CO ADSORPTION AND THE OPTICAL PROPERTIES OF INTERSTELLAR GRAINS

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Abstract. Laboratory data on the spectra of CO adsorbed on small MgO particles show that CO absorption leads to a weakening of the 220 nm band together with a shift of this band to shorter wavelengths. CO adsorption also results in the formation of a cyclic CO carbon ion that absorbs at 2.15 μm⁻¹. It is shown that this band provides a close match to a major component of the very broad structure seen in interstellar extinction at the same energy. Effects of CO adsorption on the 220 nm band and VUV extinction are discussed in light of recent observational data on stars with peculiar extinction curves.

1. Introduction

A characteristic modulation of the interstellar extinction curve near 500 nm was first noted by Whiteoak (1966) and by Walker (1967). This very broad structure (VBS) has been the subject of several observational (Hayes et al., 1973; Hayes and Rex, 1975; van Breda and Whittet, 1981) and theoretical (Huffman, 1977; Millar, 1982) studies. Generally, the VBS consists of an apparent decrease in extinction at λ⁻¹ = 1.8 μm⁻¹ together with an increase in extinction near 2.1 μm⁻¹. Further structure is likely also present at longer wavelengths. The overall amplitude of the VBS, ΔmVBS ∼ 0.018A_v, where A_v = visual extinction in magnitudes (van Breda and Whittet, 1981).

There have been various suggestions as to the origin of this feature (Borg, 1967; Manning, 1975; Huffman, 1977) Huffman’s proposal that the VBS is due to a variation in the optical constants of magnetic, Fe₃O₄ was investigated in some detail by Millar (1982) who showed that while small Fe₃O₄ particles would yield spectral structure near 1.8 μm⁻¹, the shape of this structure differed from the VBS.

We have recently provided some laboratory evidence for the existence of small MgO particles in the interstellar medium (MacLean and Duley, 1982; MacLean et al., 1982). These particles yield spectral features at 160 and 220 nm due to electronic transitions in O²⁻ ions in various coordination states. The reactivity of low coordination (L.C.) O²⁻ ions has been extensively investigated (see Che and Tench (1981) for a review) and specific reaction channels with H₂ (Coluccia and Tench, 1980) and CO (Zecchina and Stone, 1978) have been delineated.

These results are discussed in Section 2 in the context of the properties of interstellar MgO dust in diffuse clouds. Some effects of adsorption on the optical properties of MgO dust are discussed in Section 3 where it is shown that the VBS shortward of λ⁻¹ = 1.7 μm⁻¹ may be related to absorption by a surface CO complex formed via reaction between O²⁻ ions at corner sites and CO from the gas in diffuse clouds. Attendant effects on the 220 nm band are also discussed and it is shown that the weakening and shift of the 220 nm feature to shorter wavelengths observed in certain objects may be understood in terms of the chemisorption of CO.

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2. Adsorption of Molecules in Diffuse Clouds

Figure 1 shows a schematic representation of the surface of a small oxide particle such as MgO. Oxygen ions in various low coordination sites are shown explicitly and are identified by particular values of \( L \). Thus \( O_{3C}^2- \) ions are \( O^{2-} \) ions in a state of 3-fold coordination, i.e., with 3 nearest neighbour Mg\(^{2+} \) ions.

\( O^{2-} \) ions in different LC states will generally possess different reactivities (Che and Tench, 1981) and distinct optical properties (Zecchina et al., 1975). In MgO, \( O_{4C}^2- \), and \( O_{5C}^2- \) ions are responsible for a broad absorption feature at 220 nm that is similar to the well-known interstellar band at this wavelength (MacLean et al., 1982) while \( O_{3C}^2- \) ions absorb at 270 nm.

The reactivity of \( O_{LC}^2- \) ions on MgO has been shown (Garrone et al., 1980) to involve proton transfer: i.e.,

\[
O_{LC}^2- + XH \rightarrow X^- + OH_{LC}.
\]

This process occurs with \( H_2 \) at sites of low coordination: namely,

\[
Mg_{LC}^2+ O_{3C}^2- + H_2 \rightarrow (MgH)^{2+}_{LC} + (OH)^3_{5C},
\]

where \( Mg_{LC}^2+ \) is a low coordination magnesium ion adjacent to the \( O_{3C}^2- \) ion. Heterolytic dissociation of \( H_2 \) (reaction 2) can also occur at \( Mg_{LC}^2+ O_{4C}^2- \) sites (Coluccia and Tench, 1980) but the products are less strongly bound than at \( Mg_{LC}^2+ O_{5C}^2- \) sites. Chemisorption of \( H_2 \) results in the destruction of the absorption band associated with \( O_{LC}^2- \) at the reaction site. Since \( O_{5C}^2- \) sites are most reactive, the 270 nm band is greatly reduced in intensity on exposure to \( H_2 \). \( O_{4C}^2- \) and \( O_{5C}^2- \) sites are less reactive and the 220 nm feature is only slightly affected by the adsorption of \( H_2 \).

A similar effect is seen in the absorption of CO by MgO particles. Figure 2 (Zecchina and Stone, 1978) shows the effect of CO adsorption on the reflectance of a finely divided MgO powder. At low coverage, the major effect of CO adsorption is the development of a broad absorption band at 2.15 \( \mu \)m\(^{-1} \) while the 4.6 \( \mu \)m\(^{-1} \) (i.e., 220 nm) band is unchanged. With higher coverage the 2.15 \( \mu \)m\(^{-1} \) band intensifies and a new feature appears at 3.4 \( \mu \)m\(^{-1} \). At the same time the low energy side of the 4.6 \( \mu \)m\(^{-1} \) band is weakened so that this feature appears to shift to higher energies.

When reacting with the MgO surface, CO first attacks at sites of highest reactivity to yield a product absorbing at 2.15 \( \mu \)m\(^{-1} \). It has been suggested (cf. Zecchina and Stone, 1978; Guglielminotti et al., 1979) that this attack occurs at \( O_{3C}^2- \) ions (cf. Figure 1) with the formation of a resonance stabilized carbon ion (\( CO)_{6-x}^x- \) where \( x = 2 \) or 4. The nature of the product producing the band at 3.4 \( \mu \)m\(^{-1} \) is less certain although infrared spectra (Guglielminotti et al., 1979) suggest the presence of carbonate species. A narrowing and shift of the 4.6 \( \mu \)m\(^{-1} \) band occurs when CO reacts with \( O_{4C}^2- \) and \( O_{5C}^2- \) ions.

Under diffuse cloud conditions, \( H \) atoms and \( H_2 \) molecules will be the dominant collision partners with dust. It has been shown (Duley et al., 1978) that \( H + H \rightarrow H_2 \) reactions on oxide grains can occur at sites with \( H \) atoms either physically or chemically adsorbed. Laboratory data (Coluccia and Tench, 1980) now suggest that strong binding