

Geometric and Ligand Effects in the Infrared Spectra of Adsorbed Carbon Monoxide

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Received March 12, 1981; revised June 19, 1981

Coadsorption of ethylene or oxygen with carbon monoxide has been investigated using ir transmission spectroscopy. Information on the extent of "electronic" and "geometric" (dilution) effects on the ir stretching frequency of CO has been obtained by the isotopic dilution method. The increase of this frequency (blue shift) caused by oxygen can be explained mainly by a compression of the CO layer. The decrease of the frequency (red shift) caused by ethylene can be explained for more than 60% by a dilution of the CO layer.

INTRODUCTION

During a catalytic reaction the surface of a catalyst becomes covered by a mixture of species: reactants, intermediates, products, and a variety of their fragments. It is an interesting question whether (and if so, how) coadsorption leads to variations in chemical bond strengths and through that to changes in the reactivity of adsorbed species. This is by no means an academic question. For example, it could have serious consequences for our ideas on the mechanism(s) of the Fischer-Tropsch synthesis of hydrocarbons. As has been proved earlier (1), the dissociation of CO is a prerequisite for the initiation and growth of hydrocarbon chains in these reactions. If coadsorption of hydrocarbons reduced the C-O bond strength, it should imply that the reaction rate could be influenced by the presence of reaction products or intermediates. It is then obviously very important to know the exact nature of the effects of coadsorption.

In order to obtain information on this subject, ir spectroscopy is an obvious choice since it gives direct information on the C-O vibrations which can be related to the C-O bond strength. So far coadsorp-

tion of CO has been studied with several molecules, e.g., ethylisocyanide (2), pyridine (3), trimethylamine (3), benzene (4-8), acetylene (8), ethylene (8), and cyclohexane (8). A pronounced downward frequency shift (or red shift), although varying in size, has been reported for all these molecules. The hydrocarbon molecules mentioned above are all potential donors of electrons and the usual explanation is, therefore, as follows.

The donors increase the electron density in the metal resulting in an additional donation of electrons to the antibonding 2π -orbitals of adsorbed CO. In this way, the C-O bond is weakened and as a result its vibration frequency is decreased.

However, some questions remain to be answered with this mechanism. If this model gave an exact and complete description of the process, it would imply that coadsorption of CO with electron acceptors like hydrogen, oxygen, or chlorine should result in a comparable increase in the CO frequency. In one of the few reports on these coadsorbates, however, it was reported that oxygen causes an increase of the CO frequency only when both species are adsorbed on the same site (3). It seems peculiar that electron donors and acceptors should not have the expected symmetric behaviour. Another problem is that specu-

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lations on the effects of coadsorption are usually supported by analogy with the well-documented ligand effects in coordination compounds. It can be expected, however, that such effects through a single metal atom are at least larger than effects through a metal where the free electrons provide a considerable screening. On top of this, coadsorption of potassium, known as an excellent donor of electrons, has a much smaller effect on the CO frequency (9) than the electron donors mentioned above. We feel that an alternative or at least additional explanation is needed to account qualitatively and quantitatively for the effects of coadsorption.

Such an explanation may be found in the structural geometrical behaviour of the CO layer, viz., in the formation or breaking-up of CO islands. It is well known that the frequency of adsorbed CO increases with surface coverage due mainly to increased dipole-dipole coupling (10-12). If coadsorbates influenced the formation of islands of CO, i.e., the mutual distance of the CO molecules, it would have a pronounced effect on the CO frequency. This could have serious implications for practical reactions. If the frequency decrease in coadsorbed layers is due mainly to a geometrical effect of dilution, then this decrease is not caused by a reduced bond strength of CO, but only by a reduced dipole-dipole coupling. A different tendency towards dissociation cannot then be expected. If on the other hand a substantial electronic effect did operate, an increase or decrease in the CO dissociation could be possible in reactions like methanation or the Fischer-Tropsch synthesis.

The Experimental Approach

We believe that a separation of these two effects, viz., the electronic (i.e., transfer of electrons through the metal) and geometric (i.e., influence on the formation of CO islands) effects, should be simple by use of the so-called *isotopic dilution method* (11).

In this method the extent of the dipole-

dipole coupling is varied by the adsorption of mixtures of ^{12}CO and ^{13}CO . If a random part of a full layer of ^{12}CO molecules is replaced by ^{13}CO molecules the electronic interaction of the layer with the surface remains unchanged since the two species are chemically identical. However, the dipole-dipole coupling will be reduced because the ^{12}CO dipoles hardly couple with the ^{13}CO dipoles since they do not have a similar vibrational frequency. This has the following consequence (11). Upon adsorption of a mixture of ^{12}CO and ^{13}CO the ir spectrum will reveal two bands. The high-frequency band is characteristic of the ^{12}CO vibrations² and will have the frequency of a ^{12}CO layer with partly reduced dipole-dipole coupling. By extrapolating the results from experiments with several $^{12}\text{CO}/^{13}\text{CO}$ mixtures to zero content of ^{12}CO , the frequency without dipole-dipole coupling is found. This frequency differs from the singleton value (i.e., the frequency of a single isolated molecule) only by the chemical interaction with the other CO molecules. Using this method Crossley and King (12) were able to show that the frequency shift due to increasing CO coverage on Pt(111) could be ascribed almost completely to dipole-dipole coupling. This absence of an electronic effect of coadsorbed CO on the frequency of CO corroborates our doubts about the extent of an electronic effect in coadsorption with hydrocarbons.

It is obvious that any species which is adsorbed strongly enough (compared to CO) and which does not tend to form islands itself could dilute the ^{12}CO layer in a way comparable to ^{13}CO . Especially hydrocarbons could reveal this diluting effect.

² Care should be taken in the interpretation of the spectra. A simple analysis shows that the intensity is "transferred" from the low-frequency to the high-frequency band. This means that the two bands cannot simply be ascribed to separate absorptions by ^{12}CO and ^{13}CO molecules and that ir absorption is rather a collective process. In accordance with the interpretation by Hammaker *et al.* (11), however, the high-frequency band can be treated as characteristic of the ^{12}CO vibrations.

Upon dissociative adsorption the carbon skeletons are separated from each other by the split-off hydrogen. This hydrogen can then easily be displaced by CO. Available LEED data (13) for the interaction between oxygen and CO, on the other hand, indicate a tendency for CO to form more compressed islands. A blue shift of the frequency of CO can then be expected.

If the above-mentioned red shift in the frequency of adsorbed CO—caused by coadsorption with hydrocarbons—were fully attributable to a transfer of electrons into the antibonding 2π -orbitals of CO, then this effect should have the same impact on a pure ^{12}CO layer as on a ^{12}CO layer diluted by ^{13}CO . A plot of the frequency of the ir band characteristic of ^{12}CO against the isotopic composition of the adsorbed CO layer

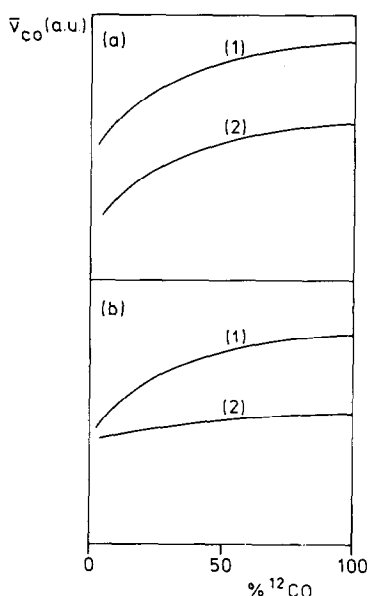


FIG. 1. Hypothetical curves for the adsorption of isotopic ($^{12}\text{CO}/^{13}\text{CO}$) mixtures. The frequency of the high-frequency ir absorption band is shown as a function of composition of the gas phase at full coverage. Curves: (1) without coadsorbed species; (2) with coadsorbed species. (a) When only a "ligand" (electronic) effect exists: the coadsorbed species causes a uniform red shift. (b) When no "ligand" effect is operative: the coadsorbed species only dilutes the CO layer, a "geometric" effect. (Frequencies always characterized by wave numbers, in cm^{-1} .)

should then consist of two *parallel* curves for experiments with and without coadsorption; the shift at infinite dilution is then equal to that for a pure ^{12}CO layer. This is illustrated in Fig. 1a.

If, on the other hand, the effect were purely geometric, i.e., if the red shift could be fully ascribed to a dilution of the CO layer, then a further dilution of ^{12}CO by ^{13}CO on the surface with preadsorbed hydrocarbons should have a reduced effect on the ir frequency of the high-frequency band. The same experiments with or without coadsorption should then produce two curves which *converge* to the same limiting value for infinite dilution, i.e., for zero dipole-dipole coupling. This is illustrated in Fig. 1b.

Following these ideas we performed experiments as described above. We used Pt as the metal, silica or alumina as carriers, and ethylene or oxygen as coadsorbates. In this way we established the extent of an electronic effect for blue shifts as well as for red shifts.

EXPERIMENTAL

The platinum-on-silica and platinum-on-alumina samples described in this paper were prepared by homogeneous precipitation with urea (14). The carrier materials were both obtained from Degussa AG Frankfurt (silica: Aerosil 300; alumina: Aluminum Oxide C). Platinum (specpure, Drijfhout) was dissolved in as little aqua regia as possible.

The average particle size of the samples was estimated by X-ray diffraction line broadening. The *in situ* treatment of the powders and the way the ir experiments were carried out were described elsewhere (15).

To investigate the nature of the influence of coadsorbates on the frequency of adsorbed CO, three types of experiments were performed.

(i) The adsorption of isotopic mixtures on the *freshly reduced* surface. After oxidation

for at least 30 min at 470 K under flowing oxygen and subsequent reduction for at least 60 min at 625 K under flowing hydrogen, each sample was cooled down under hydrogen and evacuated at room temperature for at least 15 min. Then a standard amount of CO (pure $^{12}\text{C}^{18}\text{O}$ or a mixture of the isotopes³) was admitted to a total pressure of 0.5 Torr. The mixtures were prepared by consecutive admission of the desired amounts to a vessel equipped with a calibrated Pirani gauge. Thereafter, these mixtures were expanded into the ir cell. Control experiments using a quadrupole mass spectrometer (VG-Q4) revealed that the accuracy of composition of the mixtures thus prepared was about 3%.

(ii) The adsorption of isotopic mixtures on a surface *pretreated with ethylene*. The procedure was exactly as described under (i) with one extra step. After evacuation at room temperature, 20 Torr ethylene was admitted. The sample was then heated to 330 K and cooled down again to room temperature. Thereafter, the cell with the sample was evacuated for 15 min. These experimental conditions were chosen by trial and error. The objective was to produce a substantial and well-reproducible decrease of the frequency of CO adsorbed afterwards. On the other hand, the intensity of the ir band of CO should not be reduced too much by the preadsorption of ethylene. Upon dilution of $^{12}\text{C}^{18}\text{O}$ with $^{13}\text{C}^{18}\text{O}$ a substantial reduction of the high-frequency band takes place. Isotopic experiments can therefore only be performed if the band of pure $^{12}\text{C}^{18}\text{O}$ is large enough (more than 15% loss of transmission).

(iii) The adsorption of isotopic mixtures on a surface *pretreated with oxygen*. The procedure was as described under (i) with omission of the last reduction step. After oxidation the sample was evacuated at 525 K and cooled down to room temperature under vacuum.

³ $^{12}\text{C}^{18}\text{O}$ from L'Air liquide N 20; $^{13}\text{C}^{18}\text{O}$ from Merck Sharpe & Dohme 90.5%.

RESULTS

The average particle size as determined by X-ray diffraction line broadening was less than 30 Å for both Pt/SiO₂ and Pt/Al₂O₃.

Pretreatment of the surface by ethylene did not produce any detectable bands in the region 3300–2700 cm⁻¹ or 1800–1200 cm⁻¹ of the ir spectrum, but the decrease of the absorption band intensity as well as the band frequency of CO thereafter adsorbed showed clearly that (fragments of) ethylenic species were present on the surface.

Adsorption of CO on freshly reduced Pt/Al₂O₃ produced three bands in the ir spectrum, two of which can be seen in Fig. 2. One broad band below 2000 cm⁻¹ (not shown in Fig. 2) probably due to multicoordinated CO, was too small to be used in isotopic experiments. After pretreatment by oxygen this band was fully absent. Above 2000 cm⁻¹ two bands can be distinguished (see Fig. 2), namely, the main band at 2073 cm⁻¹ and a satellite at 2080–2085 cm⁻¹. After pretreatment by ethylene only the main band was still present. However, after pretreatment by oxygen a satellite

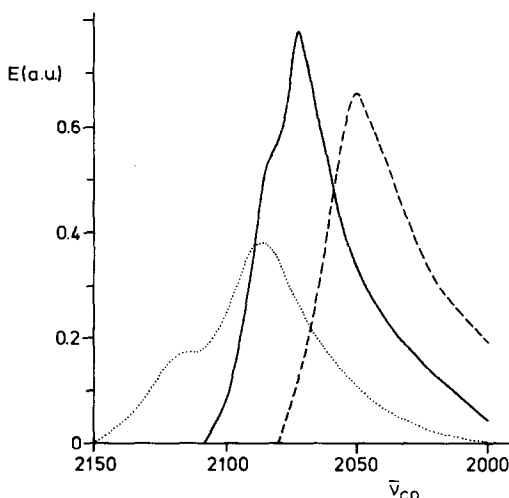


FIG. 2. Infrared spectra of CO adsorbed on Pt/Al₂O₃: (—) on a reduced surface; (···) on a surface pretreated by oxygen; (---) on a surface pretreated by ethylene. Wavenumbers in cm⁻¹.

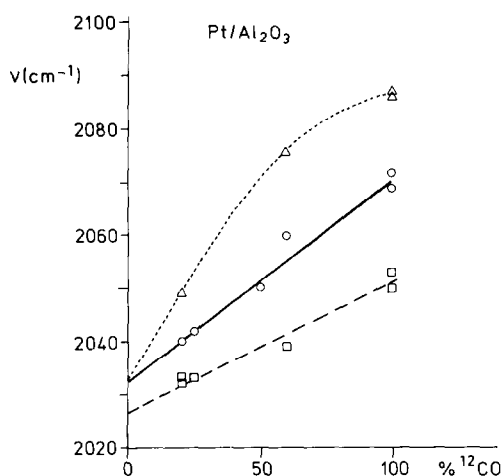


FIG. 3. Frequency as a function of isotopic composition; CO adsorbed on Pt/Al₂O₃: (○) on a reduced surface; (Δ) on a surface pretreated by oxygen; (□) on a surface pretreated by ethylene.

peak appeared again, although it was now separated 30 cm⁻¹ instead of 10 cm⁻¹ from the main band.

The influence of the pretreatment procedure on the frequency of the main band and in the ir spectrum when pure ¹²CO is adsorbed on Pt/Al₂O₃ can be clearly seen in Fig. 2.

The frequency of the main band could always be determined with an accuracy of at least ±2 cm⁻¹. The reproducibility of various experiments was better than ±3 cm⁻¹. From Fig. 2 it is clear that pretreatment by ethylene resulted in a decrease of the frequency of the subsequently adsorbed CO while pretreatment by oxygen resulted in a higher frequency as compared with CO adsorbed on a freshly reduced surface.

The main results of the isotopic experiments on Pt/Al₂O₃ are gathered in Fig. 3.⁴ Experiments with isotopic mixtures containing 20–25% ¹²CO also revealed shifts of the frequency of adsorbed CO due to pretreatment with ethylene and oxygen. These shifts were in the same direction but of a

⁴ The identification of the respective bands offered no problems; even with 25% ¹²CO the high-frequency band was of an intensity comparable to that of the low-frequency band.

clearly reduced size as compared to experiments with pure ¹²CO.

Adsorption of ¹²CO on freshly reduced Pt/SiO₂ revealed only one band at 2075 cm⁻¹ in the ir spectrum. The influence of pretreatment and of isotopic dilution on the frequency of this band was almost quantitatively comparable to the shifts of the main band in the corresponding spectra of CO on Pt/Al₂O₃. The results of the isotopic experiments on Pt/SiO₂ are collected in Fig. 4.

DISCUSSION

Although the carrier material does not seem to have any influence on the effects of pretreatment procedures or isotopic dilution, the spectra of pure ¹²CO on reduced Pt/Al₂O₃ and Pt/SiO₂ show some differences, as already mentioned above. In view of its identical behaviour upon varying conditions it does not seem unrealistic to ascribe the main peak in the spectrum of ¹²CO on Pt/Al₂O₃ to the same adsorption complex as that causing the only absorption peak in the spectrum of ¹²CO on Pt/SiO₂. This adsorption complex is probably the generally accepted single-site adsorption ("linear" CO). A band below 2000 cm⁻¹

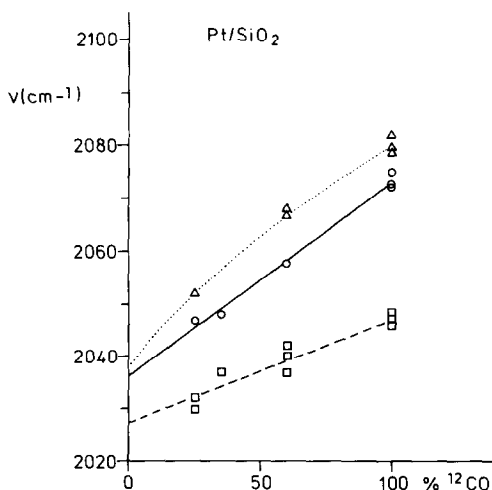


FIG. 4. Frequency as a function of isotopic composition of CO adsorbed on Pt/SiO₂: (○) on a reduced surface; (Δ) on a surface pretreated by oxygen; (□) on a surface pretreated by ethylene.

indicates the presence of multicoordinated CO. This adsorption complex requires a less smooth surface containing, for example, B_5 sites (16). The difference found between the spectra obtained with Pt/ Al_2O_3 and Pt/ SiO_2 could, therefore, imply that the carrier material (Al_2O_3 vs SiO_2) influenced the crystal surface structure. The satellite peak present in the spectra of Pt/ Al_2O_3 supports this assumption. If the surface consists of two different crystallographic planes, the satellite peaks with the higher frequency will be caused by CO adsorbed on the most densely packed plane(s). This could have the following consequences. Hydrocarbons are known to form an unreactive blocking layer preferentially on the smooth, most densely packed surfaces (17). It could be expected, therefore, that hydrocarbons would easily suppress or even eliminate CO adsorption on smooth surfaces, i.e., the CO adsorption corresponding with the higher-frequency peak. This is found in Fig. 2: after pretreatment by ethylene, the satellite peak on Pt/ Al_2O_3 is no longer visible.

Oxygen is known (13) to cause a compression of the CO layer which would predictably lead to a higher absorption frequency in the ir spectrum. This compression can be expected to be largest for the smoothest surfaces. As a result the difference between the two peaks on a surface pretreated with oxygen should be larger than that on a freshly reduced surface. This can indeed be seen in Fig. 2.

If this explanation is correct, an indication for a "dilution" effect is already obtained. If the effects of coadsorption were indeed purely electronic one would expect all bands to reveal a comparable shift due to, for example, oxygen pretreatment. More conclusive evidence about the presence and extent of a possible electronic effect can only be obtained with the isotopic experiments.

Although the blue shift in the CO frequency due to pretreatment with oxygen is not very large (10 – 15 cm^{-1}), it is neverthe-

less clear from Figs. 3 and 4 that this shift is reduced when the ^{12}CO layer is "diluted" with ^{13}CO . This means that although an electronic effect cannot be completely excluded here, it is at least accompanied by a geometric effect, viz., a compression of the CO layer.

The red shift of CO due to pretreatment with ethylene is much larger. Hence, the isotopic experiments allow a more quantitative interpretation. From Figs. 3 and 4 it is immediately clear that the shift is strongly reduced when the dipole–dipole coupling is eliminated by isotopic dilution (compare also with Fig. 1b). Tentative curves drawn through the available points indicate a residual effect upon infinite dilution of less than 10 cm^{-1} which has to be compared with the 20 – 25 cm^{-1} for the effect observed with pure ^{12}CO . This means that at least 60% (but probably even more) of the effect of ethylene on the frequency of CO on Pt can be attributed to a simple diluting effect of preadsorbed fragments in the CO layer. Ethylene adsorbed in the way described in (ii) had therefore only a relatively small electronic effect, if any, on the coadsorbed CO; its main effect is the separation of the CO dipoles.

The implications of our investigation are straightforward. We confirm that coadsorption of hydrocarbons leads, indeed, to a decrease in the ir frequency of adsorbed CO. The main reason for this reduction, however, is the diluting effect of these hydrocarbons and not the change in the CO bond strength. Therefore, one can hardly expect an "autocatalytic" effect by the formation of hydrocarbons on the surface in catalytic reactions like the Fischer–Tropsch synthesis in which the dissociation of CO is a necessary prerequisite.

CONCLUSION

The isotopic dilution method has proved to be a suitable way for the estimation of the extent of electronic vs geometric effects on the ir frequency of adsorbed CO. The

method is limited, however, to the ir bands and frequency shifts which are sufficiently large. The results obtained in this paper stress the importance of geometric rather than electronic effects when more than one species is present on the surface.

ACKNOWLEDGMENTS

The investigations were supported by the Dutch Foundation for Chemical Research (S.O.N.) with financial aid from the Dutch Organization for the Advancement of Pure Research (Z.W.O.). Fruitful discussions with Professor G. A. Somorjai are acknowledged; they were made possible by NATO Grant 1304.

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