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Monocarbide Complexes

The $\nu(\text{AlC})$ mode of AlC has been assigned to infrared bands at 629.8 and 640.1 cm^{-1} in an Ar matrix study [1], and a formal bond order of 1.5 has been determined for the AlC species [2]. It was proposed that the 629.8 cm^{-1} band might be from AlC molecules that are surrounded by Ar and the 640.1 cm^{-1} band, which is close to the value of 654.8 cm^{-1} in the emission spectrum of AlC vapor [3], from molecules on the grain surface. Both assignments are close to a calculated $\nu(\text{AlC})$ value of 629 cm^{-1} [4].

The $\nu(\text{WC})$ features at 636 , 582 , and 392 cm^{-1} in a high resolution electron energy loss spectroscopy (HREELS) study of a clean carbide-modified W(211) surface have been attributed to several different C atom sites on that surface [5] and an HREELS band at 581 cm^{-1} to a WC species on a W(110) surface [6]. An HREELS loss at c. 600 cm^{-1} has been assigned to the $\nu(\text{RuC})$ mode of adsorbed C atoms on a Ru(001) surface [7]. A Raman band at 552 cm^{-1} and an HREELS loss at 520 cm^{-1} have been attributed to adsorbed atomic C on stepped Ni(111) [8] and silica-supported Ni catalyst surfaces [9], respectively, and an HREELS band at 520 cm^{-1} to atomic C adsorbed on a Pt(210) surface [10]. The slightly lower $\nu(\text{RhC})$ frequency of $\text{Rh}\equiv\text{C}$ in Ne and Ar matrices (Table 1.1) compared with that of 1040.0 cm^{-1} in the vapor phase [11] shows a slight influence of the matrix atoms on the frequency [12]. The larger frequency shift in an Ar than a Ne matrix was attributed to weak van der Waals interactions between $\text{Rh}\equiv\text{C}$ and the more easily polarized matrix Ar atoms [12]. Although infrared bands were not detected in Ar matrix isolation studies due to expected low species concentrations, band intensities and $\nu(\text{MC})$ ($\text{M} = \text{Cu}, \text{Ag}$) frequencies were calculated for CuC (585.6 cm^{-1}) [13] and AgC (477.2 cm^{-1}) [14]. The lower $\nu(\text{UC})$ frequency of $\text{U}\equiv\text{C}$ in an Ar than a Ne matrix (Table 1.1) was attributed to a stronger interaction of $\text{U}\equiv\text{C}$ molecules with the Ar than the Ne matrix, and the frequency in the Ne matrix is closer to the calculated value of 908 cm^{-1} . It was also suggested that the higher than expected $\nu(\text{UC})$ frequency difference of 44 cm^{-1} between the Ar and Ne matrices might be from different electronic ground states of $\text{U}\equiv\text{C}$ molecules in these matrices [15, 16]. Table 1.1 summarizes infrared assignments for diatomic metal carbides.

The $\nu(\text{MO})$ mode in the Ne matrix infrared spectrum was assigned for CMO^- ($\text{M} = \text{Nb}, 877.8\text{ cm}^{-1}$; $\text{Tb}, 902.0\text{ cm}^{-1}$), and the $\nu(\text{NbC})$ and $\nu(\text{NbO})$ modes of CNbO have been assigned at 783.7 and 919.8 cm^{-1} , respectively, but CTbO was not detected [19].

Initial infrared data and discrete Fourier transform (DFT) calculations indicated that isolated CUO molecules ($\nu(\text{UC}) = 1047.3\text{ cm}^{-1}$, $\nu(\text{UO}) = 872.2\text{ cm}^{-1}$) formed in a Ne matrix but that the U atoms of CUO molecules formed weak chemical bonds with the atoms of Ar, Kr, and Xe matrices [20]. Indeed, in a 1% Ar in Ne matrix, the lower $\nu(\text{UC})$

Table 1.1 Infrared diatomic metal carbide stretching mode assignments (cm^{-1}).

Molecule	Sample phase	Experimental value	References
Al^{12}C	Ar matrix	640.1 ^{a)} 629.8 ^{a)}	[1, 4]
Al^{13}C	Ar matrix	622.8 ^{a)} 612.8 ^{a)}	[1]
SeC	Ar matrix	1029.7	[17]
	Vapor	1025	[18]
$\text{Rh}\equiv^{12}\text{C}$	Ar matrix	1024.2	[12]
$\text{Rh}\equiv^{13}\text{C}$	Ar matrix	988.2	[12]
$\text{Rh}\equiv^{12}\text{C}$	Ne matrix	1038.3	[12]
$\text{Rh}\equiv^{13}\text{C}$	Ne matrix	1002.1	[12]
$\text{Rh}\equiv^{12}\text{C}$	Vapor	1040.0	[11]
$\text{U}\equiv^{12}\text{C}$	Ar matrix	827.4	[15, 16]
$\text{U}\equiv^{13}\text{C}$	Ar matrix	797.0	[15, 16]
$\text{U}\equiv^{12}\text{C}$	Ne matrix	871.6	[15, 16]
$\text{U}\equiv^{13}\text{C}$	Ne matrix	839.6	[15, 16]

a) It was suggested in Ref. [1] that the two bands might be from two different environments for the AlC molecules, with the lower-frequency band from AlC molecules that are surrounded by Ar and the higher frequency one from those on the grain surface.

(854.0 cm^{-1}) and $\nu(\text{UO})$ (806.5 cm^{-1}) values were given as evidence for $\text{CUO}\cdot\text{Ar}$. Later matrix isolation infrared studies and DFT calculations concluded that triplet state CUO was present in pure Ar ($\nu(\text{UC}) = 887\text{ cm}^{-1}$, $\nu(\text{UO}) = 834\text{ cm}^{-1}$), Kr, and Xe matrices [21]; the CUO molecule is linear and the singlet state ($\nu(\text{UC}) = 1047.3\text{ cm}^{-1}$, $\nu(\text{UO}) = 872.2\text{ cm}^{-1}$) in a Ne matrix [22] and that the CThO molecule is nonlinear with a 109° CThO angle and a triplet ground state ($\nu(\text{ThC}) = 617.7\text{ cm}^{-1}$, $\nu(\text{ThO}) = 812.2\text{ cm}^{-1}$) [23]. There was also infrared evidence for the complexes $\text{CUO}(\text{Ar})_{4-n}(\text{Ng})_n$ ($\text{Ng} = \text{Kr}, \text{Xe}$; $n = 1-4$) [21]. In addition, the $\nu(\text{ThO})$ mode of CThO^- was assigned to a weak intensity infrared doublet at $761.7/759.6\text{ cm}^{-1}$ [23] and the $\nu(\text{UC})$ and $\nu(\text{UO})$ modes at 929.3 and 803.3 cm^{-1} , respectively, for CUO^- [22].

In an Ar matrix infrared study, it was concluded that the triplet ground state $\text{C}\equiv\text{U}\equiv\text{C}$ molecule is linear, and the $\nu_a(\text{UC})$ mode was assigned at 891.4 cm^{-1} [15, 16].

Ar matrix infrared data and frequency and intensity calculations of the three vibrational modes of M_2C ($\text{M} = \text{B}$ [24], Al [1], Si [25, 26]) indicated nonlinear structures of C_{2v} symmetry. The inability to detect some of the expected bands was consistent with the low intensities predicted in theoretical calculations, and the calculated k_{SiC} value indicated a bond order of between one and two for Si_2C [25]. Results from these studies are shown in Table 1.2. A linear structure has been proposed in vibrational studies of Se_2C in various phases [17, 27, 28], and the $\nu_s(\text{Se}_2\text{C})$, $\delta(\text{Se}_2\text{C})$, and $\nu_a(\text{Se}_2\text{C})$ modes have been assigned at c. 364, 313, and 1303 cm^{-1} , respectively [27]. An ab initio study of the structure and vibrational spectrum of Si_3C predicted a rhomboidal C_{2v} symmetry ground

Table 1.2 Theoretical and experimental vibrational assignments (cm^{-1}) for nonlinear CM_2 compounds.

Compound	Calculated ν_s	Experimental ν_s	Calculated ν_a	Experimental ν_a	Calculated δ	References
$^{11}\text{B}^{12}\text{C}^{11}\text{B}$	1481.8	1392.8	1249.3	a)	896.2	[24]
Al^{12}CAI	715.1	a)	855.3	802.0	164.6	[1]
$^{28}\text{Si}^{12}\text{C}^{28}\text{Si}$	839.5	839.5	1188.9	1188.4	134	[25, 26]

a) Band not observed.

state with two equivalent Si atoms in a nonlinear SiCSi framework and a transannular Si—C bond formed by the third Si atom [29]. These conclusions were supported by the assignment of five of the six fundamental vibrational modes of Si_3C in an Ar matrix infrared study [30].

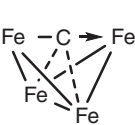
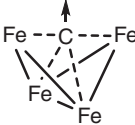
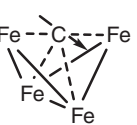
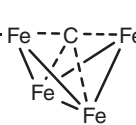
Ar matrix infrared data and calculations indicate a linear structure for $\text{HB}=\text{C}=\text{BH}$ ($\nu_a(^{10}\text{BC}^{10}\text{B}) = 1895.2 \text{ cm}^{-1}$) and its isotopomers [31]. The compound Al_3BC_3 has Al_5C trigonal bipyramids that are linked by common corners of the basal plane to produce linear $\text{C}=\text{B}=\text{C}^{5-}$ groups located between Al_3C layers [32]. In addition to vibrational assignments for the $\text{C}=\text{B}=\text{C}^{5-}$ unit ($\nu_a(\text{CBC}) = 1580 \text{ cm}^{-1}$, $\nu_s(\text{CBC}) = 1041 \text{ cm}^{-1}$, $\delta(\text{CBC}) = 735 \text{ cm}^{-1}$), Raman bands at 421 and 560 cm^{-1} were assigned to $\nu(\text{AlC})$ modes of Al_5C [32]. Some infrared assignments were given for $\text{Ga}_2\text{I}_2\{\text{C}[\text{Si}(\text{CH}_3)_3]_3\}_2$ ($\nu_a(\text{SiC}) = 658 \text{ cm}^{-1}$, $\nu_s(\text{SiC}) = 620 \text{ cm}^{-1}$) and $\text{Ga}_2\text{I}_4\{\text{C}[\text{Si}(\text{CH}_3)_3]_3\}_2$ ($\nu_a(\text{SiC}) = 660 \text{ cm}^{-1}$) [33]. Infrared and Raman data have been assigned for $(\text{CH}_3\text{Hg})_4\text{C}$ ($\nu_a(\text{Hg}_4\text{C}) = 620 \text{ cm}^{-1}$; $\nu_s(\text{Hg}_4\text{C}) = 137 \text{ cm}^{-1}$) [34], $(\text{RHg})_4\text{C}$ ($\text{R} = \text{CN}^-$, HCOO^- , CH_3COO^- , CF_3COO^- ; $\nu_a(\text{Hg}_4\text{C}) = 720\text{--}632 \text{ cm}^{-1}$; $\nu_s(\text{Hg}_4\text{C}) = 147\text{--}129 \text{ cm}^{-1}$) [35], and $(\text{XHg})_4\text{C}$ ($\text{X} = \text{F}$, Cl , Br , I ; $\nu_a(\text{Hg}_4\text{C}) = 690\text{--}623 \text{ cm}^{-1}$; $\nu_s(\text{Hg}_4\text{C}) = 165\text{--}98 \text{ cm}^{-1}$) [36]. Infrared assignments, including the $\nu(\text{GeC})$ mode, have been made for $(\text{X}_3\text{Ge})_4\text{C}$ ($\text{X}_3 = \text{H}_3$, 745 cm^{-1} ; Cl_2Br , 701 cm^{-1} ; Br_3 , 672 cm^{-1}) [37].

The $\nu_s(\text{FeC})$ mode was assigned at 443 cm^{-1} from resonance Raman data for a linear $\text{Fe}^{\text{IV}}=\text{C}=\text{Fe}^{\text{IV}}$ unit in a μ -carbido Fe tetraphenylporphyrin dimer and the $\nu_a(\text{FeC})$ mode at $939/885$ (sh) cm^{-1} from infrared data [38, 39]. It is the first reported complex with a formally dicarbenic C atom bridging a pair of transition metal atoms [39].

Vibrational data for complexes of interstitial carbide atoms in transition metal clusters with CO, or CO and other ligands have mainly included the assignment of $\nu(\text{CO})$ and $\nu(\text{metal-C})$ modes. A 1980 review compares $\nu(\text{CO})$ assignments as a function of cluster size and charge for clusters with five, six, and eight Fe, Ru, Os, Co, Rh, Fe/Rh, and Fe/Mo atoms [40]. Later studies included $\nu(\text{CO})$ assignments for carbide CO complexes with Re_6 [41], Re_7 [42], Re_8 [43], Re_7M ($\text{M} = \text{Rh}$, Ir , Pd , Pt) [44], Fe_5 [45], Ru_5 [46–49], Os_5 [49], Ru_6 [50], and Ni_n ($n = 8, 9$) [51] clusters. Changes in the number and frequency of the infrared $\nu(\text{CO})$ bands in CH_2Cl_2 solutions have been followed as $\{[\text{Co}_5\text{C}(\text{CO})_{12}]\text{Au}[\text{Co}(\text{CO})_4]\}^-$ was reduced to 2- and 3-oxidation states and $\{[\text{Co}_5\text{C}(\text{CO})_{12}]_2\text{Au}\}^-$ was oxidized to the 0 and reduced to the 2- and 3-oxidation states [52].

Infrared and Raman assignments at both 100 and 300°C have been reported for the four vibrational modes (illustrated in Table 1.3) associated with the Fe—C—Fe fragment of three tetrairon carbide CO clusters with “butterfly” Fe_4 cluster arrangements of C_{2v}

Table 1.3 Vibrational assignments (cm^{-1}) associated with carbide motion in “butterfly” tetrairon carbide CO clusters of C_{2v} symmetry at 100°C .^{a)}

								
	B₂		A₁(2)		B₁		A₁(1)	
Complex^{b)}	¹² C	¹³ C	¹² C	¹³ C	¹² C	¹³ C	¹² C	
[PPN] ₂ [Fe ₄ C(CO) ₁₂] ²⁻	929	896	666	652	608	601	272	
[HFe ₄ C(CO) ₁₂] ⁻	922	889	661	648	600		269	
Fe ₄ C(CO) ₁₃	928	895	658	645			252	

a) Reference [53].

b) Data are for the anions of the [(C₆H₅)₃P]₂N⁺ salt.

symmetry [53]. Assignments for the ¹²C/¹³C isotopomers of these modes recorded at 100°C are also given in Table 1.3. This study included carbide mode assignments for the [(C₆H₅)₃P]₂N⁺ salts of the related C_s symmetry mixed metal carbide CO complexes [Fe₃WC(CO)₁₃]²⁻ and [Fe₃RhC(CO)₁₂]⁻, with the highest carbide mode frequency at 899 and 953 cm^{-1} , respectively, a second (equivalent to the A₁(2) mode of the C_{2v} complexes) at 651 and 668 cm^{-1} , respectively, and a third at 263 and 274 cm^{-1} , respectively [53].

An X-ray diffraction study of Fe₅C(CO)₁₅ showed a C atom at the center of an approximate equilateral tetragonal pyramid formed by the Fe atoms of five Fe(CO)₃ fragments [54]. It has also been concluded [55] that previously suggested assignments [54] of infrared bands at 790 and 770 cm^{-1} to semiinterstitial C atom vibrations in Fe₅C(CO)₁₅ are likely correct. It was later noted that solid Fe₅C(CO)₁₅ exists as needle and plate polymorphs that had slightly different carbide $\nu(\text{FeC})$ frequencies at 805 and 765 cm^{-1} and 805 and 780 cm^{-1} , respectively [45]. At 298 K, isostructural Ru₅C(CO)₁₅ exhibited three semiinterstitial C atom bands (730, 738, and 757 cm^{-1}) that became five bands (735, 745, 752, 769, and 772 (sh) cm^{-1}) on cooling to 90 K [56]. Interstitial C atom vibrations have been assigned for Os₅C(CO)₁₅ (795, 777, 770, and 755 cm^{-1}) [57]. It has been reported that the complexity of the infrared spectra of M₅C(CO)₁₅ (M = Ru, Os), as was also seen for Fe₅C(CO)₁₅, is from two nonequivalent sets of molecules in the unit cells [45]. An infrared study has concluded that the dependence of the carbide $\nu(\text{MC})$ frequencies on the cluster geometry can be used as a structural indicator for M₅C(CO)₁₅ (M = Ru, Os) and several of their derivatives [58]. The $\nu(\text{CO})$ frequency for [Fe₅C(CO)₁₅]²⁻ (1735 cm^{-1}) has been noted [45, 59] to be consistent with a structure with two semi-edge-bridging CO ligands over two adjacent basal Fe–Fe bonds. This complex also has an infrared carbide $\nu(\text{FeC})$ band at 815 cm^{-1} [59].

In contrast to Ru₅C(CO)₁₅, the complexes HRu₅C(CO)₁₅X (X = Cl, Br) have a μ -hydrido-bridged butterfly Ru₅ geometry with carbide $\nu(\text{RuC})$ bands at c. 690 and 825 cm^{-1} at 298 K and a c. 5 cm^{-1} splitting of the 825 cm^{-1} band on cooling to 90 K [56].

This study included $\nu(\text{RuRu})$ and $\nu(\text{RuX})$ assignments for $\text{HRu}_5\text{C}(\text{CO})_{15}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$). A similar bridged butterfly geometry has been found for the Ru atoms in $\text{Ru}_5\text{C}(\text{CO})_{15} \cdot \text{CH}_3\text{CN}$, where the interstitial C stretching modes were assigned at 674 and 817 cm^{-1} [46]. Interstitial carbide $\nu(\text{MC})$ bands have been assigned for the ^{13}C -enriched carbide CO complexes $[\text{M}_6\text{C}(\text{CO})_n]^{m-}$ ($\text{M} = \text{Fe}, n = 16, m = 2$; $\text{Ru}, n = 16, m = 2$, and $n = 17, m = 0$) ($900\text{--}600\text{ cm}^{-1}$) [60], $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ ($735.4, 760.3$, and 772.8 cm^{-1}), and $[(\text{CH}_3)_4\text{N}]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ (753 cm^{-1}) [61].

Comparison of the infrared spectrum of $\text{Co}_6\text{C}(\text{CO})_{12}\text{S}_2$ to that of the same complex containing 90% ^{13}C led to the assignment of bands at 819 and 548 cm^{-1} in the unlabeled compound and 790 and 535.5 cm^{-1} in the ^{13}C isotopomer to the A_2'' and E' vibrations, respectively, for a C atom encapsulated at the center of a trigonal prism formed by the six Co atoms [55]. Enrichment with ^{13}C also allowed for the assignment of the interstitial $\nu(\text{MC})$ modes for $[\text{M}_6\text{C}(\text{CO})_{15}]^{2-}$ ($\text{M} = \text{Co}, \text{Rh}$) [62], and the calculation of the axial and equatorial metal carbide force constants [62]. An infrared study that used ^{13}C labeling to assign the carbide $\nu(\text{MC})$ frequencies of both the metal-capped and uncapped $\text{Re}_6(\mu\text{-C})$ and $\text{Ni}_6(\mu\text{-C})$ cores of CO clusters concluded that while a single force constant could account for the frequencies for the capped and uncapped Ni carbide clusters and the uncapped Re carbide clusters, vibrational assignments for the capped Re clusters required slightly different equatorial and axial ReC force constants [63].

