

CHARGE TRANSFER IN LUNAR MATERIALS: INTERPRETATION OF UV-VISIBLE SPECTRAL PROPERTIES OF THE MOON. J.A. Tossell*, D.J. Vaughan**, R.G. Burns***, B.M. Loeffler***, and K.H. Johnson****, *Dept. of Chemistry, University of Maryland, College Park, Maryland 20740, **Dept. of Geology, University of Aston, Birmingham, England, ***Dept. of Earth and Planetary Sciences and ****Dept. of Metallurgy and Material Sciences, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

Lunar materials have high abundances of certain transition metals, notably iron, titanium, and chromium, which absorb radiation in the visible and nearby regions of the electromagnetic spectrum. The spectra originate from excitations of electrons within individual transition metal ions (crystal field transitions), and between neighboring ions in a crystal structure as a result of charge transfer transitions. These electron transfer transitions between adjacent elements may involve cation→cation, cation→anion, and anion→cation transitions.

Charge transfer processes have been invoked to explain the intense absorption edges onsetting below 500 nm in the spectra of lunar samples (1, 2), as well as the steep declines in reflectance spectra towards the ultraviolet measured on specimens of the moon (3) and in telescopic observations of the moon's surface (4). The energies of these charge transfer transitions in oxide and silicate minerals are poorly understood (5). This has led us to calculate the electronic structures of transition metal ions in fundamental coordination polyhedral units, including regular octahedral oxide environments, such as those found in common lunar and terrestrial minerals. We summarize here data on oxygen→metal charge transfer energies obtained for the FeO_6^{9-} , FeO_6^{10-} , TiO_6^{8-} , TiO_6^{9-} , CrO_6^{9-} , and FeO_4^{6-} clusters representing Fe^{3+} , Fe^{2+} , Ti^{4+} , Ti^{3+} , and Cr^{3+} ions in octahedral coordination and Fe^{2+} in tetrahedral coordination, respectively, with oxygen.

Calculations were performed using the SCF-X_α scattered wave molecular orbital (MO) method (6). This is a first principles MO method based on the division of matter into component polyatomic clusters. For example, in a calculation on rutile (TiO_2) the TiO_6^{8-} cluster is used (7), corresponding to a Ti^{4+} ion surrounded by six O^{2-} ions. This cluster is assumed to approximate octahedrally coordinated Ti^{4+} ions in other oxides and silicates, such as ilmenite and certain pyroxenes. Similarly, hematite (Fe_2O_3), eskolaite (Cr_2O_3), wüstite (FeO), and Ti_2O_3 form the basis for calculations on octahedrally coordinated Fe^{3+} , Cr^{3+} , Fe^{2+} , and Ti^{3+} ions (7, 8). The calculated energy levels are in good agreement with transition energies obtained from x-ray photoelectron, emission and absorption spectroscopies, and from UV reflectivity and absorption spectral data (7). One calculated oxygen→ Ti^{4+} charge transfer energy, corresponding to the

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$6t_{1u} \rightarrow 2t_{2g}$ transition, lies at $33,880 \text{ cm}^{-1}$ beyond the visible region. In contrast to crystal field $d \rightarrow d$ transitions, this is a fully allowed transition and is predicted to produce an intense absorption band in the ultraviolet, the absorption edge of which may extend into the visible. Similar calculations for the FeO_6^{10-} cluster leads to an oxygen $\rightarrow \text{Fe}^{2+}$ charge transfer transition predicted at $\sim 37,500 \text{ cm}^{-1}$, in good agreement with experimentally determined spectral features for olivines and pyroxenes (9). Oxygen \rightarrow metal charge transfer energies calculated for other transition metal ions of relevance to lunar studies are summarized in table 1.

Table 1. Calculated Oxygen \rightarrow Metal Charge Transfer Transition Energies

Species	Lowest Energy of O \rightarrow M Transition (cm^{-1})
Octahedral Fe^{3+}	25,330
Octahedral Fe^{2+}	37,500
Tetrahedral Fe^{2+}	33,478
Octahedral Ti^{4+}	33,880
Octahedral Ti^{3+}	41,300
Octahedral Cr^{3+}	59,100

The present work suggests that oxygen \rightarrow metal charge transfer processes involving the more abundant Ti^{4+} and Fe^{2+} cations contribute significantly to spectral properties of lunar materials in the near UV-visible region, but that similar processes involving the less abundant Ti^{3+} and Cr^{3+} cations occur too far into the UV to be important. Evidence summarized previously (10) shows that negligible amounts of Fe^{3+} ions occur in lunar samples. The data in table 1 suggest that if ferric ions were present on the moon, contributions from oxygen $\rightarrow \text{Fe}^{3+}$ charge transfer transitions would extend absorption edges further into the visible region than is observed (11).

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