

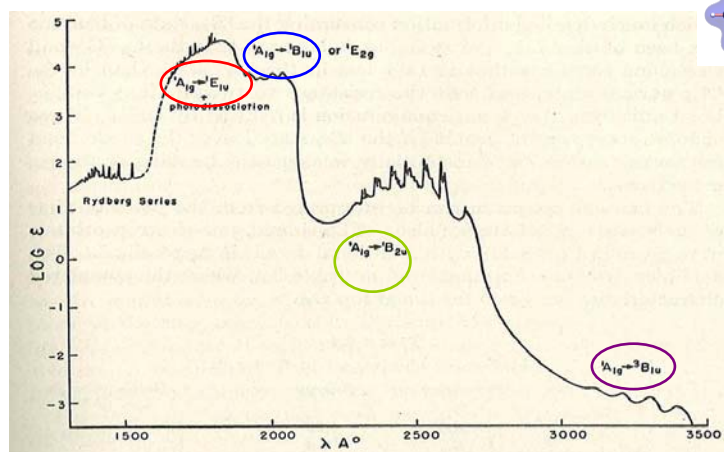
# Configurations versus States; Vibronic Coupling

C734b 2008

C734b Spectroscopy-I

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## Electronic Spectrum of Benzene



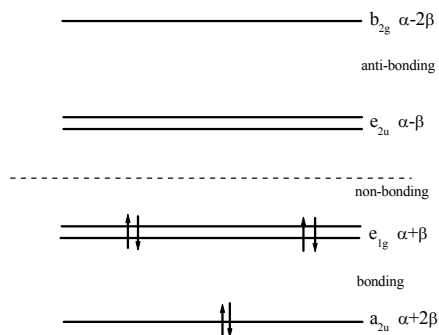
The fully allowed  $A_{1g} \rightarrow E_{1u}$  transition is assigned to the most intense transition which occurs at 180 nm. The vibronically assisted  $A_{1g} \rightarrow B_{1u}$  and  $A_{1g} \rightarrow B_{2u}$  transitions are assigned to the less intense bands at 200 and 260 nm, respectively. The spin-forbidden  $A_{1g} \rightarrow B_{1u}$  is assigned to the lowest energy and lowest intensity transition at 340 nm.

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### Why?

From previous work on the MOs of benzene, we deduced that its ground state electronic configuration was  $(a_{2u})^2(e_{1g})^2$



This is a closed shell configuration which satisfies the Pauli Exclusion Principle. As such the ground state wavefunction forms a basis for the totally symmetric IR  ${}^1\Gamma_1$  ( ${}^1A_{1g}$ )

\*This argument is general for closed shell atoms and molecules.

IR  $(a_{2u})^2$  can be found from:  $a_{2u} \otimes a_{2u}$

$(e_{1g})^4$  can be viewed as  $(1e_{1g})^2(2e_{1g})^2$ . Consider  $e_{1g} \otimes e_{1g}$

$D_{6h}$   $E$   $2C_6$   $2C_3$   $C_2$   $3C_2'$   $3C_2''$   $i$   $2S_3$   $2S_6$   $\sigma_h$   $3\sigma_d$   $3\sigma_v$

$a_{2u}$  1 1 1 1 -1 -1 -1 -1 -1 -1 1 1

$a_{2u} \otimes a_{2u}$  1 1 1 1 1 1 1 1 1 1 1 1 =  $A_{1g}$

$e_{1g}$  2 1 -1 -2 0 0 2 1 -1 -2 0 0

$e_{1g} \otimes e_{1g}$  4 1 1 4 0 0 4 1 1 4 0 0

Reduction yields:  $A_{1g} \oplus A_{2g} \oplus E_{2g}$

Same argument holds for  $(t)^6$  configurations which can be viewed as  $(1t)^2(2t)^2(3t)^2$ .

The first excited state of benzene is  $(a_{2u})^2(e_{1g})^3(e_{2u})^1$

The doubly occupied  $a_{2u}$  orbital and one of the  $e_{1g}$  orbitals are closed so they transform as  $A_{1g}$ .

Only the singly occupied orbitals need to be considered:

Excited state can be written as  $(e_{1g})^1(e_{2u})^1$

Can show that in  $D_{6h}$   $e_{1g} \otimes e_{1u} \rightarrow B_{1u} \oplus B_{2u} \oplus E_{1u}$

This means that the configuration  $(e_{1g})^1(e_{2u})^1$  leads to 3 electronic states with  $B_{1u}$ ,  $B_{2u}$ , and  $E_{1u}$  symmetry.

**The only system where configurations  $\equiv$  states are those with only one electron.**

**Next:** examine the dipole moment operator.

In  $D_{6h}$  (x,y) transform according to  $E_{1u}$  and z transforms according to  $A_{2u}$

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**Recall:**  $\Gamma_{ex} \otimes \Gamma_{\hat{o}} \otimes \Gamma_g \subset \Gamma_1$  to be allowed

$$\Gamma_g = \Gamma_1 = A_{1g}$$

Therefore need only find out if  $\Gamma_{ex} \otimes \Gamma_{\hat{o}} \subset A_{1g}$

$$B_{1u} \otimes E_{1u} = E_{2g} \quad \text{forbidden}$$

$$B_{1u} \otimes A_{2u} = B_{2g} \quad \text{forbidden}$$

$$B_{2u} \otimes E_{1u} = E_{2g} \quad \text{forbidden}$$

$$B_{2u} \otimes A_{2u} = B_{1g} \quad \text{forbidden}$$

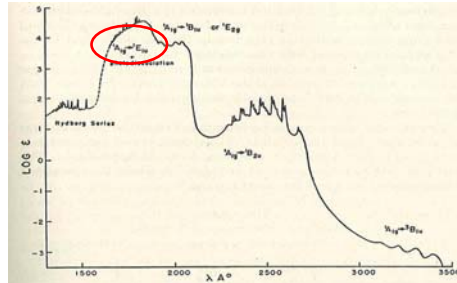
$$E_{1u} \otimes E_{1u} = A_{1g} \oplus A_{2g} \oplus E_{2g} \quad \text{allowed}$$

$$E_{1u} \otimes A_{2u} = E_{2g} \quad \text{forbidden}$$

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$\Rightarrow {}^1A_{1g} \rightarrow {}^1E_{1u} \equiv$  only symmetry allowed transition; found at  $\lambda \sim 180$  nm



**Aside:** what is the superscript on the state labels?

This is the spin multiplicity  $2S+1$ . Although each electron has spin  $s = \frac{1}{2}$ , the total spin of the system is  $S = 0$ . Therefore  $2S+1 = 1$ . These are called **singlet states**

If the electron flips its spin during a transition (violation of  $\Delta S = 0$  selection rule), then the total spin of the system is  $S = 1$ . Therefore  $2S+1 = 3$ . These are called **triplet states**.

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Not shown is a very weak band near 350 nm which is assigned to  ${}^1A_{1g} \rightarrow {}^3E_{1u}$  made partially allowed through spin-orbit coupling.

The transitions:  ${}^1A_{1g} \rightarrow {}^1B_{1u}$  and  ${}^1A_{1g} \rightarrow {}^1B_{2u}$

are symmetry-forbidden but can be made allowed through vibronic coupling

### Vibronic Coupling

The electronic wave function  $\Psi_a(\vec{r}, \vec{R})$  depends not only on the electron coordinates  $\{\vec{r}\}$  but also on the nuclear coordinates  $\{\vec{R}\}$ . Here  $a$  are the electronic quantum numbers.

Since the mass of the electron  $\ll$  mass of the nuclei, the electronic motion follows the nuclear motion **adiabatically**.

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Therefore, we can adopt the Born-Oppenheimer approximation and write the wave function as:

$$\Psi_a(\vec{r}, \vec{R}) = \psi_{a,R}(\vec{r}) \chi_{a,v}(\vec{R})$$

where  $v$  is a vibrational quantum number.

The electronic wave function depends parametrically on the positions of the nuclei. The electronic energy  $E_a(\mathbf{R})$  is calculated at a series of nuclear displacements,  $\mathbf{R}$ , which provides the potential energy  $V_a(\mathbf{R})$  for the vibrational motion.  $V_a(\mathbf{R})$  depends on the electronic state,  $a \equiv$  adiabatic potential.

It is invariant under symmetry operations.

Matrix element for vibrating molecule becomes:  $\langle \Psi_a | \hat{D} | \Psi_a \rangle \approx \langle \psi^\ell \chi^k | \hat{D} | \psi^j \chi^i \rangle$   
 $= 0$  unless  $\Gamma^\ell \otimes \Gamma^k \otimes \Gamma^j \otimes \Gamma^i \otimes \Gamma_{(x,y,x)} \subset \Gamma_1$

Since for the fundamental vibration  $\Gamma^i = \Gamma_1$  and  $\Gamma^k \equiv$  one of the IRs  $\Gamma(Q_k)$  to which the normal mode belongs, the question reduces to:

$$\text{does } \Gamma^\ell \otimes \Gamma^j \otimes \Gamma_{(x,y,z)} \subset \Gamma(Q_k)?$$

To find the symmetry forbidden transitions that are vibronically allowed you must do a normal mode analysis.

At this point it is only relevant to know that benzene has modes with  $B_{2g}$  and  $E_{2g}$  symmetry

In  $D_{6h}$  symmetry the dipole moment forms a basis for the representations:

$$A_{2u} \oplus E_{1u} = \Gamma_{(x,y,z)}$$

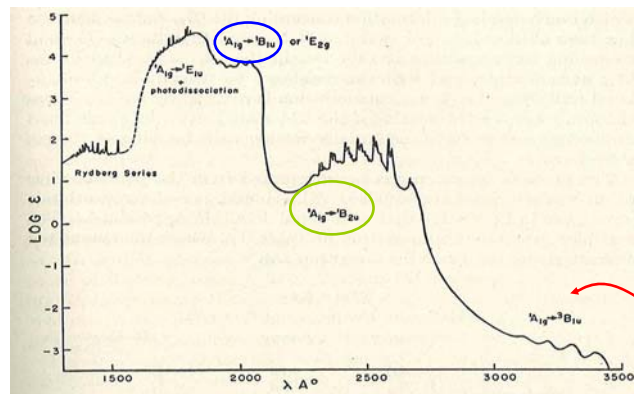
Since the ground state is  ${}^1A_{1g}$

$$\begin{aligned} \Gamma(\psi_e') \otimes \Gamma_{(x,y,z)} &= B_{1u} \otimes (A_{2u} \oplus E_{1u}) = B_{2g} \oplus E_{2g} \\ &= B_{2u} \otimes (A_{2u} \oplus E_{1u}) = B_{1g} \oplus E_{2g} \end{aligned}$$

Since  $B_{2g}$  and  $E_{2g}$  are normal modes

$$\Rightarrow {}^1A_{1g} \rightarrow {}^1B_{1u} (\approx 200 \text{ nm}); \quad {}^1A_{1g} \rightarrow {}^1B_{2u} (\approx 260 \text{ nm})$$

become allowed through vibronic coupling



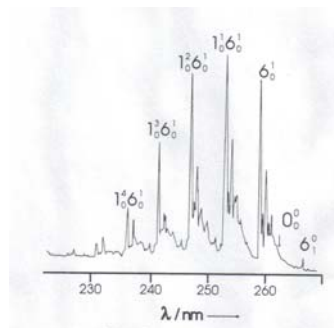
Transitions which are symmetry forbidden but vibronically allowed can be expected to be weaker than symmetry allowed transitions, and are generally broadened (due to vibrational fine structure)

**Note:** there is an even weaker spin-forbidden transition near 325 nm:  ${}^1A_{1g} \rightarrow {}^3B_{1u} (\approx 325 \text{ nm})$

Label vibronic transitions as:  $1_{v_1}^1 2_{v_2}^1 \dots$

Here 1, 2, number which normal mode is involved,  $v$  is the ground state vibrational quantum number and  $v'$  is the excited state vibrational quantum number

High resolution spectrum of  ${}^1A_{1g} \rightarrow {}^1B_{2u}$  ( $\approx 260$  nm)



6 means  $v_6$  which has  $E_{2g}$  symmetry. 1 means  $v_1$  which is the ring breathing mode and has  $A_{1g}$  symmetry  
0 indicates the origin line (electronic transition with no vibrations).

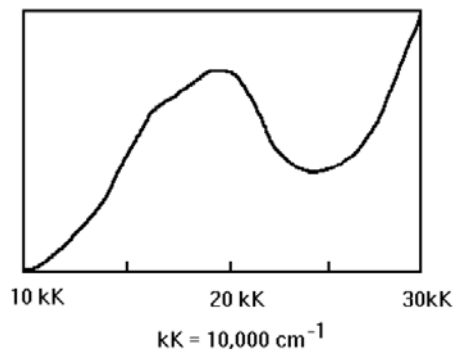
Vibronic coupling also called the Herzberg-Teller effect and represents a breakdown of the Born-Oppenheimer Approximation.

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## Electronic Spectrum of $Ti(H_2O)_6^{3+}$

Visible Absorption Spectrum of  $Ti(H_2O)_6^{3+}$



The ground state of this  $nd^1 O_h$  complex is  $t_{2g}^1$  and its first excited state is  $e_g^1$ . This means that this is a d-d transition which is symmetry forbidden by parity.

Still  $Ti(H_2O)_6^{3+}$  has an absorption at  $20,000\text{ cm}^{-1}$  ( $500\text{ nm}$ ) and a shoulder just to lower energies.

**Why?**

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First examine  $\Gamma(\psi_{ex}) \otimes \Gamma(\psi_g) = e_g \otimes t_{2g} = T_{1g} \oplus T_{2g}$  in  $O_h$

Does this direct product contain  $\Gamma_{(x,y,z)} = T_{1u}$ ? (Read off character table)

**No!**  $\Rightarrow t_{2g}^1 \rightarrow e_g^1$  is symmetry (parity forbidden)

**Next:** examine

$$\Gamma(\psi_{ex}) \otimes \Gamma(\psi_g) \otimes \Gamma_{(x,y,z)} = E_g \otimes T_{2g} \otimes T_{1u} = A_{1u} \oplus A_{2u} \oplus 2E_u \oplus 2T_{1u} \oplus 2T_{2u}$$

Can also show that normal modes for a  $ML_6$  complex form bases for:

$$A_{1g} \oplus E_g \oplus T_{2g} \oplus 2T_{1u} \oplus T_{2u}$$

Therefore parity forbidden transition can become vibronically allowed through coupling with odd parity  $T_{1u}$  and  $T_{2u}$  normal modes

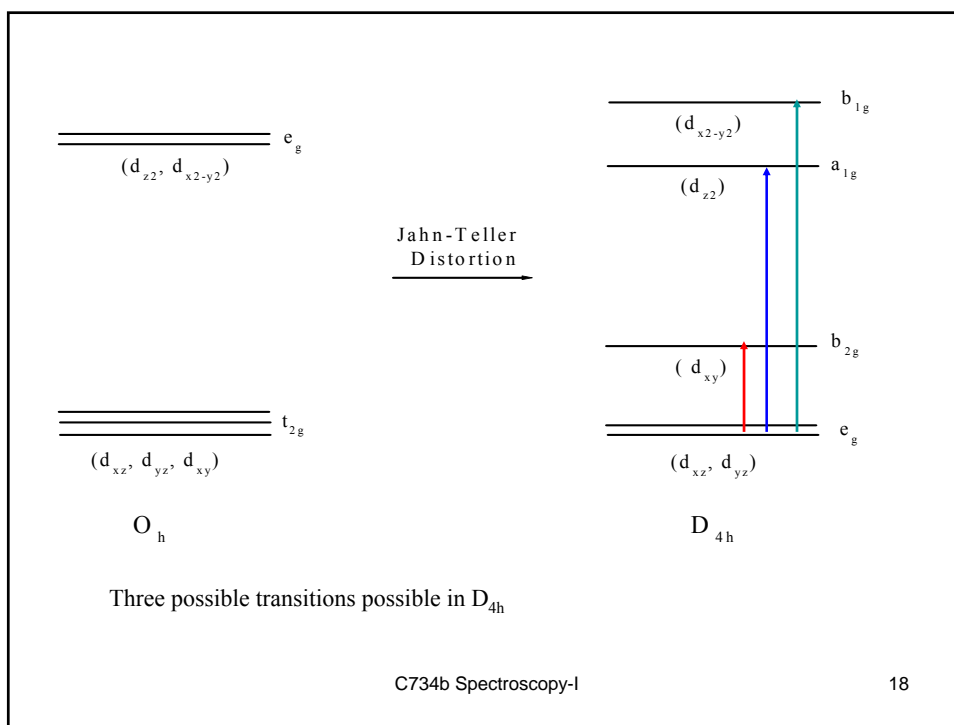
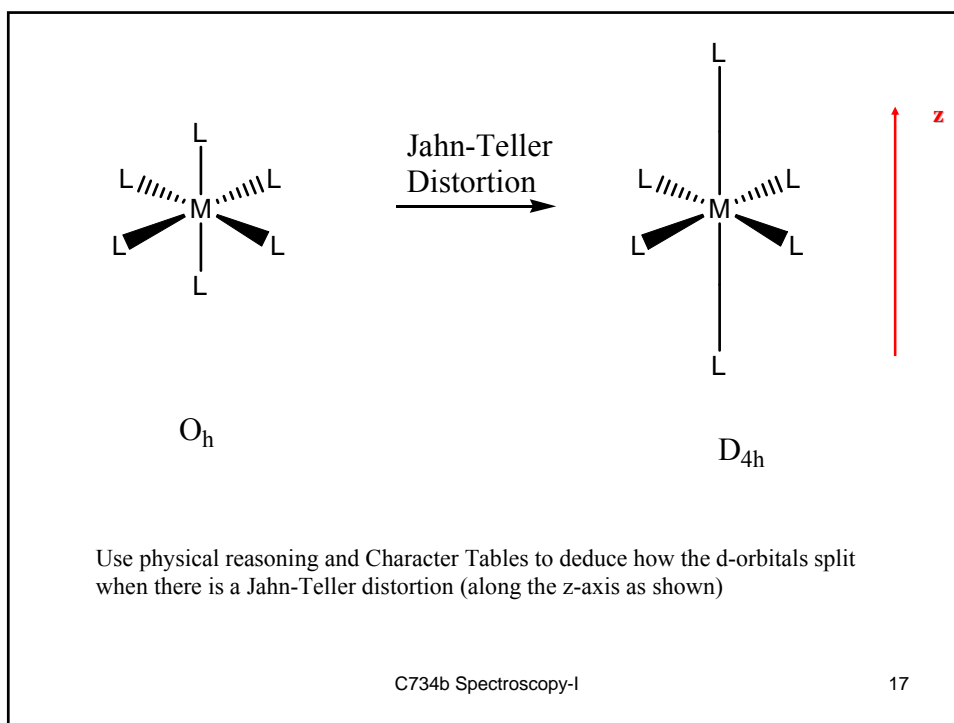
**Note:** as this is a  $d^1$  system, the spin multiplicity is  $2S+1 = 2(\frac{1}{2})+1 = 2$ .  
These are called **doublet** transitions

$\Rightarrow {}^2T_{2g} \rightarrow {}^2E_g$  accounts for the absorption band.

**Why is there additional structure?**

The additional band is associated with a lowering of the symmetry due to the Jahn-Teller effect. Here the symmetry of the  $O_h$  complex is reduced to  $D_{4h}$  by elongation of the axial ligand bond lengths.





First:  $e_g \otimes b_{2g} = e_g$  **symmetry forbidden**  $\because \Gamma_{(x,y,z)} = A_{2u} \oplus E_u$  in  $D_{4h}$

Similarly:  $e_g \otimes a_{1g} = e_g$  **symmetry forbidden**

$e_g \otimes b_{1g} = e_g$  **symmetry forbidden**

Can show that the 15 normal modes of a  $D_{4h}$  complex transform as:

$$\Gamma_{vib} = 2A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g \oplus 2A_{2u} \oplus B_{2u} \oplus 3E_u$$

Have to mix in "u" vibrational modes to make the transition vibronically allowed.  
Which ones?

Examine:  $\Gamma(\psi_{ex}) \otimes \Gamma(\psi_g) \otimes \Gamma(Q_k) = E_g \otimes \Gamma(Q_k)$

Does it contain  $\Gamma_{(x,y,z)}$  = component of dipole moment operator?

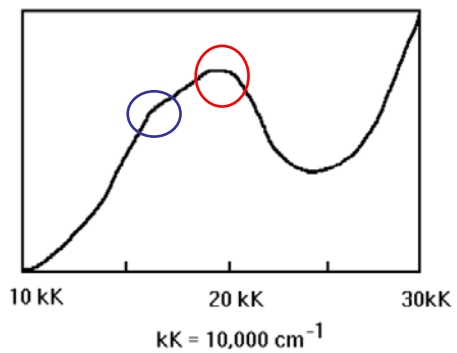
Recall:  $\Gamma_{(x,y,z)} = A_{2u} \oplus E_u$

$A_{2u} \otimes E_g = E_u$  **vibronically allowed**

$B_{2u} \otimes E_g = E_u$  **vibronically allowed**

$E_u \otimes E_g = A_{1u} \oplus A_{2u} \oplus B_{1u} \oplus B_{2u}$  **vibronically allowed**

Visible Absorption Spectrum of  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$



Highest energy transition:  ${}^2E_g \rightarrow {}^2B_{1g}$       The third  ${}^2E_g \rightarrow {}^2B_{2g}$  lies in the infrared

Lower energy shoulder:  ${}^2E_g \rightarrow {}^2A_{1g}$