Interaction of Carbon Monoxide with Alkali, Alkaline-earth, Transition, and Lanthanoid Metal Fluorides in an Argon Matrix

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The vibrational frequency of carbon monoxide has been measured for carbon monoxide when it interacts with uni-, bi-, and tri-valent metal fluorides in argon matrices. It is found to shift to higher values relative to free carbon monoxide in all cases. The shifts vary with the reciprocal of the metallic ionic radius within an isovalent group. Use of the positive shift as a relative measure of ionic character within an isovalent group is suggested.

It has been suggested that the shift to a higher stretching frequency observed when carbon monoxide is paired with metal halides [1,2] or adsorbed on ionic solid surfaces [3] is proportional to the electric field imposed on the carbon monoxide by the positive metal ion. Co-ordination is assumed to occur through the carbon. It has also been pointed out that the vibrational mode of carbon monoxide is essentially independent of the modes of the metal halide and thus reflects changes which occur only in the carbon monoxide itself.[1,2]

Previous studies [1,2] have investigated the effect on the CO stretch of changes in metal ionic radii for metal dihalides. Most of the first-row transition-metal dihalides showed anomalous shifts which were attributed to bonding effects of unfilled *d* orbitals, whereas calcium, manganese, and zinc difluorides were thought to demonstrate a proportional relation to the positive-ion electric field. We have chosen to study a broad selection of uni-, bi-, and tri-valent metal fluorides in order to evaluate the effect of charge as well as ionic radius.

EXPERIMENTAL

Commercial metal fluoride samples were vaporized from graphite cells into an argon–carbon monoxide matrix. Ratios of argon to carbon monoxide were varied from 100 to 300 : 1. Condensation was carried out for 1 h. It was found necessary to use metal fluoride concentrations yielding off-scale absorption in the metal fluoride mode in order to create observable bands in the carbon monoxide region. Approximate vaporization temperatures used for the metal fluorides are 1 100—1 200 °C for the alkaline-earth metals, 790 and 835 °C for LiF and NaF, respectively, 1 220—1 300 °C for the lanthanoids, and 1 100 and 1 160 °C for ScF_3 and YF_3, respectively. Condensation occurred on a polished copper surface which was cooled to 10 K by a commercial closed-cycle refrigerator. Infrared spectra were obtained by reflection off the metal surface after condensation and were equivalent to the traditional transmission spectra.

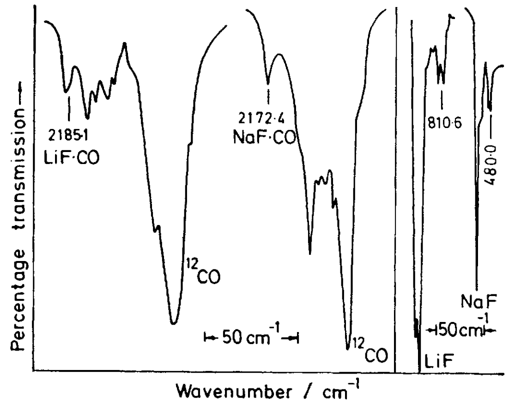

FIGURE 1 Infrared spectra of LiF and NaF co-condensed with a CO–Ar (1 : 00) mixture

RESULTS

Figure 1 shows spectra for LiF and NaF. For LiF the band at 2 185.1 cm^{-1} varies in intensity in proportion to the band of monomeric LiF at 840 cm^{-1} and is assigned to the LiF·CO pair. Bands at lower wavenumbers are assigned to interaction of CO with Li_2F_2. For NaF the band at 2 172.4 cm^{-1} is assigned to NaF·CO and the lower bands to Na_2F_2·CO. Assignments are based on intensity variations with respect to known bands of NaF monomer and dimer. Shifts to lower frequency for the metal-fluoride mode were observed and are given in Table 1.

TABLE 1

Measured wavenumbers (cm^{-1}) of metal fluoride–carbon monoxide complexes

	MX_n	MX_n·CO		MX_n·*m*CO
LiF	841.9	814.6	2 185.1	2 176.7, 2 173, 2 168
	836.9	810.6		
NaF	494.6	483.1	2 172.4	2 155.0
	489.4	480.0		
MgF_2	842.3	819.0	2 205.0	
CaF_2	558.4	553.8	2 187.3	548.2, 542.8
			2 180.4	
SrF_2			2 181.2	
			2 173.8	
			2 166.4	
BaF_2	418.7	415.0	2 172.8	
			2 163.5	
			2 159.6	
ScF_3	692.0	684.5	2 212.4	2 204
		682.2	2 208.3	
YF_3	560.9	554.7	2 197.5	2 184.3
LaF_3	478.8	476.6	2 185.2	2 119.0
		474.1		
		472.5		
NdF_3	503.2	497.0	2 187.4	2 183
GdF_3	518.9	513.8	2 194.4	2 190
		511.4		
HoF_3	535.4	527.8	2 198.2	2 194.0
		530.3		
LuF_3	551.6	547.5	2 204.8	2 194.6, 2 102.6
		543.7		

Figure 2 presents spectra of the alkaline-earth metal difluorides. All the observed bands appear to vary together and with the known monomeric metal-fluoride stretching modes. Our band at 2 187.3 cm^{-1} for CaF_2·CO appears as an unresolved shoulder in the spectra of ref. 1. If the three bands are due to differing orientations of carbon monoxide with respect to the bent metal difluoride there appear to be three distinct orientations with formation of the site of lowest shift being increasingly favoured for the heavier alkaline earths. The highest observed frequency is used in frequency-shift correlations developed here. New bands appear for the ν_3 mode of CaF_2 which vary in intensity so as to suggest stepwise addition of carbon monoxide. All observed bands are given in Table 1.

Figures 3 and 4 present spectra for ScF_3, YF_3, LaF_3, NdF_3, GdF_3, HoF_3, and LuF_3. In all cases the highest observed sharp band can be assigned to the MF_3·CO pair from studies of concentration *versus* band intensity. A broad band at lower frequency is thought to be due to interaction with dimeric MF_3 species. In some cases bands lower than that assigned to CO are observed but no assignment was made. For ScF_3 the two highest-frequency bands can be assigned to ScF_3·CO. The highest observed frequency is used in frequency-shift correlations. New bands are observed at lower frequencies for the metal-fluoride doubly degenerate ν_3 mode. In most cases two bands are observed, which could be assigned to a splitting of the ν_3 mode or to matrix site splitting. We favour the latter since one would expect a splitting of the degenerate mode in all cases, whereas YF_3 and NdF_3 give only a single band.

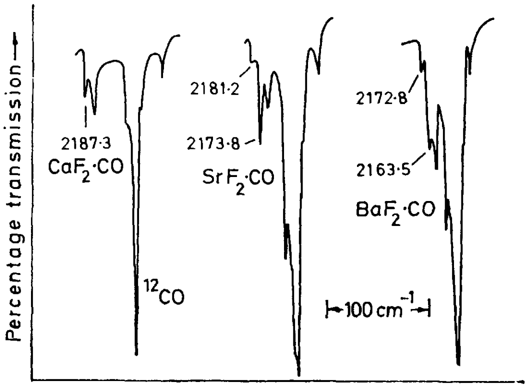

FIGURE 2 Infrared spectra of CaF_2, SrF_2, and BaF_2 co-condensed with a CO–Ar (1 : 100) mixture

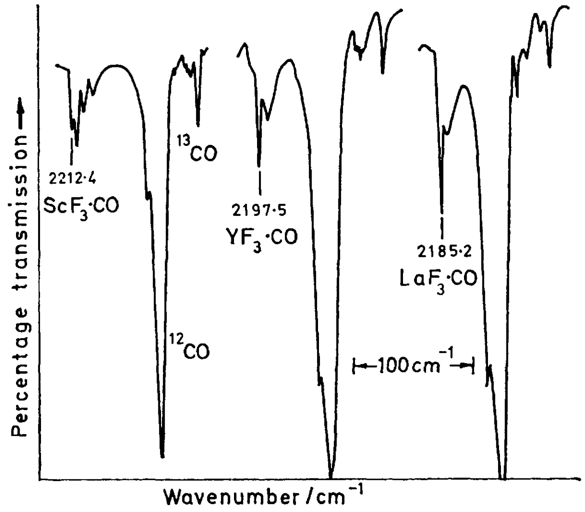

FIGURE 3 Infrared spectra of ScF_3, YF_3, and LaF_3 co-condensed with a CO–Ar (1 : 100) mixture

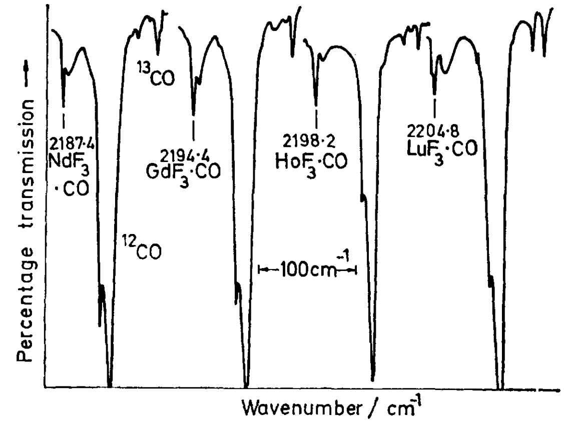

FIGURE 4 Infrared spectra of NdF_3, GdF_3, HoF_3, and LuF_3 co-condensed with a CO : Ar (1 : 100) mixture

TABLE 2

Wavenumbers shift (cm^{-1})

MF_n	$\Delta\nu$(CO)	$\Delta\nu$(MF)	$r(M^{n+})^a$/ Å	Force constant/ mdyn Å^{-1}	Relative ionic bond character (%)	Ref.
H	21.0			9.65	44	1
Li	47.1	27.3	0.68	2.50	100	*b*
Na	34.4	11.5	0.97	1.76	100	*b*
Mg	67.0	23.3	0.66	3.56	85	6, *c*
Ca	49.3	4.6	0.99	2.43	100	1, *b*, *d*
Sr	43.2		1.09	2.15	100	6, *d*
Ba	34.8	3.7	1.21	1.80	100	6, *d*
Cr	50.4	16.6	0.89	3.38	89	1, *e*
Mn	45.2	23.5	0.80	3.87	70	1, *e*
Ni	62.4	65.7	0.69	4.77	83	1, *e*
Cu	72.4	39.3	0.72	4.53	100	1, *e*
Zn	47.9	34.4	0.70	4.68	64	1, *e*
Pb	38.4	10.9	1.03	3.00	83	2, *f*
Sc	74.4	7.5, 9.8	0.732	3.86	89	*g*
Y	59.5	6.2	0.893	3.30	97	*g*
La	47.2	4.7, 6.3	1.016	2.69	100	*g*
Nd	49.4	6.2	0.995	2.93	100	*g*
Gd	56.4	5.1, 7.5	0.938	3.13	100	*g*
Ho	60.2	5.1, 7.6	0.894	3.32	100	*g*
Lu	66.8	4.1, 7.9	0.85	3.51	100	*g*
U	46.2	18	0.97			*h*

[a] Ref. 4. [b] S. E. Veazey and W. Gordy, *Phys. Rev.*, 1965, **A138**, 1303. [c] R. H. Hauge, A. S. Kanaan, and J. L. Margrave, *J.C.S. Faraday II*, 1975, 1082. Frequency shift taken from unpublished data of this laboratory. [d] V. Calder, D. E. Mann, K. S. Seshadri, M. Allavena, and D. White, *J. Chem. Phys.*, 1969, **51**, 2093. [e] J. W. Hastie, R. Hauge, and J. L. Margrave, *Chem. Comm.*, 1969, 1452. [f] R. H. Hauge, J. W. Hastie, and J. L. Margrave, *J. Mol. Spectroscopy*, 1973, **45**, 420. [g] R. D. Wesley and C. W. DeKock, *J. Chem. Phys.*, 1971, **55**, 3966; R. H. Hauge, J. W. Hastie, and J. L. Margrave, *J. Less-Common Metals*, 1971, **23**, 359. [h] K. R. Kunze, R. H. Hauge, D. Hamill, and J. L. Margrave, *J. Phys. Chem.*, 1977, **81**, 1664.

DISCUSSION

Table 2 gives the measured frequency shifts for the MF_n·CO pair. Only the highest frequency shift is listed for the alkaline-earth metal difluorides. In Figure 5 the frequency shifts are plotted against the parameter $q/(r_m + r_{CO})^2$ where r_m is the metal crystal ionic radius,[4] r_{CO} is taken as 2.00 Å, and q is the formal positive charge on the metal. As indicated by previous workers,[1,2] a relation does appear to exist between the frequency shift of carbon monoxide and the metal ionic radius. Measured shifts for a particular valence appear to vary as a function of the reciprocal of the square of the metal ionic radius. However, equally good correlations exist for higher orders of the reciprocals of the ionic radius. Thus the importance of any particular type of electrostatic interaction is not suggested. It is also clear that frequency shifts do not vary with formal charge as expected. For example, sodium, calcium, and neodymium have approximately the same ionic radius for the uni-, bi-, and tri-valent states, respectively. Thus, one might expect a simple one to two to three relationship between frequency shifts, but this is clearly not the case. It is possible that a model which considers the presence of fluoride ions and the molecular geometry of the molecular pair might account for these differences.

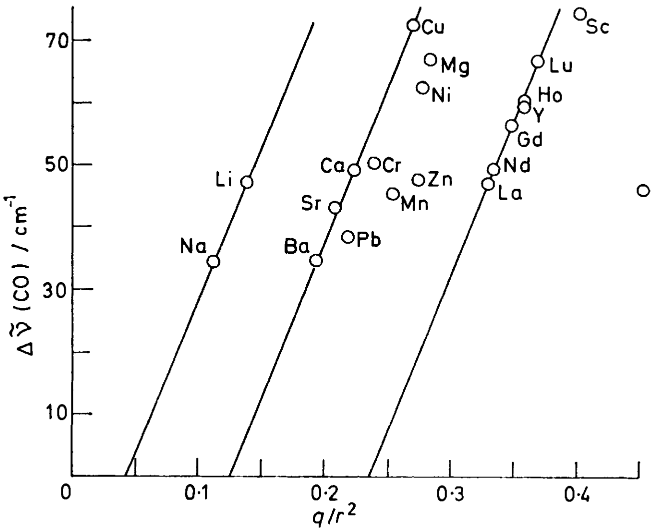

FIGURE 5 Plot of the CO frequency shift against q/r^2 where q is the formal metal charge and r is the metal ionic radius

It is instructive to attempt to calculate the frequency-shift contributions for various interactions in the $MgF_2 \cdot CO$ pair. Magnesium difluoride is assumed to be a linear array of point charges separated by 1.77 Å with a positive centre charge of 2+. The carbon monoxide interacts with its internuclear axis perpendicular to the MgF_2 axis and intersecting at the magnesium position. The distance between Mg and the point dipole and quadrupole of CO is taken as the sum of the ionic radius of Mg^{2+} (0.66 Å) and a value which is meant to represent the distance from the outer edge of the carbon atom to the centre of mass of CO. Values of 2.00 and 2.50 Å have been taken as lower and upper limits.

Frequency shifts can be caused by a change in bond strength, *i.e.* a change in force constant due to bonding changes within CO, and also by electrostatic interactions involving the vibrational dependence of the dipole ($\Delta\mu_{0-1}$), quadrupole (ΔQ_{0-1}), *etc.*, and polarizability of CO between the $v = 0$ and $v = 1$ vibrational states.[5] Available values are $\Delta\mu_{0-1}$ (expt. 1.6×10^{-2},[6] calc. 1.54×10^{-2}) and ΔQ_{zz} (calc. 1.2×10^{-2})[7] where Δr_{0-1} is 5.17×10^{-3} Å. The dipole moment is given in debyes and the quadrupole moment in Buckinghams.*

Carbon monoxide is unusual in that the absolute values of the dipole and quadrupole moments initially decrease with increasing internuclear distance thereby creating a positive shift in the observed CO frequency. A bonding change within CO might also be expected to contribute to a positive shift as ionization of CO to CO^+ gives a positive shift of 40.6 cm^{-1}. A point-charge model for $MgF_2 \cdot CO$ predicts electrostatic shifts as follows: a $\Delta\tilde{\nu}$ (charge dipole) of 47 and 26 cm^{-1} and $\Delta\tilde{\nu}$ (charge quadrupole) of 16 and 8 cm^{-1} for r_{CO} of 2.00 and 2.50 Å respectively. The total calculated shift of 63 and 34 cm^{-1} for r_{CO} of 2.0 and 2.5 Å, respectively, indicates that electrostatic interactions are important. The relative importance of a bonding change within CO and vibrational dependence of polarizability are difficult to estimate without detailed quantum-mechanical calculations for carbon monoxide in various non-linear electric fields.

It is interesting to note from Figure 5 that the bivalent elements with maximum ionic bonding exhibit a CO frequency shift behaviour which is very similar to those of the uni- and tri-valent metals. Bonding in CuF_2 has been shown to be highly ionic[8] as would be expected for the heavier alkaline-earth metal fluorides. The lower shifts of the other metal difluorides might be explained by a less ionic contribution to the bonding and a lowered electric field experienced by CO. A largely covalently bonded molecule exhibits much shorter-range intermolecular forces and results in a much smaller perturbation of the CO stretching frequency. It is possible that the ratio of measured to expected CO shift obtained by extrapolation from Figure 5 provides a relative measure of the percentage ionic bond character within an isovalent group. Such calculated values are given in Table 2.

In summary, it appears that positive CO shifts could serve as a qualitative probe of molecular ionic character for molecules with similar geometry, and perhaps will serve as a quantitative measure once the behaviour of CO in high non-linear fields is well documented.

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* Throughout this paper: 1 D ≈ 3.33×10^{-30} C m; 1 dyn = 10^{-5} N.

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