

A1) How might you use vibrational spectroscopy to determine whether an oxalate complex $M(C_2O_4)_2$ was planar or nonplanar (plane of bound oxalate ligands at right angles)?

The four C=O stretches in a metal bis(oxalato) may occur in a relatively uncluttered spectral region ($1500 - 1700 \text{ cm}^{-1}$). For a square planar geometry, the point group symmetry is D_{2h} , and for a tetrahedral coordination geometry it is D_{2d} . In D_{2h} , the four C=O stretches transform like a_g , b_{1g} , b_{2u} , and b_{3u} . The g vibrations are Raman allowed and all the u vibrations are IR allowed. In D_{2d} symmetry, the four C=O stretches transform like a_1 , b_2 , and e. Two are IR allowed and one is Raman allowed. Thus, a combination of Raman and IR spectroscopy could distinguish the two possibilities.

A2) How would you expect the IR absorptions for the S-O stretches ($1030 - 1140 \text{ cm}^{-1}$) in the sulfate ion to differ for it as a counter ion, as in $[Co(NH_3)_6][SO_4]$, versus when it binds as a monodentate ligand as in $[Co(NH_3)_5(SO_4)][Br]$?

For the free T_d sulfate ion the S-O stretches are $a_1 + t_2$. Only the t_2 stretch is allowed in the IR spectrum. When bound to the metal the attached metal shifts the unique S-OM stretch to low frequency. The three remaining S-O bonds experience a C_{3v} pseudo symmetry and they behave like $a_1 + e$ stretches. Both are IR allowed, so there should be two vibrations in the S-O stretching region ($1030 - 1140 \text{ cm}^{-1}$) when it behaves as a monodentate ligand.

A3) Determine all the vibrations present in CO_2 and N_2O . Sketch the vibrational motions. In the IR spectrum of CO_2 two intense peaks occur at 667 and 2349 cm^{-1} . How would you assign them in the proper symmetry group for a linear molecule? For N_2O three intense IR absorptions occur at 598 , 1285 , and 2224 cm^{-1} . How would you assign these vibrations? (Hint: CO_2 and N_2O are isoelectronic and closely analogous) Nitrous oxide is 310 times as effective as CO_2 as a greenhouse gas. Suggest one possible reason why.

CO_2 a σ_g^+ symmetric stretch, a doubly degenerate π_u bending vibration and a σ_u^+ antisymmetric stretch account for the $3N-5 = 4$ vibrational degrees of freedom. Only π_u^+

and Γ_u are IR allowed. The high frequency vibration (2349 cm^{-1}) is the stretch and the low frequency is the bend (667 cm^{-1}), since bending deformations always require less energy than stretches. N_2O has a Γ^+ symmetric stretch (1285 cm^{-1}), a Γ^+ asymmetric stretch (2224 cm^{-1}), and a Γ bending vibration (598 cm^{-1}). The assignments are by analogy to carbon dioxide. Although the $\text{N}=\text{O}$ and $\text{N}=\text{N}$ stretches are different, due to the similar bonding (isoelectronic with CO_2) and similar masses and bond strengths the two Γ^+ stretches mix strongly to yield normal modes very similar to those of CO_2 .

The greater number of allowed vibrational absorptions, as well as combinations and overtones leads to nitrous oxide being a stronger absorber than carbon dioxide; however, the fact that absorption in the carbon dioxide region is nearing saturation (logarithmic scale of absorbance) is also a factor.

A4) Use the energy level diagram for ferrocene on p 245 of your text to predict the lowest vibronically allowed electronic transition or transitions if several are expected to be close in energy. What is the lowest dipole allowed electronic transition? Give both the orbital transition and state symmetries. Indicate the polarization expected for the dipole allowed transition.

The lowest one electron transition is $e_{2g} \rightarrow a_{1g}$. This $e_{2g}^3 a_{1g}^1$ configuration will generate the $^1E_{2g}$ excited state. This is dipole forbidden, as the ground state is $^1A_{1g}$, but will be vibronically allowed by coupling with a vibration of symmetry such that the direct product $E_{2g} \cdot \text{vib} \cdot a_{2u}$ or $E_{2g} \cdot \text{vib} \cdot e_{1u}$ contains the totally symmetric representation. This will occur for vibrations of e_{2u} and e_{1u} symmetry. The skeletal vibrations of ferrocene include two e_{1u} vibrations corresponding to a ring tilt and a metal-ring slip (p391 of Nakamoto). Thus, this transition is vibronically allowed. The next promotion $e_{2g} \rightarrow a_{2u}$, gives rise to the excited singlet state $^1E_{2u}$. This is not dipole allowed either. The next $e_{2g} \rightarrow e_{1u}$ promotion yields $^1E_{2u}$ and $^1E_{1u}$ states. The transition $^1A_{1g} \rightarrow ^1E_{1u}$ is dipole allowed with x,y polarization.

A5) Would you expect the ferrocenium cation (obtained on one-electron oxidation) to have the same symmetry structure as ferrocene.

The ferrocenium cation has a hole in the e_{2g} orbital, which would yield a $^2E_{2g}$ ground state. This is forbidden by the Jahn-Teller distortion and should distort from D_{5d} symmetry along the a_{2g} or e_{1g} normal modes. The e_{1g} ring tilt is one possibility.