

IR Studies of Coordinatively Unsaturated Surface Compounds on Silica Gel. III. Adsorption of CO on Main Group Metal Ions

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The stretching vibration of CO adsorbed on the title compounds, containing metal ions of groups I, II and III together with Sn and Pb, has been measured. The frequency of this vibration spans the range from 2157 cm^{-1} (Cs^+) to 2232.5 cm^{-1} (Al^{3+}). An empirical relationship between this frequency and the formal charge and ion radius as variables for the characterization of the metal ions is formulated. The maximal deviation from this equation is 6.4 cm^{-1} (Tl^+) or less than 9% of the frequency range. A splitting into two bands was observed only for Be^{2+} and Mg^{2+} and is explained as due to a tetrahedral configuration with two CO molecules similar to that observed previously with Mn^{2+} . The single CO IR absorption on Mn^{2+} and a previously unassigned CO absorption band on iron (now assigned to Fe^{3+}) fit well to our empirical formula. The stretching vibrations of CO adsorbed on other transition metal ions are compared with the present results.

In the first paper of this series¹ IR spectra of CO adsorbed on a manganese(II) surface compound on silica gel were published together with those on cobalt(II) and iron(II). We have previously^{2,3} argued that the ligand field stabilisation energy might contribute to the stability of other transition metal ion CO complexes but not to those of manganese(II) (a d^5 electron system). Furthermore, the main group metal ions are not influenced by ligand field stabilisation. Therefore, it can be assumed that their CO complexes may have a similar stability as the manganese(II) CO complexes, if other conditions are similar. An investigation of such CO complexes should also reveal by comparison the

influence of the d electrons of the transition metal ions on the frequency of the adsorbed CO and by this throw some light on the nature of the metal ion – CO bond.

Similar investigations have been performed before by other workers with metal ions on zeolites⁴ and on tin oxide,⁵ as well as with metal fluoride CO complexes in low temperature argon matrices.⁶

EXPERIMENTAL

All our samples were prepared by impregnating silica gel "Merck 7733"⁷ with a solution of the metal chloride in water to give a product with 1.0×10^{-4} (mol metal ion)/(g silica gel) after dehydration at high temperatures (1000°C) in vacuum. The metal chloride water solution was prepared from commercial *p.a.* metal chlorides, with the exception of Cs, Tl and Ga, where the chlorides were prepared by reacting a water solution of the sulfates with barium chloride in water or by dissolving the metal in hot hydrochloric acid (Ga). In the case of thallium(I) and lead(II) the chlorides are probably not soluble enough in hot water to produce the surface compounds with high yield.

The dried silica gel was pressed to a sample disc and heated to 900°C in vacuum (10^{-2} Torr) in an IR cell.¹ "Preparation method 2" was used,¹ which means that together with the sample disc 0.5 to 1 g of the impregnated silica gel was placed in the IR cell. Further experimental details may be taken from Refs. 1 and 8.

After filling the IR cell with 80 Torr CO at room temperature the IR spectra were recorded at conditions also previously described.^{1,8} The CO spectra with beryllium and magnesium samples (Fig. 2)

were recorded on a Perkin-Elmer spectrophotometer 180, those of the other samples on a 580 B spectrophotometer from the same manufacturer. The resolution of the IR spectra was between 0.85 and 1.4 cm^{-1} and the error was less than $\pm 1 \text{ cm}^{-1}$.

During the measurements a CO IR absorption band was observed, which was nearly independent of the impregnation with different metal ions and could not be ascribed to CO physisorbed on the silica gel. This CO IR absorption is presumably due to CO on a metal ion present on the original silica gel. This metal ion could be removed to some 80 to 90 %, by heating the silica gel to $80 \text{ }^\circ\text{C}$ in conc. hydrochloric acid (38 %) before use (250 g SiO_2 + 200 ml HCl + 300 ml H_2O). Analysis of this solution, using atomic absorption spectrophotometry, showed 0.359 (Ca), 0.146 (Na) and 0.0038 (K) 10^{-4} (mol metal)/(g SiO_2).

Neither the vacuum heat treatment nor the purification with hydrochloric acid were optimized.

RESULTS

In order to make possible a comparison with other papers of this series, for instance in respect to the stability of the CO adsorption or the intensity of the CO IR absorption, we use the same representation of the IR spectra as before.^{1,8}

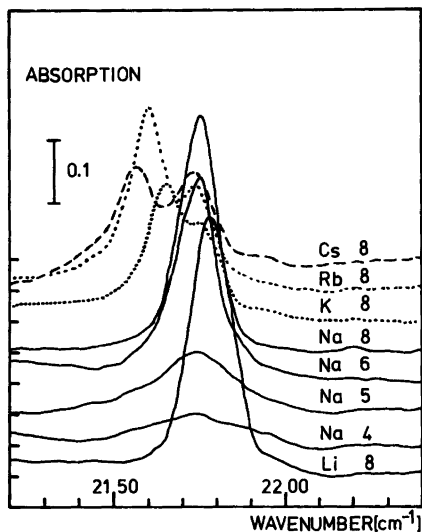


Fig. 1. IR spectra of CO adsorbed on alkali metal ions on silica gel. The numbers indicate the temperature and CO pressure (8: $-145 \text{ }^\circ\text{C}/1 \text{ Torr CO}$, 6: $-70 \text{ }^\circ\text{C}/76 \text{ Torr CO}$, 5: $-40 \text{ }^\circ\text{C}/78 \text{ Torr CO}$, 4: $-10 \text{ }^\circ\text{C}$, 80 Torr CO).

In Fig. 1 the IR spectra of CO adsorbed on alkali surface compounds are shown. Two different features can be noticed. The most important is that the position of one of the CO IR absorptions is decreasing in frequency rather regularly from lithium (2178 cm^{-1}) to sodium (2175 cm^{-1}), potassium (2165.5 cm^{-1}), rubidium (2160 cm^{-1}) and cesium (2157 cm^{-1}). The four spectra with the sodium surface compound show the weak stability of the CO adsorption, which is similar for all alkali surface compounds. All these compounds have nearly no CO adsorbed at room temperature and 80 Torr CO pressure.

The second feature is that in the case of potassium, rubidium and cesium a second absorption band is observed at 2175.5 , 2174 and 2173 cm^{-1} , respectively. This second band may be covered by the "real" one in the case of sodium and lithium and add to the absorption band observed. One can suspect that the second band is connected to a sodium surface compound, which may be present on the silica gel before impregnation.

The change in peak intensity (the extinction coefficient) is not strong, taking into account the above discussion, although potassium and cesium have somewhat smaller bands.

In Fig. 2 the CO IR spectra with beryllium and magnesium surface compounds are reproduced.

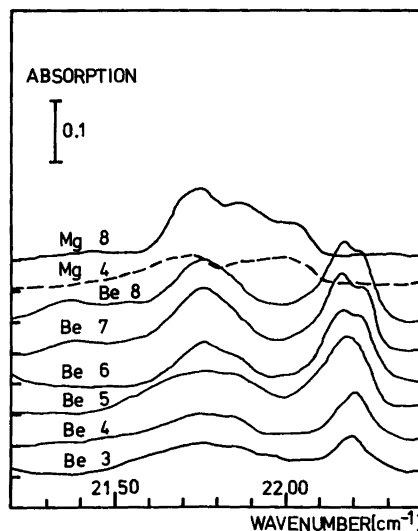


Fig. 2. IR spectra of CO adsorbed on beryllium and magnesium surface compounds on silica gel. (3: $20 \text{ }^\circ\text{C}/80 \text{ Torr CO}$) See text to Fig. 1.

Beryllium shows one absorption band at 2219 cm^{-1} at relatively high temperature, which splits at lower temperatures into two bands at 2216.5 and 2221.5 cm^{-1} . The adsorbed CO corresponding to the band at 2219 cm^{-1} is considerably more stable than the analogous sodium CO complex in Fig. 1. The peak intensity of the IR band at 2219 cm^{-1} is smaller, however.

Magnesium shows a similar behaviour as beryllium with a CO IR band at 2199 cm^{-1} at relatively high temperatures and two bands at 2186 and 2202 cm^{-1} at lower temperatures. The single band (2199 cm^{-1}) is here close to the band of the pair with the higher frequency (2202 cm^{-1}). This is similar to the CO adsorption on manganese(II), where the single band is at 2190.5 cm^{-1} and the high frequency band of the pair is at 2192 cm^{-1} .¹

In all spectra of Fig. 2 one can again observe a band around 2175 cm^{-1} , however somewhat broader than in Fig. 1.

Fig. 3 shows the CO spectra with calcium, strontium and barium surface compounds, which have bands at 2176 , 2174 and 2167.5 cm^{-1} , respectively. The band peaks of the CO adsorbed on these surface compounds move to higher wavenumbers at higher temperatures (2179.5 , 2179 and 2173 cm^{-1}), but it is not clear if this is a real effect or just produced by contamination by other metal ion

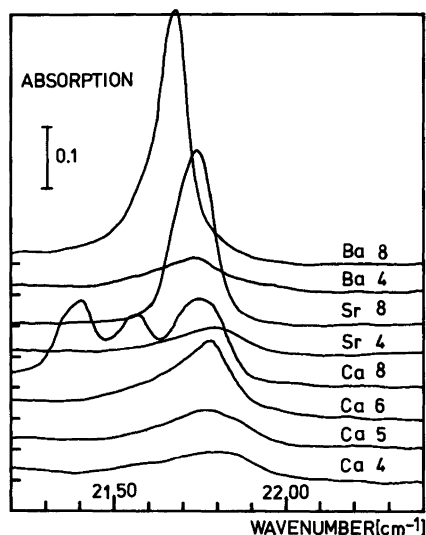


Fig. 3. IR spectra of CO adsorbed on calcium, strontium and barium surface compounds on silica gel. See text to Fig. 1.

surface compounds. The peak intensity of the CO IR bands is increasing from calcium to barium, while the stability of the CO adsorption is decreasing from beryllium (Fig. 2) to barium (Fig. 3).

In Fig. 3, spectrum Ca 8, two peaks at 2140.5 and 2156.5 cm^{-1} show the CO IR absorption bands of CO on the silica gel, which are normally subtracted in the other spectra. These bands are also often much weaker (due to our "preparation method 2") and are observed at slightly varying positions (2138 and 2156 cm^{-1} in Ref. 9).

After the investigation of the CO adsorption on alkali and alkaline-earth metal ions it became clear that the absorption band near 2175 cm^{-1} could arise from CO adsorbed on several metal ions such as lithium, sodium and calcium. This conclusion was based on the position and the stability of the absorption band. We therefore tried to remove the metal ions by heating the silica gel in conc. hydrochloric acid at $80\text{ }^{\circ}\text{C}$.

As the spectrum of SiO_2, pur (Fig. 4) shows, the CO IR absorption decreased rather drastically after such treatment. It could be restored after impregnating the silica gel with sodium chloride (spectrum $\text{SiO}_2, \text{pur, Na}$ in Fig. 4). The hydrochloric acid solution (with the contaminating metal ions) was analysed having mainly calcium, sodium and (less) potassium (see experimental section).

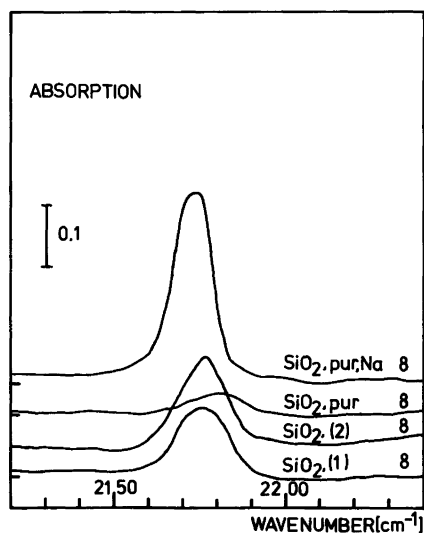


Fig. 4. IR spectra of CO adsorbed on untreated silica gel (1, 2), purified silica gel and on purified silica gel impregnated with sodium. See text to Fig. 1.

If the peak intensity of the CO IR absorption bands in spectrum SiO₂(1) and SiO₂(2) (Fig. 4) is compared with the expected peak intensity calculated using the analytical data and the peak intensities for the IR bands of CO adsorbed on calcium (spectrum Ca 8, Fig. 3) and sodium (spectrum SiO₂,pur,Na; Fig. 4) a difference of +10 or +20 %, respectively, is found. We think that this difference might be due to inaccurate intensity measurements and/or to variations of the silica gel. (Both metal concentrations (Ca, Na) are neither listed nor guaranteed by the manufacturer.) Adding the peak intensities of the IR absorption bands of adsorbed CO in spectrum SiO₂(1) and SiO₂,pur,Na (Fig. 4) one gets the same peak intensity as for CO adsorbed on the sodium surface compound in Fig. 1 (spectrum Na 8). The silica gel used for the spectra in the next two figures as well as in Fig. 3 were purified with hydrochloric acid (see experimental section).

No CO IR absorption band could be observed with samples impregnated with boric acid. However, samples with aluminium, gallium and indium showed CO IR bands, which had rather high wavenumbers (Fig. 5) at 2228.5, 2218.5 and 2209.5 cm⁻¹, respectively. The top of all three bands shifted to even higher wavenumbers at low temperatures by 4, 3 and 4 cm⁻¹. Gallium showed a second CO IR

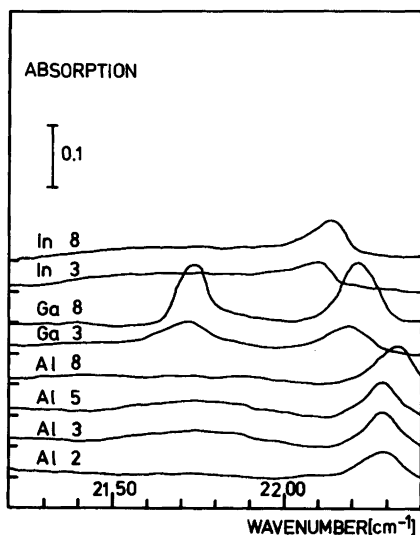


Fig. 5. IR spectra of CO adsorbed on aluminium, gallium and indium on silica gel. (2: 20 °C/20 Torr CO). See text to Fig. 1.

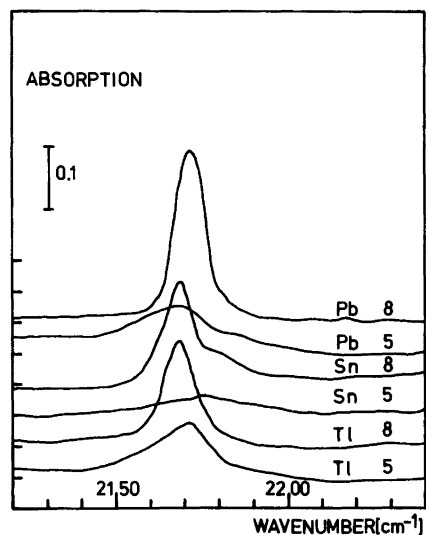


Fig. 6. IR spectra of CO adsorbed on thallium(I), tin(II) and lead(II) on silica gel. See text to Fig. 1.

absorption band at 2174 cm⁻¹, which may be due to gallium(I). The peak intensity of the CO IR absorption bands on the tri-valent cations is as weak as for beryllium(II), and the stability of the CO adsorption complex is, as it was found for beryllium(II), relatively high and comparable to transition metal ion CO complexes like those of iron(II) and cobalt(II).¹

In the last of the figures describing the spectra of the CO adsorption, the IR absorption bands of CO adsorbed on thallium(I), tin(II) and lead(II) are shown (Fig. 6). The peaks are at 2170, 2169 and 2171.5 cm⁻¹ and the stability of the CO adsorption on these metal ions is rather low.

DISCUSSION

The basic model of CO adsorption describes the CO molecule as a weak σ donor and a fairly good π acceptor¹⁰ and *vice versa* the metal ion (or metal) as a σ acceptor (electron pair acceptor = Lewis acid) and a π donor. In the present context, it is only of importance how these two aspects of the CO-metal ion bond influence the position, intensity and half width of the CO stretching vibration and what effect they have on the strength of the CO adsorption.

In respect to the position of the CO IR absorption it is generally accepted that the σ donor effect

increases the frequency of the CO stretching vibration, while the π acceptor effect decreases it. The integrated intensity of the CO IR absorption is strongly increased by the π acceptor effect and a weaker increase due to the σ donor effect has also been observed.¹¹ An influence of the two effects on the half width of the CO stretching vibration has not been noticed. Both bonding effects increase the strength of the CO adsorption.

However, the above bonding mechanism is synergic, which means that a strong σ donor effect (of the adsorbed CO) will increase the electron density at the metal ion and so increase the ability of the metal ion to show a π donor effect. Conversely, a strong π donation from the metal to the CO molecule can strengthen the σ donor properties of CO. Such a mechanism, giving contributions to the CO frequency shift in opposite directions, may cause only a small change of the CO frequency for the transition metal ion complexes (d electrons), but will enhance the stability of the CO complexes.

In discussing our results of the CO adsorption on main group metal ion surface compounds we will refer to the above remarks in order to separate the two bonding effects, of which the σ donor effect of the CO molecule should be the main contribution to the change of the CO stretching vibration from that of the CO gas (2143 cm^{-1}).

The frequency of the IR absorption of CO adsorbed on cations is often described in reference to the Coulomb law, *i.e.*, depending on the formal charge (Z) divided by the square of a distance.⁴⁻⁶

This distance is normally the sum of the ionic radius (R_i) of the cation and a distance derived from the CO molecule. However, such a Coulomb law approach overlooks the π donor effect of the transition metal ions and, furthermore, does not take into account the vibration coupling between the M-C vibration and the C-O vibration, which will always be present.¹² In our systems the M-C vibration is not observable due to the strong absorption of the silica gel support in the IR region, where this vibration should be expected. We had, therefore, to choose to use the ionic radius and formal charge only as variables of the cations in describing the spectra of CO adsorbed on the metal ion surface compounds.

In Fig. 7 the ionic radius¹³ (Pauling) is plotted against the frequency of the IR absorption of adsorbed CO. The cations can be represented by three straight lines according to their formal charge. Using the simple formula for a straight line one gets eqn. (1).

$$\bar{\nu} = \bar{\nu}_{\text{CO}_{\text{gas}}} + a - bR_i \quad (1)$$

The constant a has values of 49, 90 and 113 cm^{-1} and the constant b values of 20.7×10^8 , 51.5×10^8 and $58.6 \times 10^8\text{ cm}^{-2}$. The three straight lines in Fig. 7 are calculated by a least squares procedure using IR frequencies of CO adsorbed on uni-valent (Li, Na, K, Rb, Cs), bi-valent (Be, Mg, Ca, Sr, Ba) and tri-valent surface cations (Al, Ga, In, crosses).

A combination of the straight lines for the uni-

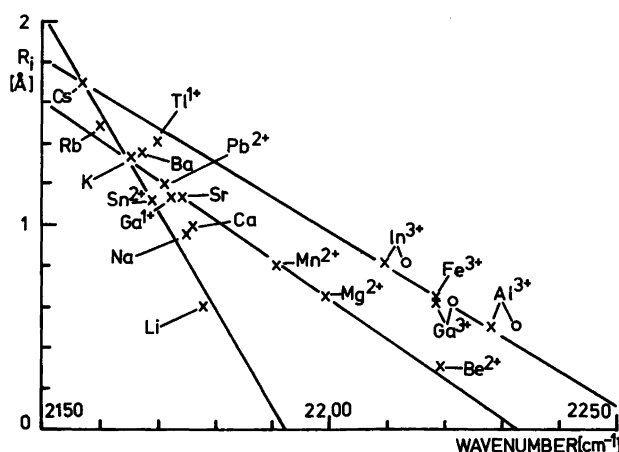


Fig. 7. Plot of ionic radius¹³ versus frequency of the IR absorption of adsorbed CO. The straight lines are calculated by a least squares procedure. See discussion.

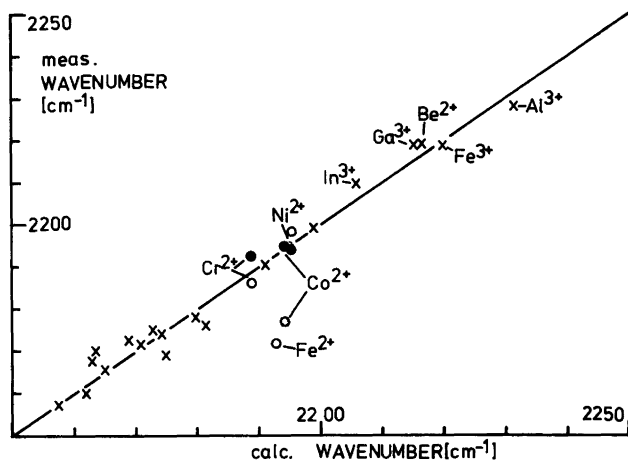


Fig. 8. Plot of measured frequency versus frequencies calculated by the empirical eqn. (2). Frequencies of *trans* (open circles) and *cis* (full circles) transition metal ion surface compounds with one adsorbed CO molecule are added. See discussion.

valent and the bi-valent cations using the formal charge (Z) gives eqn. (2).

$$\bar{\nu} = \bar{\nu}_{\text{CO}_{\text{gas}}} + a + bZ + cR_i + dZR_i \quad (2)$$

The constants have the values 9.5 cm^{-1} (a), 40 cm^{-1} (b), $10.1 \times 10^8 \text{ cm}^{-2}$ (c) and $-30.8 \times 10^8 \text{ cm}^{-2}$ (d).

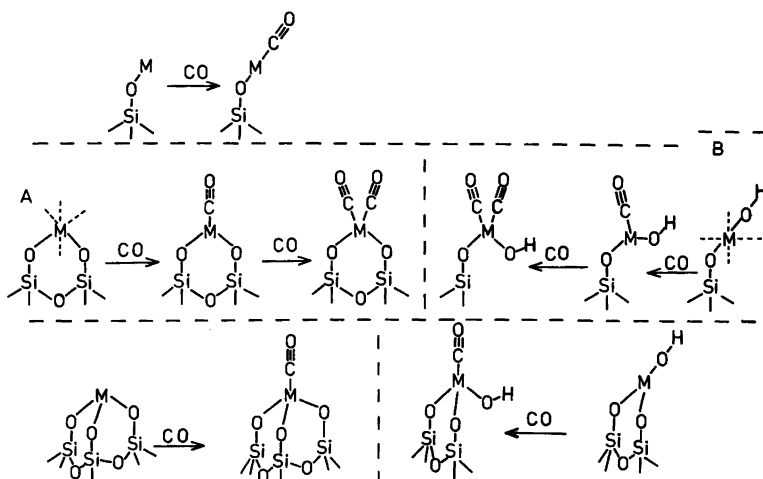
In Fig. 8 the measured frequency values for adsorbed CO are plotted against those calculated using eqn. (2). This empirical formula is valid also for the tri-valent cations, as can be seen from the figure. It is, however, not clear if a similar extension of the formal charge range as made for the tri-valent cations, is also possible in the inverse direction, *i.e.*, to metal atoms. The largest deviations of the measured CO frequencies from eqn. (2) are $+6.4(\text{Ti}^+)$, $-6.0(\text{Sn}^{2+})$ and $-5.6 \text{ cm}^{-1}(\text{Ca}^{2+})$, which means that all measured CO frequencies lie within 9% of the present CO frequency range from 2157 to 2228.5 cm^{-1} . The frequency deviations show roughly a symmetrical Gauss curve. When now turning to discuss the frequencies of CO adsorbed on transition metal ions, we will rely on these findings and calculate the CO frequencies from eqn. (2) to represent a similar-sized ion without valence d-electrons.

CO on transition metal ions. In the introduction we have used the argument that in the case of manganese(II), with no ligand field stabilisation energy, the stability of the CO adsorption complex might be similar to that of the main group metal

ions. This is, in fact, the case as can be seen by comparing the temperature and pressure dependence of the spectra of CO adsorbed on manganese(II)¹ and magnesium(II) (see results). With eqn. (2) we can now calculate the manganese(II) CO frequency (2191.3 cm^{-1}), which is nearly the same as that observed (2190.5 cm^{-1}). One can conclude from this small deviation that a half filled d electron shell has no noticeable effect on the frequency of adsorbed CO and on the stability of the CO adsorption.

This line of argument can be extended to another d^5 ion, namely iron(III). Previously we have observed a CO IR absorption band on iron impregnated samples at 2218.5 cm^{-1} , which we, at that time, could not assign.¹ As Fig. 7 shows, this band fits nicely to the straight line for the tri-valent cations. Calculating the CO frequency according to eqn. (2) gives 2219.3 cm^{-1} , which is again in good agreement with the observed CO frequency. The previous assignment of a band at 2165–2169 cm^{-1} to an iron(III) CO complex is somewhat "softened" by this argument. A future investigation of the tri-valent transition metal surface cations will hopefully clarify this disagreement.

Before we discuss the CO IR absorptions on other transition metal ions, it is necessary to put forward models for the main group metal ion surface compounds and their CO complexes. In the case of the uni-valent cations, only one configuration is possible for the surface compound, as can be seen



from the scheme. For the bi-valent cations two possibilities exist, namely a *trans* configuration ($-\text{O}-\text{M}-\text{O}-$ angle 180°) and a *cis* configuration (OMO angle less than 180° , most likely between 120 and 90°). This has been proved for the transition metal ions,^{1,8} but for the main group metal ion CO complexes (and those of manganese(II)) these two configurations may lead to the same $\text{M}-\text{CO}$ configuration, as shown in the middle of the scheme. The structure A models the *cis* configuration and the structure B the *trans* configuration. On the basis of previous discussions^{1,8} the structure A in the scheme is most likely present under our preparation conditions ("preparation method 2").

For the tri-valent surface cations three configurations can be expected with symmetries D_{3h} ("Star"), C_{3v} ("Top") and C_{2v} ("T").¹⁴ The "Top" configuration is most likely present with main group metal ion surface compounds (shown in the scheme), but a detailed discussion of the IR vibrations of CO adsorbed on tri-valent surface cations in respect to the different configurations should be postponed to the investigation of tri-valent transition metal cations, where one can expect more examples of different CO complexes.

Assuming that only such species as depicted in the scheme are present, it becomes clear that the single frequency of the CO stretching vibration in Figs. 7 and 8 refers to the complexes with only one CO molecule adsorbed.

In order to compare the CO IR absorptions of the transition metal CO complexes [except those of manganese(II)] it is necessary to discuss the *cis* and

trans surface compounds separately. For the *trans* configuration there is at present only for chromium(II) evidence that the complex with only one CO molecule really exists.^{15,1} The frequency of this adsorbed CO coincides with the frequency of the IR active vibration of the complex with two CO molecules. We assume that this behaviour is general also for the other *trans* surface compounds of bi-valent transition metal ions.

As one can see from Fig. 8, these frequencies (open circles) lie partly on line with the main group metal ions (chromium(II) and nickel(II)) as well as differ considerably from the line (cobalt(II) and iron(II)). In the latter two cases the measured frequencies are 17 and 21 cm^{-1} below the calculated ones, which is a considerably larger deviation than for any main group metal surface ion.

Previously^{2,3} we have found that the stability of the CO complexes of the above ions increases with increasing frequency of the CO IR absorption. This was stated before the *cis-trans* isomerism of the bi-valent surface compounds was established^{1,8} and so some explanatory remarks are necessary. It is clear that in the case of nickel(II) and iron(II) the *trans* surface compounds are the CO adsorption centers. With chromium(II) the *cis* compound is present,¹ but most likely only to some 10 to 20%, so that the CO complex stability refers (only) mainly to the *trans* surface compound. In the case of cobalt(II) the *cis* surface compound is exclusively present, but the CO complex of the *trans* surface compound has in this special case similar stability as that of the *cis* surface compound, which can be

seen from the CO IR spectra in Ref. 1.

The above arguments now point to the conclusion that the above-mentioned increase of the stability of the CO complexes with increasing CO stretching frequency is only valid for the *trans* surface compounds. If we now combine this correlation of the CO stretching frequency and the stability of the CO complexes with the effects of σ acceptor and π donor abilities of the transition metal ions, it is obvious that in this case the stability of the CO complexes is also mainly caused by a σ acceptor effect of the metal ion similar to that of the main group metal ions.

On the other hand, however, the stability of the above CO complexes is considerably larger than that of main group metal ions of the same formal charge and comparable ion radius. This disagreement can possibly be explained with the assumption that the transition metal ion CO complexes use to some extent the synergic bonding mechanism.

The assignment of the frequency of the *cis* surface complexes with only one CO molecule is as difficult as that for the *trans* surface compounds. Only in the case of cobalt(II) has such an assignment been attempted before.¹ We simplify again, with the assumption that the expected frequency is close to that with the higher wavenumber of the *cis* complex with two CO molecules, which is the case with cobalt(II) (2195 to 2189 cm^{-1}). Three of these frequencies are shown in Fig. 8 (full circles), which all

lie relatively close to the line of the main group metal ions.

The stability of the *cis* CO complexes with two CO molecules adsorbed diffuses, however, in a similar way as the *trans* surface complexes, so that one can propose a difference in the bonding mechanism of the CO adsorption on *trans* and *cis* surface compounds of transition metal ions.

Summarising, one can conclude that the frequencies of adsorbed CO are not drastically different between main group and transition metal surface ions with the formal charge two and comparable ionic radius, while the stability of the CO complexes is considerably higher for transition metal surface compounds.

Integrated intensity of the CO IR absorption. In respect to the integrated molar intensity of the CO IR absorption a decrease with increasing frequency can be concluded from Fig. 9. It should, however, be kept in mind that Fig. 9 is based on the assumption that the formation of the surface compounds is similar in quantity to those of transition metal ions (75% of the overall metal content), which is not proved. In addition, the formation of the CO complexes with low frequencies (below 2170 cm^{-1} , low stability) may not be completed at the low temperatures used in our measurements. Nonetheless, we propose that the broken line in Fig. 9 represents some upper limit for the integrated intensity of the CO IR absorption of CO adsorbed on main group

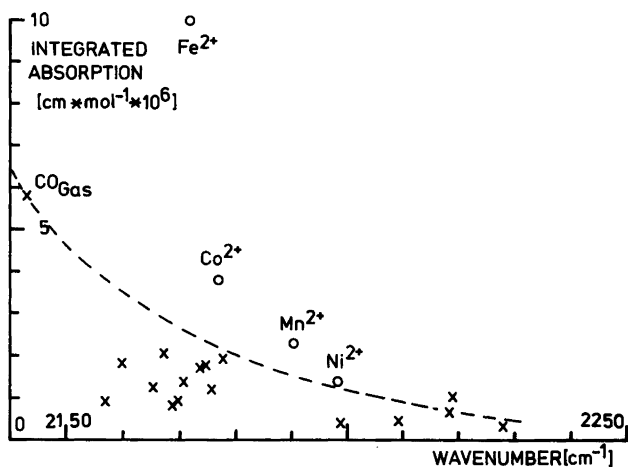


Fig. 9. Plot of integrated intensity of the IR absorption of adsorbed CO against frequency of the CO IR absorption. The broken line is thought to be an upper limit of the integrated intensity of CO adsorbed by main group metal ions on silica gel.

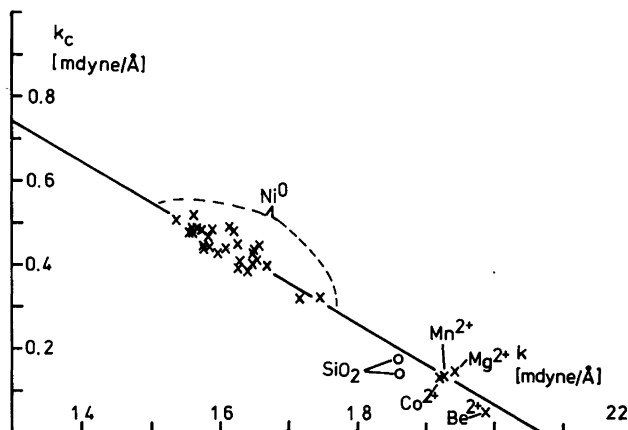


Fig. 10 Plot of the stretching interaction CO-CO constant k_c versus stretching force constant k for tetrahedral complexes with two CO molecules. The crosses in the middle represent nickel(0) complexes from Ref. 17. For further details see discussion.

surface compounds. Although we used the same equation for the calculation of the integrated intensity (eqn. (4) in Ref. 11) we find an inverse trend with frequencies higher than that of CO gas (2143 cm^{-1}), which is contrary to the results reported by Seanor and Amberg.¹¹

Two items support the general correctness of our calculation of the integrated intensity: (1) The integrated intensity of the CO molecule^{11,16} itself is $5.8 \times 10^6\text{ cm mol}^{-1}$, which is only about three times higher than our values for the IR absorption band of CO adsorbed on main group metal ion surface compounds. Support for the dashed line comes also from the known fact that the integrated intensity of CO vibrations in carbonyls is very high, for example $\text{Ni}(\text{CO})_4$ (2057 cm^{-1}) has a integrated intensity of 320 (CCl_4) or $456 \times 10^6\text{ cm mol}^{-1}$ (THF).¹⁶ (2) If one calculates the integrated intensity of the IR absorption band for CO adsorbed on Ni^0 from the figures in Ref. 8, an integrated intensity of $570 \times 10^6\text{ cm mol}^{-1}$ is found, which is close to the comparable values for $\text{Ni}(\text{CO})_4$.

As can be seen in Fig. 9, the integrated intensity of the CO stretching vibration is close to the dashed line representing the main group metal ion surface compounds in the case of *trans* cobalt(II), manganese(II) and *trans* nickel(II) and much higher in the case of *trans* iron(II) (and, presumably, *trans* chromium(II)).

In a previous paper of this series⁸ an empirical dependence of the stretching interaction CO-CO constant ("splitting force constant") k_c of a tetra-

hedral configuration with two CO molecules on the stretching force constant k of the two CO molecules of such a configuration was shown. In Fig. 10 the values for the magnesium(II) and beryllium(II) complexes are plotted in a similar way, together with those for tetrahedral nickel(0) complexes¹⁷ (slightly selected) and two values for the cobalt(II) and manganese(II) CO complexes. The least squares straight line through these values (crosses in Fig. 10) hits the force constant axis at 20.66 mdyne/Å or 2262 cm^{-1} .

The two open circles in Fig. 10 represent the IR absorption bands of CO physisorbed on the silica gel from above and are relatively close to the straight line. We take this as some evidence that the physisorbed CO is adsorbed at a tetrahedral system, which is most likely the oxygen atom of siloxan bridges on the silica gel surface ($-\text{Si}-\text{O}-\text{Si}-$). This would mean that physisorbed CO is not bonded by an undirected force, as van der Waals forces are normally interpreted, but by a tetrahedral system with relatively directed bonds.

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