Reflectance Spectra of CO Chemisorbed on MgO, and Evidence for the Formation of Cyclic Adsorbed Species

By Adriano Zecchina and Frank S. Stone*
(*School of Chemistry and Chemical Engineering, University of Bath, Bath* BA2 7AY)

Summary U.v.–visible reflectance spectra of CO chemisorbed on high surface area MgO show electron transfer and the development of conjugated adsorbed $(CO)_n^{m-}$ species.

Reflectance spectroscopy in the u.v., visible, and near i.r. regions has so far been used very little in adsorption studies of simple molecules on oxide surfaces. There has been work[1] on large molecules containing chromophores absorbing in the visible or near u.v., where differences between the spectra of the molecule in solution and in the adsorbed state have been used to study charge distribution and structure in the adsorbed species. Reflectance has also been applied to study *d–d* spectra of transition metal ions and modifications due to changes in co-ordination at surfaces.[2] By a suitable choice of system, we considered it possible to observe in one and the same reflectance spectrum both the internal electronic transitions of adsorbed species and those of the surface ions of the adsorbent. No such studies have so far been reported, yet they offer, in principle, a very direct method of studying the interaction between adsorbate and adsorbent. We show below that the chemisorption of CO on MgO provides a novel illustration of this method.

The adsorbent MgO was prepared in a high surface area form (*ca.* 280 $m^2 g^{-1}$) by controlled decomposition *in vacuo* of $Mg(OH)_2$ prepared from Specpure magnesium (Johnson & Matthey). A silica reflectance cell was designed to fit exactly into the entrance port of the reflectance attachment of a Pye Unicam SP 700 spectrometer. The reference specimen was a low surface area silica powder obtained by finely grinding an optical window of Suprasil. The cell was attached to a vacuum manifold so that gas could be dosed for measurement of u.v. and visible reflectance spectra *in situ*. A track enabled the vacuum manifold and cell to be wheeled aside for outgassing, prior to exact re-siting for further spectral measurements.

MgO was first outgassed at 800 °C. O_2 was then admitted at room temperature and the reflectance spectrum recorded (Figure, Curve 1). A pressure of oxygen (typically 1 Torr) is necessary in order to quench the surface fluorescence and thus obtain the true spectrum of high surface area MgO. The absorption band at 46,000 cm^{-1} and the shoulder at *ca.* 37,000 cm^{-1} are characteristic of high surface area MgO and they correspond to the energies of excitation of surface states (surface excitons).[3] A surface exciton involves a charge transfer from a surface oxide ion to the neighbouring surface Mg ions. Its frequency is influenced by the co-ordination of the ions involved, such that the lower the co-ordination of the ions the lower the excitation energy.[3] Hence the band at *ca.* 37,000 cm^{-1} corresponds to surface ions which are more unsaturated (and consequently more reactive in chemisorption) than those associated with the 46,000 cm^{-1} band.

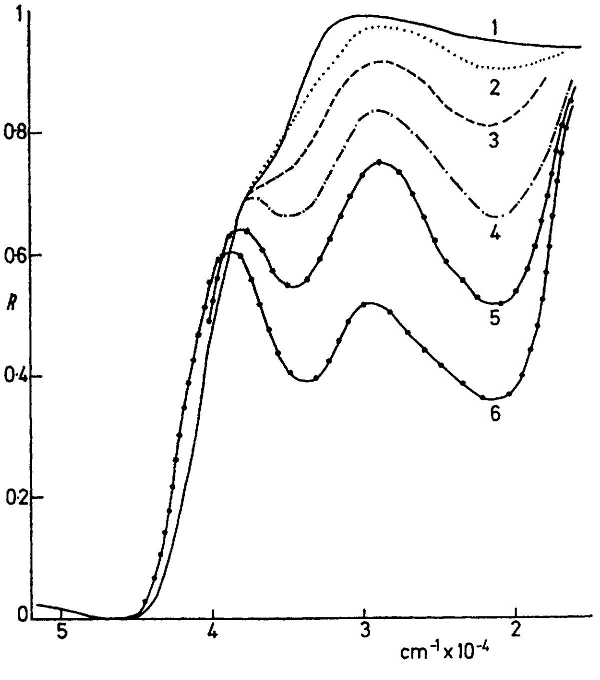
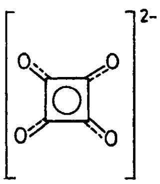


FIGURE. Reflectance *vs.* wavenumber for MgO outgassed at 800 °C. Curve 1: reference spectrum (in presence of 1 Torr O_2 to quench fluorescence). Curves 2—6: spectra after dosing CO to the evacuated surface at increasing pressures (up to 110 Torr).

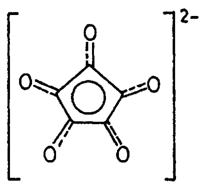
Curves 2-6 in the Figure were obtained by successively exposing the evacuated MgO for approximately 15 min to a series of increasing CO pressures at room temperature. Two strong absorptions develop at 34,000 and 21,500 cm^{-1} respectively. The oxide acquires a pink colour due to the absorption at 21,500 cm^{-1}. Simultaneously with the development of these bands, there is a decrease in the intensity of the absorption between 39,000 and 45,000 cm^{-1}, showing that as coverage increases during the adsorption of CO low frequency excitons are destroyed. For MgO outgassed only at 500 °C the shoulder at 37,000 cm^{-1} is absent: exposure of this oxide to CO does not give rise to the bands at 34,000 and 21,500 cm^{-1}. Thus the surface states involved are mainly those associated with the 37,000 cm^{-1} shoulder, which shows that low-co-ordinate surface sites are being used in the CO adsorption which gives rise to these bands.

The new bands are obviously due to internal electronic transitions in adsorbed species formed from CO, but the species are not CO$^-$ (ref. 4), CO$_2^-$ (ref. 4), CO$_3^{2-}$ (ref. 5), carboxylate,[6] or oxalate,[7] since the u.v. absorptions of these entities occur at much higher frequencies. Radical species such as CO$^-$ and CO$_2^-$, known already from e.s.r. studies,[8] are also ruled out because their coverages on MgO ($<0{\cdot}01\%$) are insufficient to justify the observed intensity of absorption.

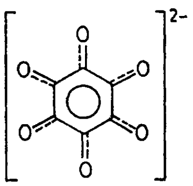
We believe that the bands arise from the $\pi^* \leftarrow \pi$ transition of aromatic oxocarbon anions such as (CO)$_n^{2-}$ where n = 4, 5, or 6[9] [(I), (II), or (III)]. The double negative charge stabilizes the polymeric CO and the source of this charge on the adsorbed species is likely to be the surface oxide ions. This accounts for the decrease of surface exciton absorption. The charge transfer to adsorbed species will be easier for the ions of low co-ordination, which explains why the exciton absorption most affected is that occurring at the lowest frequencies.



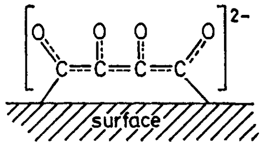
(I)



(II)



(III)



(IV)

The two bands formed on exposure to CO are due to different species, since they have different resistances to evacuation at room temperature. The band at 21,500 cm^{-1} (species A) decreases slowly on pumping at room temperature, and after 20 h has disappeared. The band at 34,000 cm^{-1} (species B) shows a slight *increase* in intensity in the first stages of pumping, but then remains unchanged. Re-exposure to CO regenerates the 21,500 cm^{-1} band and decreases the intensity of the 34,000 cm^{-1} band to its original value. This behaviour indicates that species A may be partially transformed into species B by removing CO from the surface, and *vice versa.*

The above observation is in good accord with the hypothesis that polymeric species are present on the surface. Species A and B could be (CO)$_n^{2-}$ ions with different values of n (and hence different ring dimensions). For instance, a 6-membered ring (III) for species A (21,500 cm^{-1}) and a 4- or 5-membered ring [(I) or (II)] for species B would be in agreement with the known spectra of the analogous compounds.[9] An alternative possibility is that species A alone is cyclic, and that species B absorbing at higher frequencies is an *open* conjugated structure (IV) derived from it by loss of one or more CO molecules.

The work suggests that reflectance spectroscopy in the visible and near u.v. regions might be applied much more widely in surface chemistry by making use of the influence of adsorption on the spectra of the surface states of finely divided oxides and by choosing simple adsorbates such as CO capable of yielding chromophores by intermolecular reaction in the adsorbed state.

A.Z., on leave from the Institute of Physical Chemistry, University of Turin, thanks the Italian National Research Council (C.N.R.) for financial support.

(*Received*, 30*th May* 1974; *Com.* 623.)

---

[1] H. P. Leftin and M. C. Hobson, *Adv. Catalysis*, 1963, **14**, 115; H. Zeitlin, R. Frei, and M. McCarter, *J. Catalysis*, 1965, **4**, 77; G. Kortüm, 'Reflectance Spectroscopy,' Springer, Heidelberg, 1969.

[2] K. Klier, *Catalysis Rev.*, 1967, **1**, 207; B. J. Hathaway and C. E. Lewis, *J. Chem. Soc.*, 1969, 1176, 1183, 2295.

[3] A. Zecchina, M. G. Lofthouse, and F. S. Stone, in preparation.

[4] A. Habersbergerova, I. Janovsky, and P. Kourim, *Radiation Res. Rev.*, 1972, **4**, 123, and papers cited therein.

[5] A. Muller, H. Seidel, and W. Ritter, *Spectrochim. Acta*, 1967, **23A**, 1619.

[6] H. H. Jaffe and M. Orchin, 'Theory and Application of Ultraviolet Spectroscopy,' Wiley, New York, 1962.

[7] D. P. Graddon, *J. Inorg. Nuclear Chem.*, 1956, **3**, 308.

[8] J. H. Lunsford and J. P. Jayne, *J. Chem. Phys.*, 1966, **44**, 1492.

[9] R. West in 'Non-benzenoid Aromatics,' Vol. 1, p. 31, ed. J. P. Snyder, Academic Press, New York, 1969.