REASSIGNMENT OF THE IRON(III) ABSORPTION BANDS IN THE SPECTRA OF MARS. David M. Sherman, Dept. of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

Absorption features in the near-infrared and visible region reflectance spectra of Mars have been assigned to specific Fe$^{3+}$ crystal-field and O$_2^-$ + Fe$^{3+}$ charge transfer transitions [1]. Recently, we have obtained near-ultraviolet absorption spectra of iron oxides [2] and have also determined the energies of O$_2^-$ + Fe$^{3+}$ charge-transfer (LMCT) transitions from accurate SCF-X$\alpha$-SW molecular orbital calculations on Fe$_6^+$ and Fe$_4^+$ clusters [3]. (The new calculations are an improvement over those of [4] insofar as the "overlapping sphere" approach to the molecular potential was used.) Both the theoretical and experimental results, together with existing data in the literature, show that some of the previous Fe$^{3+}$ band assignments in the spectra of Mars need to be revised.

Theory of Fe$^{3+}$ spectra in minerals.

Figure 1 gives the Tanabe-Sugano diagram for the electronic states of Fe$^{3+}$ in either octahedral or tetrahedral coordination. The ground $^6A_1$ state arises from the one-electron orbital configuration $(t_2^a)^3(e^a)^2$ where a implies a spin-up orbital. The first two excited states, $^4T_1$ and $^4T_2$, arise from the configuration $(t_2^a)^3(e^a)^1(t_2^b)^1$ where b indicates a spin-down orbital. In this configuration, the $e^a$ orbital is occupied by only one electron; hence, this configuration will undergo a Jahn-Teller splitting. Although usually not recognized as such, this effect is observed in the spectra of Fe$^{3+}$ minerals as splittings of the $^4T_1$ and $^4T_2$ absorption bands. The rest of the ligand field states in Fig. 1 arise from the "spin-flip" configurations $(t_2^a)^2(e^a)^2(t_2^b)^1$ and $(t_2^a)^3(e^a)^1(e^b)^1$. Relative to the ground configuration, the energies of these configurations are independent of 10Dq. The states arising from these configurations occur at nearly constant energies in different Fe$^{3+}$ oxides and silicates. (The small dependence of the high energy $^4T_1$ and $^4T_2$ states on 10Dq is due to configurational interaction.) In these minerals, the $^4E,^4A_1(^4G)$ state occurs at ca. 23 kK (0.43 m) while the $^4E(^4D)$ state occurs at ca. 27 kK (0.37 m).

For octahedrally coordinated Fe$^{3+}$, the lowest energy LMCT transition is from a $t_{1u}^\beta$ 0 2p non-bonding orbital to the $t_{2g}^\beta$ Fe$^{3+}$ "crystal field" orbital. From the SCF-X$\alpha$-SW molecular orbital calculations, the energy of this transition is estimated to be 37.9 kK (0.26 m) for an Fe$_6^+$ cluster with an Fe-0 distance of 2.05 Å.

The Fe$^{3+}$ ligand field transitions are expected to be both spin- and parity-forbidden. In many systems, however, these transitions become allowed through the coupling of adjacent Fe$^{3+}$ centers by Fe-0-Fe superexchange [5]. In addition to intensifying the Fe$^{3+}$ ligand field transitions, the Fe-0-Fe coupling allows for a new type of electronic transition, namely, the simultaneous excitation of two Fe$^{3+}$ centers by a single photon. These transitions occur at energies given approximately by the sum of two Fe$^{3+}$ ligand field transition energies. At present, these transitions are not fully understood and, in many systems, their identities are uncertain. These phenomena have useful implications for the spectrum of Mars and have been discussed by [6].
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Figure 2 shows the near UV to visible region spectrum of goethite and maghemite. These spectra are very similar to those of the other iron oxides and Fe\textsuperscript{3+} smectites [7]. Features corresponding to the \(^{4}\text{T}_1\text{(}^{4}\text{G})\) and \(^{4}\text{E(}^{4}\text{D})\) states occur at their expected energies. The energy of the \(^{4}\text{T}_1\text{(}^{4}\text{G})\) state is already known (e.g. [8]). From these three state energies, we can calculate the ligand field parameters \(10Dq\), \(B\) and \(C\) and use these to estimate the energies of the other ligand field states. These energies can then be used to assign the remaining features in the spectrum. This procedure gives an internally consistent assignment scheme and physically reasonable values for \(10Dq\), \(B\) and \(C\). The values for \(10Dq\) are in good agreement with that estimated from the \((\text{FeO}_6)^{9-}\) MO calculation (15.8 kK). The highest energy features are assigned to LMCT transitions. Their energies are in good agreement with those estimated by the MO results. The only feature which cannot be directly explained by either the ligand field theory or the MO calculations is the band at 0.49-0.53 \(\mu\). This can be assigned to either a split component (via the dynamic Jahn-Teller effect) of the \(^{6}\text{T}_2\text{(}^{4}\text{G})\) band or to the lowest energy Fe-Fe pair transition, \(^{6}\text{A}_1+^{6}\text{A}_1+^{4}\text{T}_1+^{4}\text{T}_1\). Its absence in the spectra of magnetically dilute systems [e.g. 9] suggests that the latter assignment is correct.

Application to the spectrum of Mars.

Table 1 gives the range of energies observed for transitions in different Fe\textsuperscript{3+} oxides and silicates together with a new band assignment scheme for the spectra of Mars. The band positions in the spectrum of Mars are only approximate. In the Martian spectrum, the visible region absorption edge is due mainly to the Fe\textsuperscript{3+} ligand field transitions (intensified by the Fe-O-Fe superexchange interactions) and the Fe-Fe pair excitation. When higher-resolution spectra of Mars become available, these band assignments may allow for an estimate of the ligand field parameters of Fe\textsuperscript{3+} in the Martian mineralogy. It is uncertain, however, whether this would be mineralogically diagnostic since these quantities show little variation among iron oxides and silicates [10].