W(CO)_6\}\text{–}M^*{}_{56}Y + 9/2nO_2 \xrightarrow{h\nu} n(WO_3)\text{–}M^*{}_{56}Y + 6nCO_2 \quad (1)$$

**Table 1.** Observed and calculated $\nu(CO)$ frequencies ($cm^{-1}$) of regular trigonal pyramidal $W(^{12}CO)_n(^{13}CO)_{3-n}$–$Cs_{56}Y$.

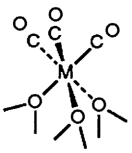
| Species | Obs.[a] | Calc. | Assignment |
|---|---|---|---|
| $W(^{12}CO)_3$–$Cs_{56}Y$ | 1895 | 1892 | $A_1$ |
| ($C_{3v}$) | 1741 | 1738 | E |
| $W(^{12}CO)_2(^{13}CO)$–$Cs_{56}Y$ | 1880 | 1880 | A′ |
| ($C_s$) | 1741 | 1738 | A″ |
| | 1709 | 1710 | A′ |
| $W(^{12}CO)(^{13}CO)_2$–$Cs_{56}Y$ | 1866 | 1867 | A′ |
| ($C_s$) | 1718 | 1722 | A′ |
| | 1699 | 1699 | A″ |
| $W(^{13}CO)_3$–$Cs_{56}Y$ | 1851 | 1850 | $A_1$ |
| ($C_{3v}$) | 1699 | 1699 | E |

[a] Best-fit Cotton–Kraihanzel force constants are: $f_r = 12.95$; $f_{rr} = 0.75$ mdyn/Å. RMS error in the eigenvalues is 1.744 $cm^{-1}$

**Table 2.** Observed and calculated $\nu(CO)$ frequencies ($cm^{-1}$) of distorted trigonal pyramidal $Mo(^{12}CO)_n(^{13}CO)_{3-n}$–$Li_{56}Y$.

| Species | Obs. | Calc.[a] | Assignment |
|---|---|---|---|
| $Mo(^{12}CO)_3$–$Li_{56}Y$ | 1925 | 1925 | A′ |
| ($C_s$) | 1798 | 1795 | A″ |
| | 1760 | 1758 | A′ |
| $Mo(^{12}CO)_2(^{13}CO)$–$Li_{56}Y$ | 1925 | 1925 | A′ |
| ($C_s$) | 1798 | 1795 | A″ |
| | 1716 | 1718 | A′ |
| $Mo(^{12}CO)_2(^{13}CO)$–$Li_{56}Y$ | 1909 | 1907 | A |
| ($C_1$) | 1769 | 1772 | A |
| | 1760 | 1758 | A |
| $Mo(^{12}CO)(^{13}CO)_2$–$Li_{56}Y$ | 1909 | 1907 | A |
| ($C_1$) | 1769 | 1772 | A |
| | 1716 | 1718 | A |
| $Mo(^{12}CO)(^{13}CO)_2$–$Li_{56}Y$ | 1880 | 1882 | A′ |
| ($C_s$) | 1760 | 1758 | A′ |
| | 1755 | 1755 | A″ |
| $Mo(^{13}CO)_3$–$Li_{56}Y$ | 1880 | 1882 | A′ |
| ($C_s$) | 1755 | 1755 | A″ |
| | 1716 | 1718 | A′ |

[a] Best fit Cotton–Kraihanzel force constants are: $f_r = 12.48$; $f_r' = 13.99$; $f_{rr} = 1.11$; $f_{rr}' = 0.98$ mdyn/Å. RMS error in the eigenvalues is 2.055 $cm^{-1}$.



**(I)**

In the course of an extensive study[2] of thermal decarbonylation, ligand-exchange, and photo-oxidation chemistry of $M(CO)_6$–$M^*_{56}Y$, where M = Cr, Mo, or W; M* = Li, Na, K, Rb, or Cs, it proved possible for the first time to define unequivocally the stoicheiometry and structure of an IMC reactive intermediate, $M(CO)_3$–$M^*_{56}Y$ using mixed $^{12}CO/^{13}CO$ vibrational isotope labelling techniques. The following is a summary of this work.

Briefly, the *in situ* thermal vacuum decarbonylation of $M(CO)_6$–$M^*_{56}Y$ at 100—150 °C can be organized to proceed through two intermediate stages to produce cleanly a single, well defined subcarbonylmetal species denoted $M(CO)_3$–$M^*_{56}Y$ [reaction (2)].†

$$M(CO)_6\text{–}M^*_{56}Y \xrightarrow[in\ vacuo]{100\text{—}150\,^{\circ}C} M(CO)_3\text{–}M^*_{56}Y + 3CO \quad (2)$$

Of the fifteen $M(CO)_3$–$M^*_{56}Y$ species possible with M = Cr, Mo, or W, and M* = Li, Na, K, Rb, or Cs only the two high atomic number combinations $Mo(CO)_3$–$Cs_{56}Y$ and $W(CO)_3$–$Cs_{56}Y$ display the diagnostic $A_1 + E$ ν(CO) vibrational patterns of an anchored $C_{3v}$ trigonal pyramidal tricarbonyl moiety, while the remaining thirteen samples show $2A' + A''$ ν(CO) patterns signalling a $C_s$ distorted version of the above $C_{3v}$ species. Although trapping experiments[2] using tridentate ligands like benzene and cyclohepta-1,3,5-triene provide indirect but compelling proof of the proposed intrazeolite tricarbonylmetal(0) stoicheiometry [reaction (3)], direct proof derives from mixed $^{12}CO/^{13}CO$ isotope labelling experiments of the kind in reaction (4), where $m$ = 0—6; $n$ = 0—3. The $W(^{12}CO)_m(^{13}CO)_{6-m}$–$Cs_{56}Y$ and $Mo(^{12}CO)_m(^{13}CO)_{6-m}$–$Li_{56}Y$ precursors‡ will be used to exemplify the method for elucidation of stoicheiometry and structure of the respective regular trigonal pyramidal $W(^{12}CO)_n(^{13}CO)_{3-n}$–$Cs_{56}Y$ and distorted trigonal pyramidal $Mo(^{12}CO)_n(^{13}CO)_{3-n}$–$Li_{56}Y$ tricarbonyl moieties.

$$M(CO)_3\text{–}M^*_{56}Y + C_6H_6 \longrightarrow (\eta^6\text{-}C_6H_6)M(CO)_3\text{–}M^*_{56}Y \quad (3)$$

$$M(^{12}CO)_m(^{13}CO)_{6-m}\text{–}M^*_{56}Y \xrightarrow{100\text{—}150\,^{\circ}C} M(^{12}CO)_n(^{13}CO)_{3-n}\text{–}M^*_{56}Y + (3-m+n)^{13}CO + (m-n)^{12}CO \quad (4)$$

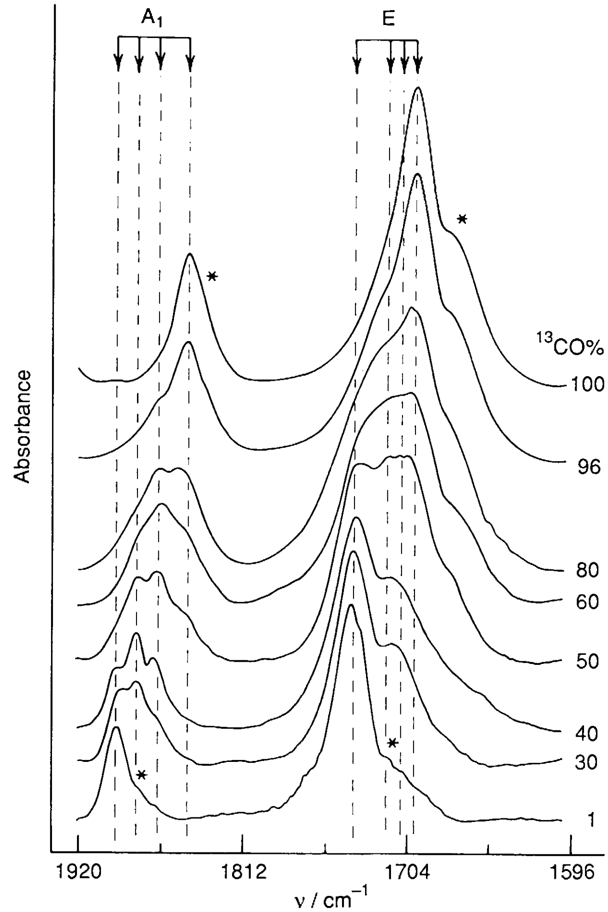


**Figure 1.** Mid-IR $^{12}CO/^{13}CO$ vibrational isotope spectral patterns of the $A_1 + E$ ν(CO) modes of $W(^{12}CO)_n(^{13}CO)_{3-n}$–$Cs_{56}Y$, (where $n$ = 0—3) with various levels of $^{13}CO$ enrichment. A low concentration of a second trapping site of $W(^{12}CO)_n(^{13}CO)_{3-n}$–$Cs_{56}Y$ is indicated by an asterisk.

Thus, the $A_1 + E$ ν(CO) modes of the postulated $C_{3v}$ $W(^{12}CO)_3$–$Cs_{56}Y$ occur at 1895 and 1741 $cm^{-1}$ respectively. The $^{12}CO/^{13}CO$ mixed isotope vibrational patterns for the parent $A_1$ and E ν(CO) modes of $W(^{12}CO)_n(^{13}CO)_{3-n}$–$Cs_{56}Y$ utilizing 1, 30, 40, 50, 60, 80, 96, and 100% $^{13}CO$ enrichment are depicted in Figure 1. The isotopic quartet structure on both the parent $A_1$ and E ν(CO) fundamentals ($n$ = 0—3) unequivocally establishes the $W(CO)_3$ subcarbonyl stoicheiometry with perfect $C_{3v}$ trigonal pyramidal symmetry. The acceptable fit (RMS error, 1.7 $cm^{-1}$) between the calculated (Cotton–Kraihanzel force field)[3] and observed ν(CO) frequencies for the four expected mixed isotopic molecules ($n$ = 0—3) listed in Table 1 provides additional support for the vibrational assignments, stoicheiometry, and $C_{3v}$ structure of $W(CO)_3$–$Cs_{56}Y$.

By contrast, the $Mo(^{12}CO)_3$–$Li_{56}Y$ moiety displays $A' + A'' + A'$ ν(CO) modes at 1925, 1798, and 1760 $cm^{-1}$ respectively. The $^{12}CO/^{13}CO$ isotope patterns for various $^{13}CO$ enrichments consist of a triplet, triplet, and doublet structure running from the parent high frequency $A'$, through the middle $A''$ to the low frequency $A'$ ν(CO) mode respectively. This observation together with the calculated frequencies (RMS error, 2.0 $cm^{-1}$) (Table 2) establishes the tricarbonyl stoicheiometry and distorted $C_s$ pyramidal geometry for $Mo(^{12}CO)_{3-n}(^{13}CO)_n$–$Li_{56}Y$, where $n$ = 0—3.

The question of whether the tricarbonylmetal(0) fragment is anchored in the α-cage of zeolite Y *via* extraframework

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† After vacuum thermal dehydration and calcining at 450 °C the zeolite wafers were exposed to the hexacarbonylmetal(0) vapour at room temperature in a mid-IR transmission UV-VIS reflectance cell specially designed for *in situ* treatments (G. A. Ozin and J. P. Godber, *J. Phys. Chem.*, 1988, **92**, 4980). Partial decarbonylation of $M(CO)_6$–$M^*_{56}Y$ was achieved by heating the impregnated wafer at 100—150 °C for 30 min in dynamic vacuum. Various alkali-metal zeolites were prepared from the sodium zeolite Y (UOP, Union Carbide, Tarrytown, NY) by use of standard ion-exchange techniques (J. Dwyer and A. Dyer, *Chem. Ind.*. 1984, 237).

‡ The selective $^{12}CO/^{13}CO$ labelling of the intrazeolite precursor hexacarbonylmetal(0) moiety is most easily accomplished by conducting a thermal (90 °C) or photochemical (room temp.; λ > 240 nm broadband) reaction of intrazeolite $M(^{12}CO)_6$–$M^*_{56}Y$ with $^{13}CO$ using a pressure of 50 Torr.

cations through the metal centre or oxygen-end of the carbonyl, or to a framework oxygen site through the metal centre has been answered by an EXAFS structure determination of a representative sample, namely $Mo(CO)_3$–$Rb_{56}Y$.[2] The absence of a direct Mo · · · Rb bonding interaction, together with carbonyl and oxygen co-ordination numbers close to three favours the oxygen framework anchoring site model (**I**).

Finally, the occurrence and origin of the observed $C_{3v}$ to $C_s$ structural distortion amongst the fifteen $M(CO)_3$–$M^*_{56}Y$ samples is traced *via* optical reflectance spectroscopy and molecular orbital analysis[2] to the operation of a second order Jahn–Teller effect. In essence, it is the coupling between the closely spaced HOMO 1e and LUMO 2e states of $C_{3v}$ $M(CO)_3$–$M^*_{56}Y$ through a degenerate e-type vibrational motion ($e \times e = a_1 + a_2 + e$) that leads to the observed distortion to the lower symmetry $C_s$ species.[4] This will be favoured for those circumstances that boast a small HOMO–LUMO energy gap, namely low atomic number elements for both M and M*. On this basis it is easy to appreciate why it is that in the fifteen $M(CO)_3$–$M^*_{56}Y$ samples, it is *only* the M = Mo, W and M* = Cs systems that exist with the regular $C_{3v}$ trigonal pyramidal geometry; the rest undergo a static second-order Jahn–Teller distortion and settle down in the $C_s$ distorted trigonal pyramidal form.

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