an increased importance in bond making in the activation process and the negative ΔS_d^* values associated with the lower ΔH_d^* indicating an ordering in the transition state consistent with the binding of additional solvent molecules in the transition state. It is only in dimethylformamide that activation data are available for the decomplexation of both $[Na{\cdot}C21C_5]^+$ and $[Na{\cdot}C211]^+$ (Table III). The latter cryptate is characterized by a much greater ΔH_d^* and a substantial and positive ΔS_d^* which contrasts with the negative ΔS_d^* characterizing $[Na{\cdot}C21C_5]^+$. This is consistent with the mechanistic proposals developed above in which bond breaking is more important in the decomplexation activation process starting from ground-state c in Figure 3 for $[Na{\cdot}C211]^+$ than in the activation process for $[Na{\cdot}C21C_5]^+$, probably because Na^+ is more accessible to solvent in the latter case. (The k_d values characterizing $[Na{\cdot}C21C_5]^+$ and $[Na{\cdot}C211]^+$ are substantially greater than the k_d value characterizing the inclusive cryptate $[Na{\cdot}C221]^+$ (Table III) consistent with the rate-determining step for the decomplexation of the latter species involving a change from the inclusive to the exclusive form.)

In acetonitrile, acetone, methanol, and dimethylformamide, k_f characterizing $[Na{\cdot}C21C_5]^+$ varies by a factor of 2.55 only which shows that the summation of the free energy changes accompanying the partial desolvation of Na^+ and the formation of Na^+ to $C21C_5$ bonds in the activation process are similar. In propylene carbonate and pyridine k_f is decreased which infers that the contributions to ΔG_f^* arising from the desolvation of Na^+ (and possibly solvation changes of $C21C_5$) in these solvents are substantially greater than in the other four solvents. Thus propylene carbonate and pyridine in particular produce k_f and k_d values which are unexpected on the basis of the trends in these parameters observed for the other solvents studied. There are insufficient data available to ascertain if these kinetic differences induced by propylene carbonate and pyridine are general in cryptate systems, but the observation[5] of $10^3 k_d(298.2\ K) = 0.13$ and $13.0\ s^{-1}$ in pyridine and dimethylformamide, respectively, for the $[Li{\cdot}C211]^+$ system indicates that pyridine produces small k_d values in one other cryptate system at least.

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Registry No. $C_{21}C_5$, 72640-82-5; $[Na{\cdot}C_{21}C_5]^+$, 104911-16-2; Na, 7440-23-5.

Supplementary Material Available: Tables of experimental k_d ($= 1/\tau_c$) and experimental temperatures plotted in Figure 2 and corresponding to solutions i–xii of Table I (4 pages). Ordering information is given on any current masthead page.

Interaction between Lithium and Carbon Monoxide. 1. A Matrix Infrared Study

O. Ayed, A. Loutellier, L. Manceron, and J. P. Perchard*

Contribution from the Laboratoire de Spectrochimie Moléculaire, Université Pierre et Marie Curie, 75320 Paris Cédex 05, France.

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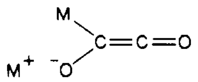
Abstract: Codeposition of lithium atoms and carbon monoxide molecules in an inert medium (Krypton) at 12 K led to the spontaneous formation of numerous products classified in three groups. The first group is constituted by four mononuclear species $Li(CO)_n$ with n = 1, 2, 3, and $\geqslant 4$. In these cases, structures, vibrational spectra, and bonding have been discussed with the help of isotopic substitutions ($^6Li/^7Li$, $^{12}C/^{13}C$, $^{16}O/^{18}O$). The structural properties of the well-identified monolithium species are closely related to carbonyls of transition metals, but with stronger perturbations with Li for equal coordination numbers. The second group involves species with several Li atoms and one or two CO molecules in which the carbonyl groups are only weakly coupled in spite of larger perturbations than with mononuclear species. The third group corresponds to species identified by stretching modes of either CO single bonds or strongly coupled double bonds therefore species in which true chemical bonds are formed between carbonyls.

The state of knowledge of the carbonyl chemistry of alkali metals has remained up to now astonishingly low compared to that relating to transition metals. The reaction between alkali atoms (M) dissolved in liquid ammonia and carbon monoxide was reported for the first time in 1933 by Pearson[1] for M = Li. After evaporation of ammonia, a white solid with one-to-one stoichiometry was isolated with the following properties: it is stable at room temperature and decomposes at about 500 °C, with formation of Li_2CO_3, Li_2O, and C; it reacts vigorously with water, with formation of Li_2CO_3, C, and H_2. More recently the structure of the reaction product for M = K has been determined by X-ray crystallography.[2] The product has been shown to be potassium acetylenediolate (KOC≡COK) with the following internuclear distances (Å): K–O, 2.67; C–O, 1.28; C–C, 1.21.

Also evidence has been presented[3] suggesting that in liquid ammonia another compound with the structure



is formed along with the acetylenediolate salt. On the other hand, some infrared spectra were reported for Li–CO complexes trapped in inert matrices by Margrave and co-workers.[4] But to our knowledge, no detailed analysis of these data has been subsequently published.

This lack of interest in alkali metal carbonyls from the chemists and physicochemists (no specific publication on this topic since 1963) is probably due to the absence of applications of these carbonyls in preparative chemistry. However, the nature of the interaction between alkali metal atoms and carbon monoxide could be of major interest in catalysis, since it has been recognized[5] that the catalytic properties of transition metal surfaces are modified

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(1) Pearson, T. G. *Nature (London)* **1933**, *131*, 166.

(2) Weiss, E.; Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 1121; *Z. Anorg. Allg. Chem.* **1964**, *330*, 251.

(3) Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 2111.

(4) Ozin, G. A.; Moskovits, M. In *Cryochemistry*; Wiley: New York, 1976; p 345.

(5) Dry, M. E.; Shingles, T.; Boshoff, L. J.; Oosthuizen, G. J. *J. Catal.* **1969**, *15*, 190. See also: Broden, G.; Gafner, G.; Bonzel, H. P. *Surf. Sci.* **1979**, *84*, 295.

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by addition of submonolayer amounts of alkali metals. Studies about these interactions, based on heat of adsorption and on desorption temperature of CO (other ligands such as NO, N_2, N_2O, C_6H_6) coadsorbed with alkali metal,[6] indicate that electronic interactions between the adsorbates and the metal atoms do occur. These interactions are in particular responsible for large charges in adsorption energy and CO vibrational frequency which shifts from ca. 2000 cm^{-1} (CO adsorbed clean Pt surface) down to 1400 cm^{-1} for the most tightly bound CO molecules on the metal surface in the presence of potassium. These observations are consistent with the existence of a CO dissociation process which has been evidenced by Hoffmann et al.[7] and Crowell et al.[8] The mechanism of such a process is still unclear. Some authors suggested that it is connected with an enhancement of the net electronic density of the catalyst, through charge transfer from the alkali atom toward the transition metal atoms; there is then electron back-donation into the antibonding orbitals of the CO molecule. Very recently[9] a direct interaction, corresponding to the formation of a surface complex between the alkali metal and the CO, has been evidenced by the observation of simultaneous desorption of potassium and CO.

In order to go into greater depth regarding the nature of the direct interaction between alkali atoms (monomer and small aggregates) and carbon monoxide, we have undertaken an infrared study of the Li/CO system trapped in krypton matrices. Extensive experiments, carried out over a wide range of experimental conditions, have allowed us to identify several complexes and to determine their structural properties from isotopic dilution experiments. However, the complexity of the infrared spectra does not allow a full understanding of the data and suggests complementary approaches in both theoretical and experimental fields. On the one hand, ab initio calculations have been performed for some $Li_m(CO)_n$ aggregates ($m = 1$, $n = 1$; $m = 1$, $n = 2$; $m = 2$, $n = 1$); they are published in the following paper (referred to as part 2) in this issue.[10] On the other hand, complementary infrared studies involving the binary Li–CO system and other alkali atoms (Na, K) trapped in Kr/CO mixtures are currently in progress. They will be the object of separate publications.

In this paper we shall describe, in the first part, the infrared spectra of Li/CO/Kr matrices and propose, in the second part, an assignment of some bands in terms of low-stoichiometry complexes.

Experimental Section

Lithium metal was vaporized from a stainless steel crucible heated in the temperature range 370–490 °C. The vaporization temperature was determined by using a copper-constantan thermocouple immersed in melted lithium. The lithium effusion rate was measured with a quartz crystal microbalance. An atomic beam of lithium was codeposited with carbon monoxide in an excess of krypton onto a KBr or CsI plate cooled to 13–14 K by means of a closed-cycle helium cryostat (Air Products CSW 202). The CO/Kr gas mixture was premixed according to standard manometric technique. After about a 20-min deposition, the UV-visible spectrum of the sample was recorded in order to control the Li/Li_2 ratio; then deposition was carried out for 6 to 14 h prior to infrared spectra recording. Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer, with spectral slit width between 4 and 1 cm^{-1} and frequency accuracy of 1 cm^{-1}. UV-visible spectra were recorded on a Cary 14. Photolysis of the matrices was performed using Xe lamp (150 W) and prism monochromator.

High-purity lithium metal (99.95%) was obtained from Alfa Inorganics. An isotopically enriched sample of the metal (95% in ^6Li) was furnished by the French Commissariat à l'Energie Atomique (CEA). Carbon monoxide (99.5%) and enriched sample containing 99% of ^{13}CO and 91% of $^{13}C^{18}O$ were purchased from Matheson and the CEA, respectively. Air Liquide krypton (99.995%) was used without further purification.

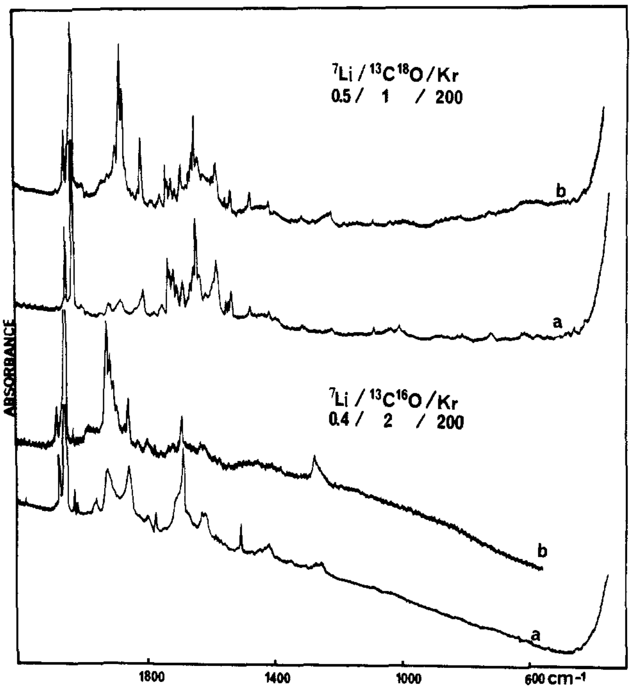

Figure 1. Infrared spectra of Kr matrices doped by natural Li and two different isotopic species of carbon monoxide: upper traces, $^7Li/^{13}C^{18}O/Kr = 0.5/1/200$; lower traces, $^7Li/^{13}C^{16}O/Kr = 0.4/2/200$. (a) Spectrum recorded after deposition at 14 K in the dark; (b) spectrum recorded after annealing at 50 K for 10 mn in the dark, (recording temperature, 14 K).

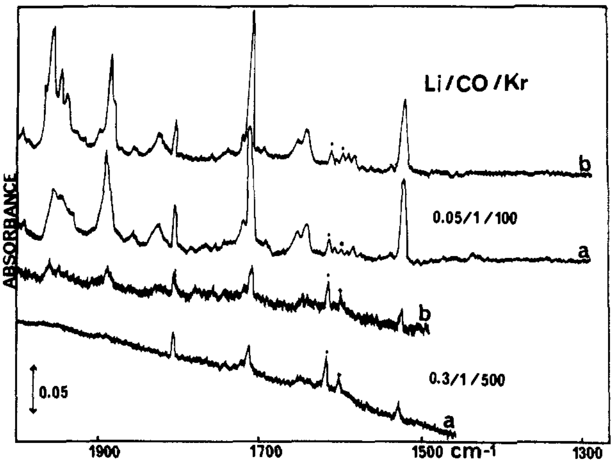

Figure 2. Infrared spectra of natural CO and Li in solid krypton in the spectral range 2000–1300 cm^{-1}: upper traces, Li/CO/Kr = 0.05/1/100; lower traces, Li/CO/Kr = 0.3/1/500. (a) After deposition, (b) after annealing at 50 K. The starred lines are due to impurity traces of H_2O.

Results

Codeposition of CO and Li in krypton gives rise to a huge number of CO bands in the 2000–1000-cm^{-1} spectral range (Figure 1 and Table I)), while absorptions below 700 cm^{-1} are scarce and difficult to observe owing to their very weak intensities as compared to those of the CO stretching bands. As a rule, an increase in Li/CO molar ratio leads to the appearance of several low-frequency CO bands between 1500 and 1000 cm^{-1}, while at high CO concentration (Kr/CO ~ 100) bands in the 1800–2000-cm^{-1} range are strikingly enhanced.

The presentation of the spectral data will be detailed by successively examining each absorption of $^{12}C^{16}O$ in interaction with Li. Isotopic counterparts will be reported as well as effects of isotopic dilution obtained for equimolar mixtures of $^{12}C^{16}O/^{13}C^{16}O$ and $^{13}C^{16}O/^{13}C^{18}O$. The third mixture ($^{12}C^{16}O/^{13}C^{18}O$) is es-

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[6] Garfunkel, E. L.; Crowell, J. E.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 310. Garfunkel, E. L.; Maj, J. J.; Frost, J. C.; Farias, M. H.; Somorjai, G. A. *Ibid.* **1983**, *87*, 3629. Garfunkel, E. L.; Farias, M. H.; Somorjai, G. A. *J. Am. Chem. Soc.* **1985**, *107* 349.

[7] Hoffmann, F. M.; de Paola, R. A. *Phys. Rev. Lett.* **1984**, *52*, 1697.

[8] Crowell, J. E.; Tysoe, N. T.; Somorjai, G. A. *J. Phys. Chem.* **1985**, *89*, 1598.

[9] Lee, J.; Arias, J.; Hanrahan, C. P.; Martin, R. M. *J. Chem. Phys.* **1985**, *82*, 487.

[10] Silvi, B.; Ayed, O.; Person, W. B. *J. Am. Chem. Soc.*, following paper in this issue.

Table I. Reaction Product Absorptions in the 2100–1000-cm^{-1} Region for Li + CO in Krypton and Assignment to Li$_m$(CO)$_n$ or *m*:*n* Complexes[a]

$^{12}C^{16}O$			$^{13}C^{16}O$			$^{13}C^{18}O$			assignment	
2065.5	w	+	2019.5	w	+	1971	w	+	ν_s	1:3
						1910	*			
1997.5	*	+/–	1953.5	*	–	1906		–		1:2
1991	w		1947.5	w		1902	w			
1957.5	s	++	1915.5	s	++	1866	s	++	ν_d	1:4 or 6
1948	s	++	1907	s	++	1858	s	++		
1937	m	+	1897	m	+	1848	m	+		
1932	w	+								
1924	w	+				1835	w	+		
1898	w	+	1857.5	w	+					
1888	m	+	1847.5	m	+	1801	m	+	ν_d	1:3
1824.5										
	w	+	1786	w,b	+	1742	w,b	+		
1818										
1806	m	–	1764.5	m	–	1723.5	m	–		1:1
1801	*		1760	*		1719	*			
1792	*		1752	*		1710	*			
1788	w	–	1748	w	–	1707	w	–		
1780	w	+	1744	w	+					
1774	w	+	1737	w	–	1695	w			
1757	w	+	1720	w	+					
1742	w		1705	w						
1721.5	*		1686	*		1643	*			
		+/–			+/–			+/–		1:2
1712.5	s		1677	s		1634	s			
1655			1620			1579				
	w	–		w	–		w	–		
1645			1610.5			1569				
1613	w		1577.5	w		1540	w			2:2
1601			1570			1531				
1596	w		1560	w		1523.5				2:1
1532.5	m	+	1499	m	+	1462	m	+		
1470	w		1439	w		1404	w			3:1
1446	w		1410	w		1381				
			1268			1230				
1294	w, br	+		w, br	+		w, br	+		
			1254			1220				
1273	w		1246	w		1212	w			
1267.5	w		1240.5	w		1208	w			
1132	w	–	1107	w	–	1076	w	–		
1049	w, br	–	1028	w, br	–	1000	w, br	–		

[a] Relative band intensities refer to spectra recorded at 13 K: +,–, intensity increases, decreases after annealing; +/–, intensity increases for Kr/CO > 200 and decreases in the opposite case; *, the band intensities strongly vary according to the sample but the growth of all these lines is correlated.

pecially difficult to analyze because the $^{13}C^{18}O$ sample contains a small amount of $^{13}C^{16}O$, leading to the simultaneous presence of the three carbon monoxide isotopic precursors in the matrix.

A. Spectra Obtained at High Dilution in Lithium. Experiments carried out at Kr/CO molar ratio between 700 and 1500 and Kr/Li greater than 1000 allow the observation of a main line at 1806 cm^{-1} and weaker features at 1712 and 1530 cm^{-1} before annealing (Figure 2); after annealing several bands around 1950 cm^{-1} and another one at 1888 cm^{-1} appear. When the Kr/CO molar fraction decreases from 500 to 100, with the Kr/Li ratio keeping a value larger than 1000, other weak features are measured at about 1825 and 1750 cm^{-1}. These bands will be successively examined, in the order of their appearance, for increasing CO molar fraction in the matrix.

The 1806-cm^{-1} band. This is the only one to appear for matrices with CO/Li/Kr = 0.3/1/1500. In some experiments this band appears as a doublet at 1806–1801 cm^{-1} and in a few cases the low-frequency component is the only one present. We were not able to define the experimental conditions required for the growth of one band rather than the other. None of them is induced by the presence of H_2O and O_2 as impurity traces in the matrix. Nevertheless, an interesting point is that the electronic spectrum of Li displays in the Li atom absorption region (600–700 nm) a different pattern according to the presence of either the 1806- or 1801-cm^{-1} line. In the first case (1806 cm^{-1} predominant), the Li spectrum corresponds to the usual one, namely, with a main triplet at 660–675–685 nm;[11] in the second case, one observes a broad doublet at 625–645 nm (Figure 3). Thus the presence of the splitting of the CO stretching mode is probably tied to the existence of several trapping sites for the lithium atoms. This remark will be also useful for interpretation of several other CO

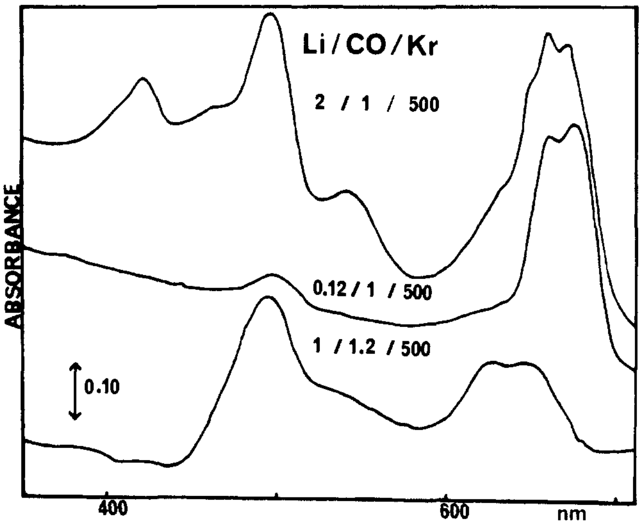

Figure 3. UV-visible absorption spectra of Kr matrices doped with natural Li and CO for various concentrations in Li. The lower trace corresponds to an "abnormal" spectrum with blue-shifted bands for the Li monomer. The corresponding infrared spectrum displays a band at 1801 cm^{-1} instead of 1806 cm^{-1}.

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(11) Andrews, L.; Pimentel, G. C. *J. Chem. Phys.* **1967**, *47*, 2905; Welker, T.; Martin, T. P. *Ibid.* **1979**, *70*, 5683.

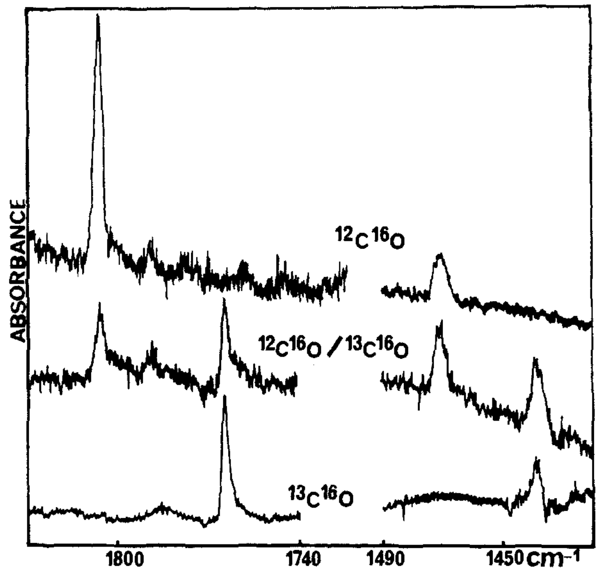

Figure 4. Comparison between infrared spectra of Li/CO/Kr matrices for different isotopic compositions in carbon monoxide. For the 1810–1740-cm^{-1} spectral region the composition is typically 1/2/1000; for the 1490-1430-cm^{-1} region it is 3/2/1000. All the spectra were recorded after deposition.

absorption bands whose behavior upon annealing is likewise typical of the presence of multiple trapping sites. The $^{13}C^{16}O$ and $^{13}C^{18}O$ counterparts of the 1806–1801-cm^{-1} lines are respectively measured at 1764.5–1760.5 and 1723.5–1719 cm^{-1}. For isotopic mixtures no other feature is observed at intermediate frequency (Figure 4). Consequently these bands have to be assigned to single CO oscillators, i.e., to monocarbonyl species; observations of these bands at high dilution in lithium make their assignment to the monolithium monocarbonyl (1:1) species unquestionable.

The 1712–1991-cm^{-1} Bands. The intensity ratio between the bands at 1712 and 1991 cm^{-1} has been found to be constant in large CO or Li concentration ranges, leading to the conclusion that they have to be assigned to the same species. Each of these lines appears as a doublet at 1712–1721 and 1991–1996 cm^{-1}. The intensity ratio between the two components of each doublet varies according to the deposition conditions in a way which parallels the behavior of the 1806–1801 doublet; the upper limit of 4 for the 1712/1721 intensity ratio is reached when the 1806-cm^{-1} line is the only one to be present, while a lower limit of 1 is obtained when the 1801-cm^{-1} line is preponderant. A comparable evolution is observed for the 1991/1996 doublet. On the other hand the 1712/1991 and 1721/1996 intensity ratios remain constant whatever the experimental conditions, of the order of 16 and 3.5, respectively.

The intensity of these two doublets increases with respect to that of the 1806–1801 one when the Kr/CO molar ratio decreases and also after annealing for diluted samples; for Kr/CO ratios less than 200, on the contrary, annealing does not lead to any intensity increase. Isotopic counterparts are given in Table I; for isotopic mixtures new doublets appear halfway between the frequencies of pure species (for $^{12}C/^{13}C$ isotopic dilution, see figure 5). This pattern is typical of two equivalent CO within the aggregate;[12] furthermore since the bands are observed at high dilution in Li, the aggregate is likely to be the monolithium dicarbonyl species.

The 1533-cm^{-1} Band. This band is slightly broadened on its high-frequency side. It grows in the same proportion as the 1722–1712-cm^{-1} doublet, the 1712/1533 intensity ratio keeping a constant value of 2.3 ± 0.5, whatever are the dopant concentrations. After irradiation with the full light of a Xe lamp, this ratio decreases and is of the order of 1 after 1 h exposure. For isotopic mixtures remarkably small splittings are evidenced (Figure 5) with an unusual decoupling effect consisting of the appearance of a *red*-shifted line with respect to that observed for the pure light isotope and a *blue*-shifted one with respect to that of the pure heavy isotope. In both cases the splitting is 3 to 5 cm^{-1} and the two components of each doublet have the same intensity for equal concentrations of isotopic species.

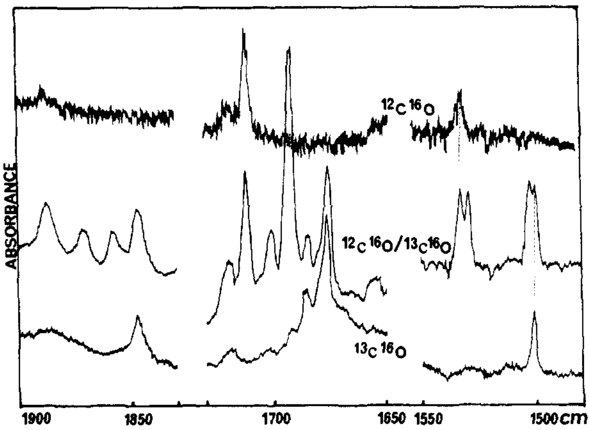

Figure 5. Comparison between infrared spectra of Li/CO/Kr matrices for different isotopic compositions in carbon monoxide. For the upper traces (natural CO), the composition is 1/1.4/1000; for the others it is 1/2.2/1000. All the spectra were recorded after deposition.

The 1888–2065-cm^{-1} Bands. Systematic intensity measurements have shown that there exists a constant intensity ratio, of the order of 0.07, between these two bands, which consequently have to be assigned to the same aggregate. The properties of the stronger line at 1888 cm^{-1} are as follows: (i) it is always accompanied by a weak satellite at 1898 cm^{-1} and is observed before annealing for Kr/CO ratio less that 200; (ii) for larger values it is observed only after annealing; (iii) its intensity with respect to the 1712–1721-cm^{-1} system varies according to the Kr/CO ratio and the annealing temperature. As a rule, the 1712/1888 intensity ratio increases when the CO molar fraction or the annealing temperature decreases. In $^{12}C/^{13}C$ isotopic dilution experiments there appear (Figure 5) two new lines at intermediate frequencies. The same pattern is also observed in $^{13}C^{16}O/^{13}C^{18}O$ mixtures. A decoupling effect has also been observed for the weak high-frequency band in the spectrum of a sample containing equal proportions of ^{12}CO and ^{13}CO; in this case a new line appears at 2052 cm^{-1} with a much higher intensity than that of the two lines at 2065 and 2020 cm^{-1} assigned respectively to isotopically pure ^{12}CO and ^{13}CO species. Therefore, these absorptions belong to a species containing three equivalent CO oscillators.[12]

The 1957–1924-cm^{-1} System. This species is seen with very low Li concentration. For Kr/CO molar ratio of the order of 100 a broad absorption with ill-defined submaxima is observed after deposition. With lower concentration in CO this multiplet is observed only after annealing (Figure 2) or when the deposition temperature of the sample is higher than 30 K. In both cases the system is constituted by at most five components (1957.5, 1948, 1937, 1932, and 1924 cm^{-1}) whose intensities decrease in the order of decreasing frequencies. These absorptions grow strongly upon annealing, mainly that at 1957.5 cm^{-1} which becomes strongest of the whole spectrum. The bands are then well-separated from each other, but the weak ones at 1932 and 1924 cm^{-1} are missing in some experiments. The relative intensity of the 1948-cm^{-1} band with respect to that of the 1957-cm^{-1} band varies from 0.8 to 0.2, but this evolution has not been correlated to any experimental factor. Likewise the relative intensities of the low-frequency bands vary, but are in any case at most 0.15 times that of the 1957 cm^{-1} line. On the other hand, the intensity of this last one with respect to that of the 1888-cm^{-1} band is seen to increase when the CO molar fraction increases, either before or after annealing. In isotopic dilution experiments involving equal concentration of ^{12}CO and ^{13}CO, there appears (Figure 6) a broad and symmetrical band centered at 1930 cm^{-1} which can reasonably be assigned to a decoupling effect within the species responsible for the strongest line at 1957 (^{12}CO) or 1915 cm^{-1} (^{13}CO). This shows unam-

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(12) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2496.

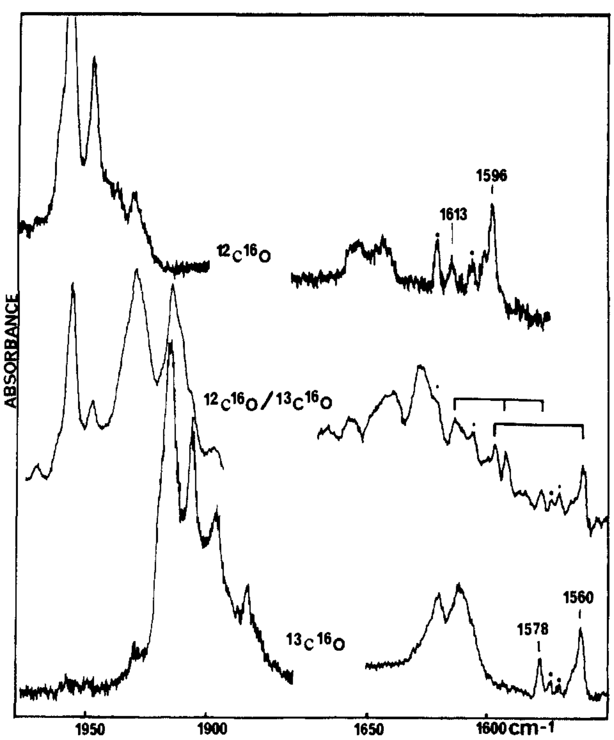

Figure 6. Comparison between infrared spectra of Li/CO/Kr matrices for different isotopic compositions in carbon monoxide. For the 2000–1900-cm^{-1} spectral region the composition is typically 1/2.5/1000 (spectra recorded after annealing); for the 1650–1550-cm^{-1} region the composition is 3/2.5/1000 (spectra recorded after deposition). The starred peaks are due to H_2O impurity traces.

biguously that the species responsible for this absorption contains one Li atom but several equivalent CO groups, the concentration study indicating that its CO stoichiometry is larger than that of the 1888-cm^{-1} species (i.e., more than three CO). Similar absorptions at 1966/56 cm^{-1} are by far the main features before exposure of the sample to visible light in the spectra of Li/CO binary mixtures which will be described in a forthcoming paper.[22]

The 1824-cm^{-1} Band. This rather broad line, which is observed only after deposition for Kr/CO molar fractions smaller than 250, has been resolved in some spectra into two components 6 cm^{-1} apart. It weakly increases upon annealing and has been clearly identified in the spectra of the other CO isotopic species with the usual shift. Unfortunately, isotopic decoupling behavior cannot be observed because of the presence of the strong line at 1806 cm^{-1}.

The 1757-cm^{-1} Band. This band is observed only after deposition for Kr/CO molar ratios smaller than 250; it grows after annealing and is observed even for CO-diluted samples (see, for instance, Figure 7). In $^{12}CO/^{13}CO$ mixed samples a new narrow line at 1739.5 cm^{-1} is probably assignable to the corresponding mixed species.

B. Spectra Obtained at High Concentration in Lithium. A large number of experiments have been carried out for evaporation temperatures of lithium higher than 450 °C which, according to our deposition conditions, corresponds to Kr/Li molar fractions smaller than 500. Visible spectra show (Figure 3) evidence for the presence of appreciable quantities of Li$_n$ aggregates.[11] Under these conditions new absorptions are observed in the infrared spectra. They are classified in the order of appearance for increasing CO concentration: (i) for Kr/CO molar fraction as high as 1000, the presence of two narrow lines at 1596 and 1470 cm^{-1}; (ii) for Kr/CO molar ratio equal to or less than 400, observation of many weak features spread over the whole 2000–1000-cm^{-1} spectral range.

(a) Bands Observed at Low CO Concentration. The 1596-cm^{-1} Band. The intensity of this narrow line with respect to that of the 1806-cm^{-1} band previously described is found independent of the CO concentration at fixed Kr/Li molar ratio. Conversely the 1596/1806 intensity ratio increases with increasing molar fraction of Li in the matrix. Although the analysis of the 1650–1570-cm^{-1} spectral region is made difficult by the presence of free and lithium complexed water[13] absorptions, we have concluded that no other feature than those due to pure ^{12}CO and ^{13}CO species (at 1560 cm^{-1} for ^{13}CO) is observed in isotopic mixtures involving these two species (Figure 8).

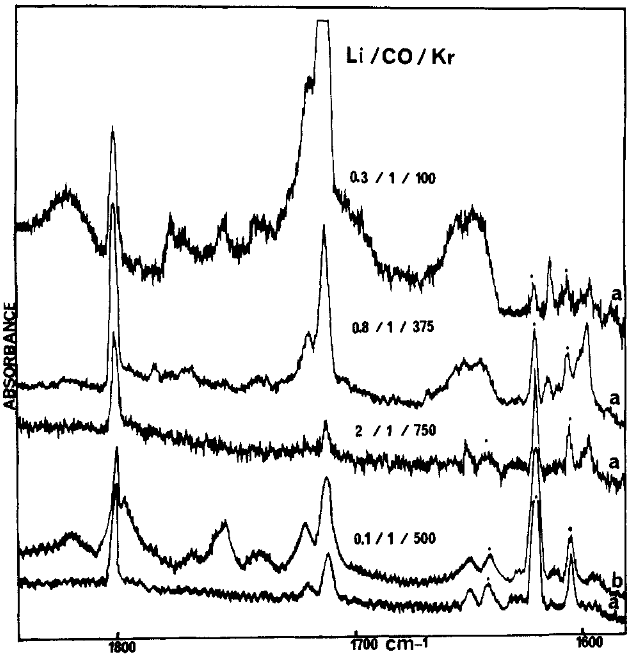

Figure 7. Comparison between infrared spectra in the 1800–1600-cm^{-1} region for different Li/CO/Kr molar ratios: (a) after deposition, (b) after annealing at 50 K. The starred lines are due to impurity traces of H_2O.

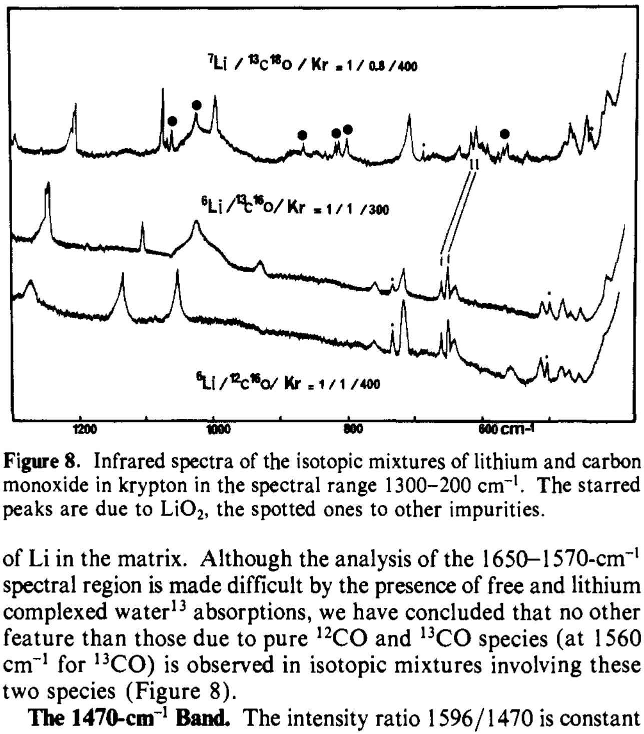

Figure 8. Infrared spectra of the isotopic mixtures of lithium and carbon monoxide in krypton in the spectral range 1300–200 cm^{-1}. The starred peaks are due to LiO_2, the spotted ones to other impurities.

The 1470-cm^{-1} Band. The intensity ratio 1596/1470 is constant at fixed Li and variable CO concentrations but decreases with the Kr/Li molar ratio. The 1470-cm^{-1} band is not observed for values less than 400. In isotopic dilution experiments this band behaves the same as the 1596-cm^{-1} one, i.e., without appearance of new signals at intermediate frequency between those observed for pure species (Figure 4). These observations indicate that this species, like those related to the 1806- and 1596-cm^{-1} features, contains one single CO group but has an even higher Li stoichiometry than these two latter species.

(b) Bands Observed for Kr/CO Molar Ratios Equal To or Smaller Than 400. When the Kr/CO molar fraction reaches 400, a large number of weak features appear, favored by high CO

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(13) Manceron, L.; Loutellier, A.; Perchard, J. P. *Chem. Phys.* **1985**, *92*, 75.

concentration. They will be examined successively, in the order of decreasing frequencies.

The 1790–1740-cm^{-1} Region. A complicated pattern of weak bands is identified in this spectral domain. A precise study of their behavior is made difficult because of their proximity to strong bands, which precludes any observation of decoupling effects in isotopic mixture experiments. However, certain conclusions can be drawn from careful comparisons.

The 1788-cm^{-1} band disappears upon annealing but is present for Kr/CO molar ratio of the order of 300.

The 1780-cm^{-1} band has been observed after deposition for Kr/CO molar fraction of 100 and only after annealing for samples diluted in CO but rich in Li.

The 1774-cm^{-1} band is observed after deposition for Kr/CO molar fraction of 325, i.e., for CO concentration smaller than required for the appearance of the previous one at 1780 cm^{-1}. However, the 1780/1774 intensity ratio is less than unity when the Kr/CO ratio is of the order of 100.

The 1742-cm^{-1} band is always weak and broad, without noticeable increase upon annealing.

The 1655–1645-cm^{-1} Doublet. The intensity ratio 1655/1645 of the two rather broad components of this doublet is roughly 0.7 whatever the experimental conditions. After annealing one observes a slight intensity decrease of this doublet. ^{13}CO isotopic counterparts are measured at 1620 and 1611 cm^{-1}, the first line overlapping the main component of the bending mode of H_2O. In ^{12}CO/^{13}CO isotopic dilution experiments a rather complicated pattern is observed, with two broad absorptions centered at about 1639 and 1627 cm^{-1} (Figure 6).

The 1613-cm^{-1} Band. The intensity increase of the 1613-cm^{-1} band is clearly correlated to the increase of the CO molar fraction, at constant Li concentration (Kr/Li equal to or smaller than 400). Compared to the 1596-cm^{-1} band previously described, its intensity is weaker for Kr/CO larger than 200 but becomes stronger when this molar ratio reaches 100 provided the Kr/Li ratio is kept constant, of the order of 300. ^{13}CO enrichment yields a triplet structure (Figure 6) at 1613, 1592, and 1578 in which the central band is relatively more intense. The 1613-cm^{-1} band, like the 1596-cm^{-1} one, tends to decrease in intensity upon annealing.

The 1446-cm^{-1} Band. This broad band is very sensitive to annealing and disappears at a temperature higher than 40 K. At constant Kr/Li molar ratio (of the order 300), the 1446/1470 intensity ratio is seen to strongly increase with the CO molar ratio, varying from 1 to 10 for Kr/CO ratio decreasing from 400 to 100. ^{13}CO enrichment yields a broad band centered at about 1430 cm^{-1}, suggesting the existence of a decoupling effect with appearance of a new absorption at intermediate frequency between those of pure ^{12}CO and ^{13}CO species (1410 cm^{-1} for ^{13}CO).

The 1300–1000-cm^{-1} Region. Three groups of weak bands are identified (Figure 8) in this region, at about 1300, 1130, and 1050 cm^{-1}. All these bands show a ^{12}C/^{13}C and ^{16}O/^{18}O isotopic shift but are insensitive to ^{6}Li/^{7}Li substitution. Their relative intensities vary according to CO and Li concentrations; the 1270-cm^{-1} band is the strongest for Kr/CO = 100 while the one at 1050 cm^{-1} grows when lithium molar fraction increases. The structure of the band at 1270 cm^{-1} varies with the CO concentration and after annealing, as shown in Figure 9 for a ^{13}C^{16}O/Li/Kr mixture; in all cases a broad band at higher frequency is superimposed after annealing on the rather narrow lines observed after deposition. Inversely, annealing causes a nearly complete disappearance of the bands at 1132 and 1050 cm^{-1}. Mixed isotope experiments allow us to differentiate the behavior of the two first groups of bands. On the one hand, for the first group observed before annealing at about 1270 cm^{-1} (^{12}C^{16}O), there appears a new line half-way between those belonging to pure species; for example, for ^{12}C^{16}O/^{13}C^{16}O mixtures, the main new line is measured at 1253 cm^{-1} (1266 for ^{12}C^{16}O and 1240 for ^{13}C^{16}O). On the other hand, for the second absorption measured at 1132 cm^{-1} for ^{12}C^{16}O, isotopic dilution does not lead to the appearance of new features. The ^{12}C^{16}O–^{13}C^{16}O isotope pattern is merely the superposition of the spectra obtained for pure ^{12}C^{16}O (1132 cm^{-1}) and ^{13}C^{16}O (1107 cm^{-1}). As for the last band at 1050 cm^{-1} for ^{12}C^{16}O, it is broad and accompanied by poorly reproducible shoulders so that decoupling effects cannot be ascertained.

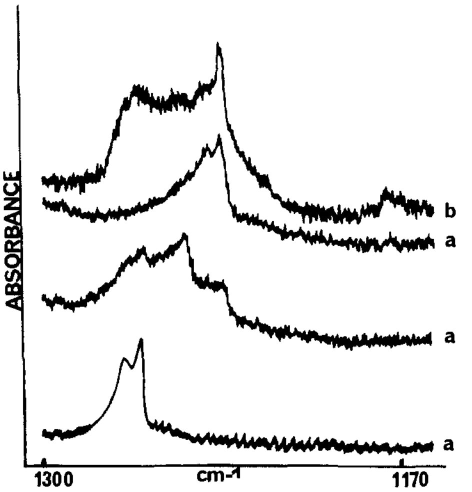

Figure 9. ^{12}CO/^{13}CO isotopic effect in the 1300–1200-cm^{-1} spectral range: (1) ^{12}CO/Li/Kr = 1/1/400, (2) ^{12}CO/^{13}CO/Li/Kr = 0.5/0.5/1/400, (3) ^{13}CO/Li/Kr = 1/1/500. Spectra recorded before (a) and after (b) annealing.

Table II. Reaction Product Absorptions below 1000 cm^{-1} for Li + CO in Krypton[a]

^{12}CO		^{13}CO		^{13}C^{18}O
^{6}Li	^{7}Li	^{6}Li	^{7}Li	^{7}Li
717 br	705 br	717 br	710	710 br
660	620	658	617.5	613.5 } 1:1
649.5	610	648	608.5	605.5 }
640	600		590	
558				560 br
510 br		507	500	475
477		473	470	466
453	450	451	449	447, 439
	428		426	423
414	412	414		411

[a] All these lines are weak and decrease in intensity upon annealing, except those in the 480–450-cm^{-1} region.

C. Absorptions below 1000 cm^{-1}. As in the case of Li/H_2O/Kr mixtures,[13] there exists (Table II) a large number of very weak bands between 900 and 400 cm^{-1} which are hardly correlated to high-frequency CO modes.

Figure 8 displays the spectra obtained for the three CO isotopic species at roughly the same molar ratio in either ^{7}Li or ^{6}Li. The main remarks about these spectra are the following. (i) some bands in the 950–800-cm^{-1} frequency range are not reproducible from one experiment to the other and are tentatively assigned to impurity traces (other than LiO_2 and Li_2O_2 which have also been identified);[14] (ii) the strongest line below 1000 cm^{-1} is measured around 700 cm^{-1} (it is weakly sensitive to ^{6}Li/^{7}Li substitution and decreases after annealing); (iii) a well-defined doublet is measured between 660 and 610 cm^{-1}, with large ^{6}Li/^{7}Li and weak CO isotopic shifts (this doublet is clearly correlated to the 1806-cm^{-1} band (^{12}C^{16}O), with a constant 1806/doublet 610 intensity ratio of the order of 5); (iv) a doublet around 500 cm^{-1} is seen to be sensitive to Li isotopic substitution while some other at lower frequency are not significantly shifted, whatever are the isotopic species.

Discussion

The data analysis will be divided into five parts, the first four treating separately the different products grouped according their CO stoichiometry, which takes successively the values 1, 2, 3, 4, or 6. This choice is suggested by the identification of clear-cut CO isotopic patterns typical of couplng between several identical

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(14) Andrews, L. *J. Chem. Phys.* **1969**, *50*, 4288; **1971**, *54*, 4935. Hatzenbühler, D. A.; Andrews, L. *Ibid.* **1972**, *56*, 3398.

Table III. Comparison between Observed and Calculated Frequencies of the LiCO 1:1 Complex Trapped in Krypton

		ν_{CO}[a]		$\nu_{\mathrm{CO...Li}}$[b]	
		obsd	calcd	obsd	calcd
	$^{6}\mathrm{Li}$			660–649.5	660.0–649.4
$^{12}\mathrm{C}^{16}\mathrm{O}$		1806–1801	1806.4–1801.8		
	$^{7}\mathrm{Li}$			620–610	620.0–610.0
	$^{6}\mathrm{Li}$			658–648	658.0–647.4
$^{13}\mathrm{C}^{16}\mathrm{O}$		1764.5–1760.5	1766.2–1761.6		
	$^{7}\mathrm{Li}$			617.5–608.5	617.9–607.9
	$^{6}\mathrm{Li}$				654.4–643.8
$^{13}\mathrm{C}^{18}\mathrm{O}$		1723.5–1719	1721.5–1717.1		
	$^{7}\mathrm{Li}$			613.5–605.5	614.0–604.1

[a] CO force constants for the two sites: F_{CO} = 13.199 and 13.131 mdyn Å^{-1}. [b] Li–CO stretching force constants for the two bands associated to the complex with CO stretching mode at 1806 and 1801 cm^{-1}. $F_{\mathrm{Li-CO}}$ = 1.270 and 1.229 mdyn Å^{-1}.

oscillators. However, this classification still leaves unassigned many weak lines, properties of which are discussed in a fifth part. The structural implications deduced from the spectra will be considered in this analysis; here again many questions remain unanswered, especially in the case of complexes with CO frequencies lower than 1400 cm^{-1}. For such large CO perturbations chemical reactions occur within the aggregates that cannot be simply deduced from spectral data. For example, the possibility of forming the acetylenediolate LiOCCOLi as in liquid ammonia[2] is difficult to take into account in the absence of IR data for this crystal which has been studied only by X-ray diffraction.

A. Complexes of the Type $\mathrm{Li}_m\mathrm{CO}$. Complexes involving only one CO molecule are characterized by the absence of new bands in isotopic mixtures, spectra of which are simply the superposition of those of each isotopic species, without decoupling effect. However, one must keep in mind that the possibility of two equivalent but uncoupled CO molecules in a highly symmetrical aggregate would give rise to the same pattern.

Four systems, measured in the case of $^{12}\mathrm{C}^{16}\mathrm{O}$ at 1806–1801, 1596, 1470, and 1132 cm^{-1}, behave in this way. The three first will be considered successively in this order.

The 1806–1801-cm^{-1} System. The fact that either the 1806- or the 1801 cm^{-1} band is preponderant at high dilution in both reactants, for Kr/Li and Kr/CO ratios as large as 5000 and 1500, respectively, favors their assignment to the 1:1 complex. The existence of two CO bands, 5 cm^{-1} apart, for this species means that this complex exists with only one structure occupying two different sites in the krypton matrix. On the other hand, the 1806-cm^{-1} band has been correlated to a weaker doublet in the spectral range 650–600 cm^{-1} characterized by a large $^{6}\mathrm{Li}/^{7}\mathrm{Li}$ and a small CO isotopic shifts. As a consequence this doublet is likely to be assigned to the intermolecular stretching mode; as to the third mode of this complex, which probably lies at lower frequency, we have not been able to assign it.

Since the three modes of the complex are likely to be uncoupled, force constants have been calculated separately for the two stretching modes ν(CO) and ν(Li–CO). The first one is deduced from two sets of three independent frequencies since the CO mode gives rise to a doublet for each of the three CO isotopic species; for the second mode two force constants have also been calculated since two bands are observed in the 600-cm^{-1} region for each isotopic species. However, it must be kept in mind that the complex responsible for the 1806-cm^{-1} band (for $^{12}\mathrm{C}^{16}\mathrm{O}$) gives rise to this doublet while the Li–CO band corresponding to the CO frequency at 1801 cm^{-1} has not been identified. Comparison between calculated and observed frequencies is made in Table III. The force constants of the intermolecular Li–CO stretching mode have been calculated in the hypothesis that the CO molecule moves as a point mass, i.e., that the G element for this mode is $(m_{\mathrm{Li}}^{-1} + m_{\mathrm{CO}}^{-1})$. The good agreement between observed and calculated frequencies justifies this assumption. This result is different from the one obtained by Andrews and Pimentel[15] for the LiON complex, for which the Li stretching mode situated at roughly the same frequency is more sensitive to the $^{16}\mathrm{O}/^{18}\mathrm{O}$ isotopic substitution than to the $^{14}\mathrm{N}/^{15}\mathrm{N}$ one [$\nu(^{7}\mathrm{Li{-}}^{14}\mathrm{N}^{16}\mathrm{O})/\nu(^{7}\mathrm{Li{-}}^{15}\mathrm{N}^{16}\mathrm{O}) = 1.000\,92$, $\nu(^{7}\mathrm{Li{-}}^{14}\mathrm{N}^{16}\mathrm{O})/\nu(^{7}\mathrm{Li{-}}^{14}\mathrm{N}^{18}\mathrm{O}) = 1.008\,68$ instead of 1.003 06 and 1.005 97 using the same approximation]. This observation allowed the authors to conclude a bent NO···Li structure in which the Li atom faces the oxygen. In our case, as one as can see in Tables II and III, if the mode also involves Li motion to a great extent, it is equally sensitive to $^{12}\mathrm{C}/^{13}\mathrm{C}$ and $^{16}\mathrm{O}/^{18}\mathrm{O}$ substitution [$\nu(^{7}\mathrm{Li}^{12}\mathrm{C}^{16}\mathrm{O})/\nu(^{7}\mathrm{Li}^{13}\mathrm{C}^{16}\mathrm{O}) = 1.0040$, ν-$(^{7}\mathrm{Li}^{13}\mathrm{C}^{16}\mathrm{O})/\nu^{7}\mathrm{Li}^{13}\mathrm{C}^{18}\mathrm{O}) = 1.0065$ compared to 1.0040 and 1.0063 using the same point mass approximation]. If the above-mentioned simple calculation justifies the assignment to a Li(CO) stretching mode, a more precise determination of the structure (Li···CO, Li···OC, or T-shaped) is honestly *impossible* without the knowledge of the third (bending) mode of this species. No prior knowledge of this frequency leaves the question mathematically undetermined, and different values of the LiOC bond angle would yield different possible force constants sets.[15] One can say at the most that a bent (LiON-like structure) appears more unlikely.

A last remark about this complex is the closeness of the carbonyl frequencies in LiCO and HCO (1806 and 1861 cm^{-1}, respectively), which may suggest comparable bonding in both cases, in spite of a large ionization potential difference between Li and H (5.4 and 13.6 eV, respectively). Ab initio calculations for the HCO and HOC radicals have shown[16] that the first one is more stable by about 23 kcal mol^{-1}. The HCO angle is 130° and the unpaired electron is located in a σ-type orbital with significant amount of hydrogen character. Thus the CO frequency for this radical shows that it is not necessary to invoke the existence of electron transfer within the Li–CO pair to justify the large red shift observed for the CO stretching mode. A full comprehension of both structural and vibrational properties of the 1:1 complex will be otained in part 2 of this work.

The 1596-cm^{-1} Band. The observation of this band only at high concentration in Li but with high dilution in CO suggests assignment to a $\mathrm{Li}_n\mathrm{CO}$ (or n:1) complex; furthermore, since it is the first band (after the 1806-cm^{-1} line) assignable to a n:1 complex to appear when the Li/Kr molar ratio increases, with concomitant growth of the absorption band of Li_2 at 495 nm (indicating a second-order stoichiometry in Li), it is therefore likely to be assigned to a 2:1 species. If structure prediction could only be speculative, one is, however, struck by the fact that the ν(CO) frequency shift vs. ν(LiCO), although large, is smaller than for corresponding quantities for other diatomics for which ionic models have been suggested.

	ν_{XY} (cm^{-1}) ($-100\Delta\nu/\nu$)		
XY =	O_2 (ref 14)	NO (ref 15)	CO
XY	1552	1886	2135
Li(XY)	1096 (29%)	1352 (28%)	1806 (15%)
Li_2(XY)	842 (46%)	881 (53%)	1596 (25%)

This might be indicative of slight differences in the nature of the bonding and this problem will be discussed in part 2.

The 1470-cm^{-1} Band. The appearance of this band after the 1596-cm^{-1} line, with increasing Li molar fraction, suggests its assignment to a 3:1 species. The frequency is very close to that measured for the CO molecules adsorbed on a transition metal catalyst covered with a submonolayer of potassium atoms (1460 cm^{-1}, see ref 7). In this case a side-on bonding of the CO molecule on the surface has been proposed, with the molecular axis parallel to or inclined toward the metal surface. Any structural determination is, of course, impossible in light of only one CO stretching mode, but it is interesting that CO perturbation equivalent to that of chemisorbed CO is already reproduced in aggregates containing only three (or possibly four) metal atoms.

B. Complexes of the Type $\mathrm{Li}_m(\mathrm{CO})_2$. Dicarbonyl complexes with two identical CO groups are expected to give rise to a triplet

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(15) Andrews, L.; Pimentel, G. C. *J. Chem. Phys.* **1966**, *44*, 2361. Tevault, D. E.; Andrews, L. *J. Phys. Chem.* **1973**, *77*, 1640.

(16) Bruna, P. J.; Buenker, R. J.; Peyerimhoff, S. D. *J. Mol. Struct.* **1976**, *32*, 217.

Table IV. Comparison between Experimental and Calculated Frequencies of the Li(CO)$_2$ Complex Trapped in Sites I and II of a Krypton Matrix

	site I[a]		site II[b]	
	calcd	obsd	calcd	obsd
$(^{12}C^{16}O)_2$	1990.9	1991	1998.1	1997.5
	1714.2	1712.5	1723.8	1721.5
$(^{13}C^{16}O)_2$	1946.6	1947.5	1953.6	1953.5
	1676.0	1677	1685.4	1686
$(^{13}C^{18}O)_2$	1897.3	1902	1904.2	1906
	1633.6	1634	1642.8	1643
$^{12}C^{16}O$, $^{13}C^{16}O$	1970.3	1970.5	1977.4	1976.5
	1693.5	1693.5	1703.1	1704.5
$^{12}C^{16}O$, $^{13}C^{18}O$	1951.0	1953	1958.1	1958.5
	1667.0	1667	1676.3	1676
$^{13}C^{16}O$, $^{13}C^{18}O$	1923.9		1930.9	1930.5
	1652.8	1654	1662.1	1663

[a] Site I: $F_{CO} = 13.941$, $f_{CO-CO} = 2.071$ mdyn Å^{-1}. [b] Site II: $F_{CO} = 14.066$, $f_{CO-CO} = 2.062$ mdyn Å^{-1}.

pattern for isotopically mixed CO samples.[15] Two systems display such a typical effect, which are located, for $^{12}C^{16}O$, at 1712–1991 and 1613 cm^{-1}.

The 1712–1991-cm^{-1} System. As previously discussed, the observation of these bands at high dilution in lithium and the typical isotopic pattern make the assignment of these bands to the Li(CO)$_2$ species unambiguous. Each of these bands is, in fact, split into two components with the same behavior in isotopic dilution experiments. The intensity ratio of the two lines of each doublet varies according to the experiments in a way which parallels that of the 1806/1801 bands assigned to the 1:1 species. For this reason the splitting is believed to arise from a site effect. In the following, the site responsible for the bands at 1712–1991 cm^{-1} will be referred to as site I and the other responsible for the bands at 1721–1996 cm^{-1} as site II. The observation for each site of one strong and one weak band suggests the equivalence of the two CO submolecules whose internuclear axes are nearly colinear. Such structures (with, in some cases, the same site effect) have already been observed for other M(CO)$_2$ complexes with M = Pt,[17] Pd,[18] Cu,[19] Ag[20] and Au.[21] Calculations have been performed in this hypothesis. The strong 1712–1721-cm^{-1} doublet is assigned to the out-of-phase CO stretching mode, the one at 1991–1996 cm^{-1} to the in-phase mode. Table IV compares the observed and calculated values for all observed CO modes; the agreement is excellent and provides convincing evidence for the correctness of the mononuclear C_{2v} Li(CO)$_2$ structural assignment. Furthermore, in the hypothesis of the additivity of bond dipole moments, the angle θ between the two oscillators can be deduced from the observed intensity ratio between the in-phase and out-of-phase modes I_s/I_a by the relationship:

$$I_s/I_a = (1 + \cos\theta)/(1 - \cos\theta)$$

Applied to sites I and II this model leads to θ values of 152 and 124°, respectively.

The 1613-cm^{-1} Band. Since this band is observed at high concentration in both dopants and displays the basic pattern of a dicarbonyl in isotopic decoupling experiments, it is tentatively assigned to the 2:2 species. Frequency calculations yield the set of frequencies shown in Table V. The agreement between the calculated and observed modes is good and supports the assignment of the bands to a Li$_n$(CO)$_2$ aggregate in which the two CO groups are equivalent. The in-phase high-frequency CO stretching modes (expected at about 1700 cm^{-1} for $^{12}C^{16}O$) have not been observed even for isotopically mixed species because of their low absorbance, leading to the conclusion that the angle between the two internuclear CO axes is not far from 180°. Let us remark, however, that a value of about 150° as calculated for the 1:2 species in site I, would lead to an absorbance for the in-phase mode too weak to be detected with the present signal-to-noise ratio.

Table V. Comparison between Calculated and Observed CO Stretching Frequencies for the Li$_2$(CO)$_2$ Species Trapped in a Krypton Matrix[a]

	calcd	obsd
$(^{12}C^{16}O)_2$	1703.6	
	1614.1	1613
$(^{13}C^{16}O)_2$	1665.6	
	1578.1	1577.5
$(^{13}C^{18}O)_2$	1623.5	
	1538.2	1540
$(^{12}C^{16}O, ^{13}C^{16}O)$	1688.3	
	1592.4	1591.5
$(^{12}C^{16}O, ^{13}C^{18}O)$	1678.4	
	1561.3	1561.5
$(^{13}C^{16}O, ^{13}C^{18}O)$	1649.2	
	1553.5	1554

[a] $F_{CO} = 11.124$, $f_{CO-CO} = 0.600$ mdyn Å^{-1}.

Table VI. Comparison between Experimental and Calculated Frequencies of the Li(CO)$_3$ Complex Trapped in Krypton[a]

	calcd	obsd	assignment
$(^{12}C^{16}O)_3$	2066.1	2065.5	ν_s
	1889.6	1888	ν_d
$(^{13}C^{16}O)_3$	2020.3	2019.5	ν_s
	1847.4	1847.5	ν_d
$(^{13}C^{18}O)_3$	1967.9	1971	ν_s
	1799.5	1801	ν_d
$(^{12}C^{16}O)_n(^{13}C^{16}O)_{3-n}$	1859.2	1858.5	$n = 2$ ν_a
	2053.3	2052.5	$n = 1$ ν_s
	1872.9	1871	$n = 1$ ν_a
$(^{12}C^{16}O)_n(^{13}C^{18}O)_{3-n}$	1820.3	1821	$n = 2$ ν_a
	1827.9		$n = 1$ ν_a
$(^{13}C^{16}O)_n(^{13}C^{18}O)_{3-n}$	1812.6	1814	$n = 2$ ν_a
	1827.9	1828	$n = 1$ ν_a

[a] $F = 15.365$, $f = 0.942$ mdyn Å^{-1}.

C. Complexes of the Type Li(CO)$_3$. Quartet patterns typical of a highly symmetrical tricarbonyl species[12] are observed in isotopic dilution experiments in the 1900–1800-cm^{-1} spectral range. Such quartets were identified, for instance, for Ag(CO)$_3$ trapped in argon.[19] With $^{12}C^{16}O$ the (CO)$_3$ stretching degenerate mode is measured at 1888 cm^{-1}, while the symmetrical one is observed at 2065 cm^{-1}, with a low intensity with respect to the first one. A force-field calculation supports (Table VI) the assignment of these bands to a n:3 aggregate. The value $n = 1$ is the most probable since this species is observed even at low concentration in lithium. The appearance of the in-phase mode suggests a nonplanar C_{3v} symmetry. Using the results of the force-field calculations, the angle θ between the CO axis is determined from the relationship:

$$I_s/I_d = (1 + 2\cos\theta)L_{1s}^2/(1 - \cos\theta)L_{1d}^2$$

where L_{1s} and L_{1d} are the amplitude of the CO stretching motion for the symmetrical and degenerate modes, respectively. From the experimental value $I_s/I_d = 0.07$, one gets $\theta = 113.7°$. Let us recall that a value of 120° corresponds to the D_{3h} (planar) symmetry.

D. Complexes of the Type Li(CO)$_n$, $n > 3$. The spectral features observed in the 1960–1920-cm^{-1} domain for natural CO

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[17] Kündig, E.; McIntosh, D.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7234.

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[20] McIntosh, D.; Ozin, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 3167.

[21] McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 51.

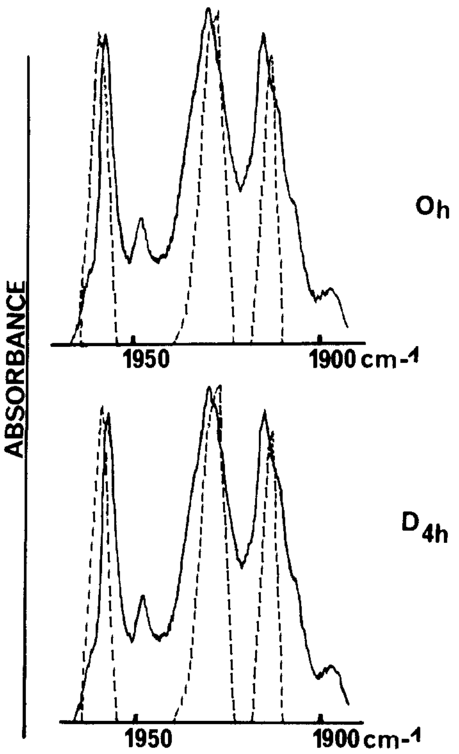

Figure 10. Comparison between experimental (full line) and calculated (dotted line) spectra in the 1950–1910-cm^{-1} spectral range for two kinds of aggregate: $Li(CO)_4$, D_{4h} symmetry, and $Li(CO)_6$, O_h symmetry. Values of the force constants (mdyn Å^{-1}) for D_{4h} are $F = 16.157$, $f_{cis} = 0.332$, $f_{trans} = 0.664$; for O_h, $F = 16.048$, $f_{cis} = 0.222$, $f_{trans} = 0.554$. Band profiles have been calculated for triangular band shapes with full width at half-maximum equal to 5 cm^{-1}.

have been analyzed in the hypothesis that the species responsible for these bands is of the type $Li(CO)_n$ with n larger than 3. These species can be considered as the ultimate step of aggregation of CO molecules around a single lithium atom since the corresponding bands grow in intensity at the expense of all the others for low Kr/CO molar ratios, even at low Li concentration. Furthermore, the strongest bands in the spectra of Li/CO binary mixtures are also observed between 1970 and 1900 cm^{-1}.[22] Determination of the CO stoichiometry has been discussed on the basis of the isotopic patterns characterized by a poorly resolved broad band closer to that arising from the pure heavy CO isotope than that due to the pure light one. Calculations have been performed for tetra- and hexacarbonyl monolithium complexes, in the hypothesis that the band multiplicity arises from site effects. Accordingly the species are characterized by only one band at 1957.5, 1915.5, and 1866 for $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{13}C^{18}O$, respectively.

$Li(CO)_n$, n = 4 or 6? It appeared rapidly that the T_d symmetry was not able to account for isotopic patterns. Indeed, the mixed isotope bands are spread over a large frequency range, and the synthetic spectrum drawn with bandwidths of 4 cm^{-1} (as observed for the bands of isotopically pure species) is much better resolved than the observed one. Other structures with lower symmetry (C_{3v}, C_{2v}) were also considered; none of them allowed a correct fit to the experimental spectra, the decoupling pattern being in all cases spread over the whole spectral domain between the two main bands characterizing each of the isotopically pure species. The best results for lithium tetracarbonyl have been obtained in the hypothesis of a D_{4h} (planar) structure. As shown in Figure 10, the fit between observed and calculated spectra for a $^{12}CO/^{13}CO = 1/1$ isotopic mixture is good, as far as band frequencies and relative intensities are concerned. The central absorption, which is the sum of four bands due to mixed $Li(^{12}CO)_x(^{13}CO)_{4-x}$ species ($1 < x < 3$), has been calculated using bandwidths of 5 cm^{-1} for each component (as observed for the band at 1957.5 cm^{-1} of natural CO). Its position and overall profile are quite correct, but its bandwidth is much narrower than observed (8 cm^{-1} instead of 14 cm^{-1}).

It has also been possible to account for the spectral data in the hypothesis of an octahedral (O_h symmetry) structure for the complex. The calculated spectrum shown in Figure 10 approximately fits the experimental one; the absorption due to decoupling effects has its maximum at about 1928 cm^{-1} and is found to be very unsymmetrical and, as is the case of the $Li(CO)_4$ (D_{4h}) species, narrower than observed. The choice between the assignment of this species to $Li(CO)_4$ or $Li(CO)_6$ remains uncertain in the state of our experimental data.

E. Comments on the Vibrational Properties of the Nonidentified Species. Among the large number of bands which have not been assigned previously, there are some whose behavior deserves special comments because of either their unexpected shifts in mixed isotope experiments or their frequency domains. We shall consider successively the band at 1532 cm^{-1} and those between 1300 and 1000 cm^{-1}, which have to be assigned to CO stretching modes because of their ^{13}C and ^{18}O isotope shifts.

Band at 1532-cm^{-1}. This band appears at relatively low concentration in both dopants, and has the same behavior as the stronger absorption at 1712 cm^{-1}, already assigned to a $Li(CO)_2$ species, with the difference that it slightly grows upon UV–vis irradiation at the expense of the 1712-cm^{-1} one. Furthermore, the quartet pattern with the new components at 1529.5 and 1502 cm^{-1} intermediate inbetween the positions of the pure ^{12}CO and ^{13}CO species at 1532.5 and 1499 cm^{-1} for ^{12}CO + ^{13}CO mixtures makes clear that this species contains two nonequivalent carbon atoms. A similar experiment performed with $^{13}C^{16}O$ + $^{13}C^{18}O$ yields a comparable quartet from which one can deduce that this species also contains two nonequivalent O atoms. From the magnitude and sign of the $^{13}C/^{12}C$ and $^{16}O/^{18}O$ shifts one could tentatively propose that this absorption is due to a C=O stretching coupled to one C—C and one C—O oscillator linked to the same carbonyl carbon. In that case the position of the two new absorptions appearing with ^{12}CO + ^{13}CO or $^{13}C^{16}O$ + $^{13}C^{18}O$ mixtures could be explained: one, red shifted vs. pure $^{12}C^{16}O$ (or $^{13}C^{16}O$) position, corresponding to ^{13}C (or ^{18}O) substitution in the β position with a ^{12}C (or a ^{16}O) in the carbonyl group, the other (blue shifted) being due to the other isomer with a ^{12}C (or ^{16}O) in β whereas the carbonyl carbon (or the oxygen) is substituted.

We wish to emphasize, however, that because of the absence of observation of other correlated absorption, it is very delicate to draw a more definite conclusion about this species in which extensive chemical modification of one of the carbonyl groups has obviously taken place.

Bands between 1300 and 1000 cm^{-1}. A set of three bands appear in the 1300–1000 cm^{-1} region (at 1270, 1132, and 1050 cm^{-1} for natural CO) in the same experimental conditions, namely, at high molar fraction in both dopants. Their sensitivity to CO isotopic substitution but not to the $^6Li/^7Li$ one suggests their assignment to CO stretching modes. Their very low frequencies indicate either a strong coupling between several CO/CC oscillators or a strong weakening of the CO force constant, whose value is typical of a single CO bond. The chemical species identified by Büchner[2,3] could be at the origin of such bands. The one with a ketene structure, $Li^{+-}OCLi{=}C{=}O$, is expected to give rise to a strong band around 2100 cm^{-1} ($\nu_a(C{=}C{=}O)$) and weaker ones in the range 1300–1000 cm^{-1} ($\nu_s(C{=}C{=}O)$ and $\nu(CO^-)$). The first one overlaps the strong band due to uncomplexed CO; the others possibly correspond to the weak absorptions at 1132 and 1050 cm^{-1}.

As for the acetylenediolate species $(OC{\equiv}CO)^{2-}$, it is characterized in the infrared by an out-of-phase CO stretching mode which, taking into account the CO distance of 1.28 Å obtained by X-ray diffraction,[2] could be located at about 1300 cm^{-1}. Frequency calculations have been performed in this hypothesis. The comparison between experimental and calculated frequencies of the infrared-active stretching mode shown in Table VII leads to the conclusion that such an interpretation is realistic, though

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[22] Loutellier, A., to be submitted for publication.

Table VII. Comparison between Experimental and Calculated Frequencies of the Infrared Active Stretching Mode of the $[O{-}C{\equiv}C{-}O]^{2-}$ Dianion Trapped in Krypton

	calcd	obsd
$^{16}O^{12}C^{12}C^{16}O$	1268.5	1267.5
$^{16}O^{13}C^{13}C^{16}O$	1240.2	1240.5
$^{18}O^{13}C^{13}C^{18}O$	1208.0	1208
$^{16}O^{12}C^{13}C^{16}O$	1253.6	1253
$^{16}O^{12}C^{13}C^{18}O$	1237.9	1236
$^{16}O^{13}C^{13}C^{18}O$	1224.8	

not fully convincing in the absence of the observation of the IR-active bending mode or the two other Raman-active stretching modes.

Conclusion

One can gather in three groups the aggregates which have been identified more or less confidently in this study. The first group is constituted by species of the type Li(CO)$_n$, with n = 1, 2, 3 and 4, or 6. This last stoichiometry, which corresponds to the most stable monolithiocarbonyl, remains undefined since both hypotheses fit the spectral data reasonably well. The existence of a planar tetracarbonyl is surprising since such a structure is rather uncommon and unexpected for an alkali metal atom. The presence of a lithium hexacarbonyl is also surprising since intermediate tetra- and pentacarbonyl are missing. As a matter of fact, the band multiplicity observed in the 1950–1920-cm^{-1} range for natural CO (intermediate between the features due to hexa- and tricarbonyls) could arise from such species, but the bands are too weak to be analyzed on isotopic grounds. The structural properties of the identified monolithium carbonyls are closely related to the carbonyls of transition metal described, in particular, by Ozin. But the vibrational perturbations of the CO molecules are much stronger with Li, as evidenced in Figure 11 in which the CO force constants and their evolution with n are reported for Li, Ag,[20] and Ni.[23] One should note the monotonic trend for Li and Ni and the amonotonic one for Ag, although force constants are closer between Li and Ag than between Li and Ni. So it is difficult to draw a parallel between the interaction mechanism from an alkali to a transition metal atom.

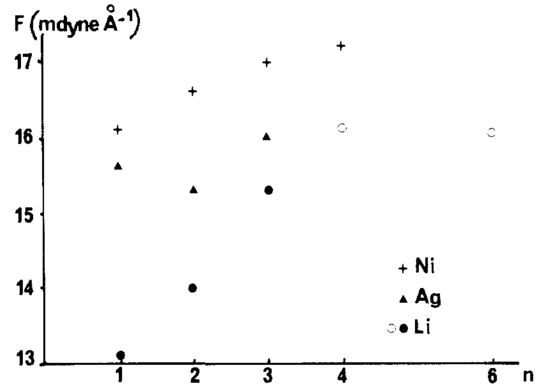

Figure 11. Evolution of the stretching force constant F of CO engaged in monometal complexes M(CO)$_n$ as a function of M and n. For M = Li (present study) there is no determination of the value of n for the complex of highest stoichiometry (see text).

The second group corresponds to species involving two or three Li atoms and one or two CO molecules, in which the CO molecules are believed to retain their own individuality. The CO vibrational perturbations are larger than those observed for monolithium carbonyls, corresponding to CO force constants as low as 10 mdyn Å^{-1}. Such values are expected in the case of multiple bridging, as discussed, for instance, by Herrmann et al.[24] in metal carbonyl complexes where two or three transition metal atoms interact with one CO molecule. For instance, one can imagine a double attack of the CO molecule (i.e., of the type LiCOLi) and possibly a bridge between the π system of the carbonyl and a further metal atom. This situation is comparable to that encountered in the experiments of coadsorption of CO and K on Ru described by Hoffmann et al.,[7] where the CO frequency measured at 1465 cm^{-1} is explained by a side-on bonding, the molecular axis being parallel to or inclined toward the metal surface.

The third group is constituted by species in which true chemical bonds between carbonyls have been formed. A typical example is the acetylenediolate, which has been identified in the solid phase but whose IR spectrum is unfortunately unknown. These species are believed to be characterized by several bands in the 1300–1000-cm^{-1} spectral range, corresponding to stretching modes of either CO single bonds or strongly coupled double bond, as in the case of ketene.

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(23) Kündig, E.; Moskovits, M.; Ozin, G. A. *J. Mol. Struct.* **1972**, *14*, 137.

(24) Herrmann, W. A.; Biersack, H. Ziegler, M. L.; Weidenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.