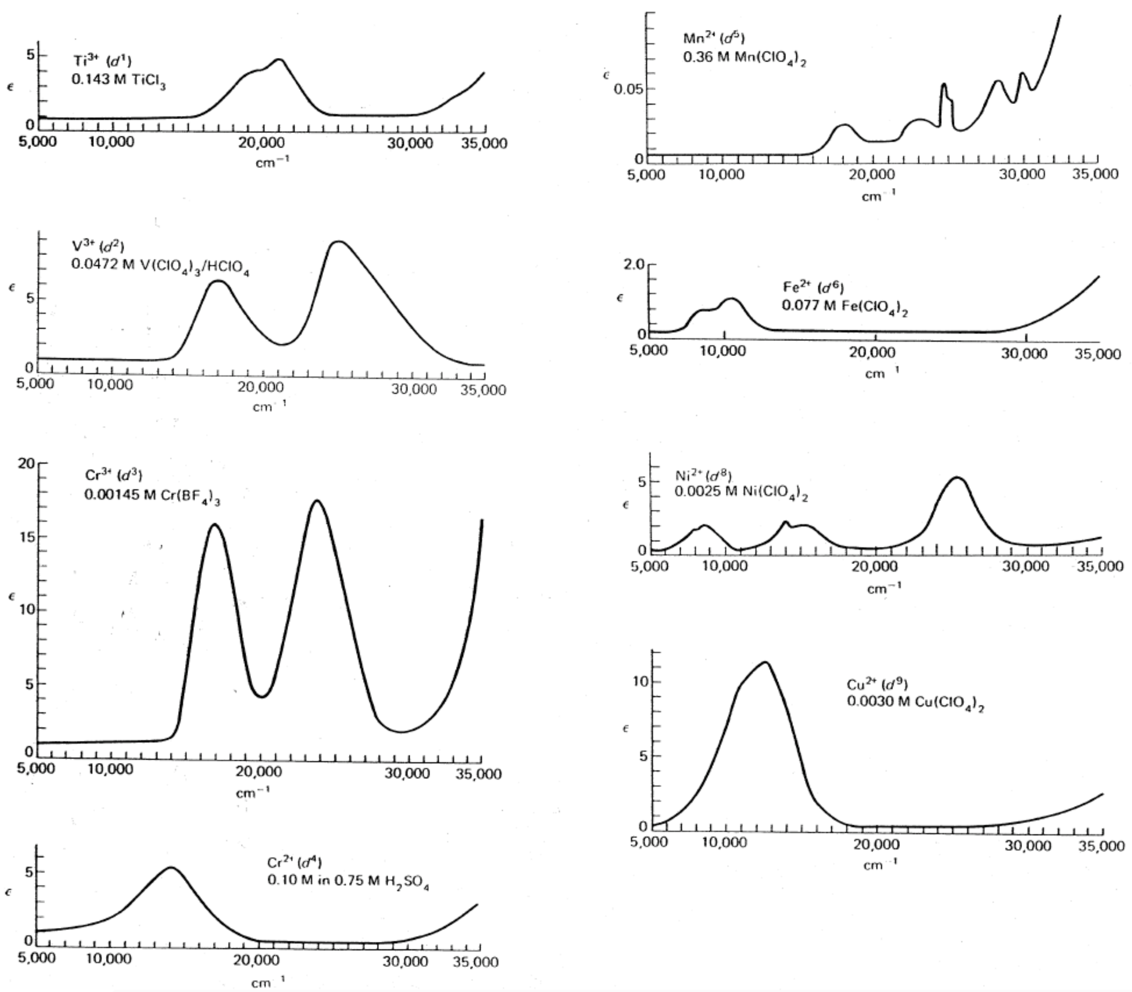
Assign the electronic absorption spectra of the following ions in water.



Answers

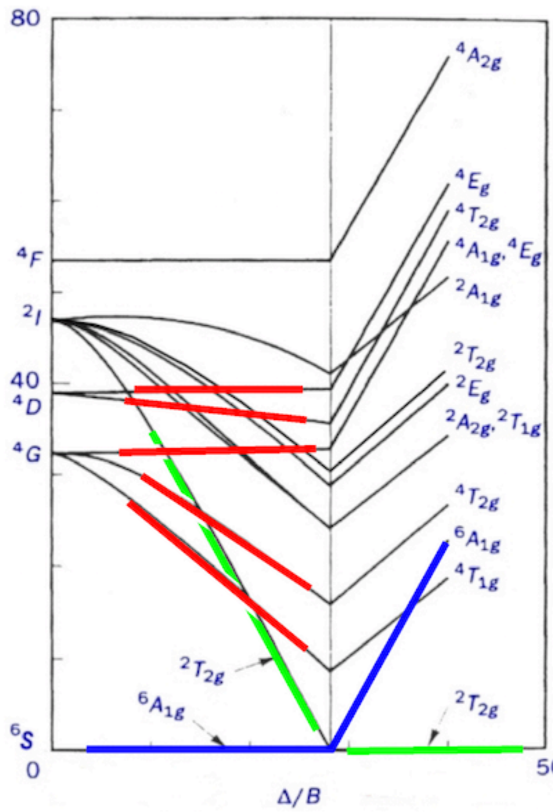
d^1 Ti^{3+}. A $^2T_{2g}$ to ^2E_g dd transition split because of Jahn-Teller distortion.

d^2 V^{3+}. The complex will have a $^3T_{1g}$ ground state corresponding to a $t_{2g}^2\ e_g^0$ configuration. The first excited state will arise from a $t_{2g}^1\ e_g^1$ configuration - the $^3T_{2g}$ state in the Orgel diagram. This will be the lowest energy transition and is found at about 18,000 cm^{-1}. The Orgel diagram predicts two transitions to $^3T_{1g}$ and at higher energy to $^3A_{2g}$, which correspond well with the observed transitions at about 25,500 cm^{-1} and shoulder at 30,000 cm^{-1}. (The asymmetric shape of the 26,000 cm^{-1} transition suggests a second transition at higher energy that is not clearly resolved, or that the third transition is not observed.)

d^3 Cr^{3+}. The ground configuration of t_{2g}^3 corresponds to a $^4A_{2g}$ state. From this state, there are two excitations to $^4T_{1g}$ and $^4T_{2g}$ possible, fairly close in energy - 17,000 and 24,000 cm^{-1}. There is a third spin-allowed transition at higher energy that is not observed.

d^4 Cr^{2+}. The ground state is a ^5E_g which can only be excited to the $^5T_{2g}$, which is observed at about 15,000 cm^{-1}.

d^5 Mn^{2+}. No Orgel diagram because there are no spin-allowed dd transitions possible. Looking at the Tanabe-Sugano diagram, there is only one state with a multiplicity of 6 (blue). Therefore, there are no spin-allowed transitions in the visible - the absorbance scale is in the 10^{-2} range, which is indicative of spin-forbidden transitions. These transitions will occur to the multitude of quartet states available (red lines). Transition to the doublet (green) is not observed because it requires movement/spin flip of two electrons. See Tanabe-Sugano diagram below.



d^6 Fe^{2+}. The ^5D term of the free d^6 ion (at the origin of the d^6 Orgel diagram) shows that it splits into $^5T_{2g}$ and ^5E_g states in the presence of a weak octahedral ligand field, such as six waters. The transition at about 10,000 cm^{-1} is an excitation from the $^5T_{2g}$ state to the ^5E_g. It is split into two peaks because of Jahn-Teller distortions in the ground and excited states.

d^8 Ni^{2+}. There are three triplet excited states in the d^8 Orgel diagram: $^3T_{2g}$, $^3T_{1g}$(F) and $^3T_{1g}$(P). Three different excitations are expected, observed at 7500, 15 000, and 25 000 cm^{-1}.

d^9 Cu^{2+}. Since one "hole" in the electronic structure of d^9 is similar to one electron in the d^1 structure. There should be a singlet transition split into two because of the Jahn-Teller effect, as is seen at about 13,000 cm^{-1}.