5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #30: What is in a Character Table and How do we use it?

Last time

matrix representations of symmetry operators
representations of group — same multiplication table as symmetry operators
characters of matrix representations (all we need for most applications)
generate representation from convenient set of objects (basis vectors)

GOT
character table
irreducible representations ← generalization of odd/even
notation — symmetry label for multi-dimensional integral with several non-commuting symmetry operators
} GOAL

reduction of reducible representations

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generate and reduce reducible representations

how do we get and use the fancy labels to the right of characters
(a, b, c)↔(x, y, z) [conventions for x, y, z,
$I_a \le I_b \le I_c$ for a, b, c]
selection rules: pure rotation and rotation-vibration and Raman.
nature of various types of vibration.

Example:

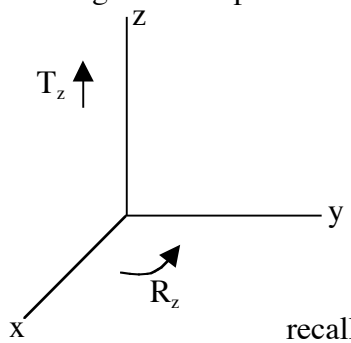
D_{3h}	E	$2C_3(z)$	$3C_2(\perp)$	$\sigma_h(xy)$	$2S_3(z)$	$3\sigma_v$	(rotational level symmetries and perturbations) Rotations, Translations, IR selection rules, p–orbitals electronic selection rules (magnetic dipole)	Polarizability, Raman Selection Rules, d–orbitals
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	–1	1	1	–1	R_z	
E'	2	–1	0	2	–1	0	(x,y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	–1	–1	–1		
A_2''	1	1	–1	–1	–1	1	z	
E''	2	–1	0	–2	1	0	(R_x,R_y)	(xy, yz)

totally symmetric

order of group $g = 12 = \sum_\nu n_\nu^2$ (n_ν is order of ν-th irreducible representation) equal to number of classes: 1 + 2 + 3 + 1 + 2 + 3

R_z "belongs to" A_2', z (or T_z) belongs to A_2''

Use picture to generate representation



	E	C_3	C_2	σ_h	S_3	σ_v	
R_z	1	1	–1	1	+1	–1	A'_2
T_z	1	1	–1	–1	–1	1	A''_2

show with cartoons why $R_z \leftrightarrow A'_2$ from these characters

recall $'$, $''\leftrightarrow\sigma_h$

$1,2\leftrightarrow\sigma_v$

(x,y) means symmetry operation transforms x into y (must generate 2D representation using x and y)

Selection rules: integrand must contain totally symmetric representation.

$$\int \psi_i \, \hat{O}p \, \psi_f \, d\tau \neq 0$$

Direct Product: $\Gamma(\psi_i) \otimes \Gamma(\hat{O}p)$ must include $\Gamma(\psi_f)$ because direct product of any irreducible representation with itself contains the totally symmetric representation.

$$\chi^{\Gamma_i \otimes \Gamma_j} \equiv \left(\chi^i(R_1)\chi^j(R_1), \chi^i(R_2)\chi^j(R_2), \ldots\right)$$

Example: $E' \otimes E'' = (4\ 1\ 0\ -4\ -1\ 0)$
(the irreducible representations must all be $''$)

shortcuts

$A \otimes B = B$ $\quad '\otimes''=''$

$g \otimes u = u$ $\quad 1 \otimes 2 = 2$

Decomposition of (4 1 0 –4 –1 0):

$$a_{A'_2} = \frac{1}{12}[4\cdot1\cdot1 + 1\cdot2\cdot1 + 0 - 4\cdot1\cdot1 - 1\cdot2\cdot1 + 0] = 0$$

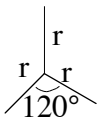
$$a_{E''} = \frac{1}{12}[4\cdot2\cdot1 + 1\cdot2(-1) + 0 - 4\cdot1\cdot(-2) - 1\cdot2\cdot1 + 0] = 1$$

$$a_{A''_1} = 1$$

$$a_{A''_2} = 1$$

So now we know how to work out all selection rules.

Best to work specific example of D_{3h} molecule BCl_3.

Generate 3N dimensional representation. 

planar

	E	C_3	$C_2(\perp)$	σ_h	S_3	σ_v
χ^{red} =	12	$1 + 2\cos\frac{2\pi}{3}$	2(1–2)	4(2–1)	$-1+2\cos\frac{2\pi}{3}$	2(2–1)
	12	0	–2	4	–2	2

$\chi^{red} = \chi^{A_1'} + 3\chi^{E'} + 2\chi^{A_2''} + \chi^{A_2'} + \chi^{E''}$ (total of 12 degrees of freedom)

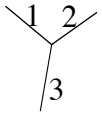
3 translations $E' \leftrightarrow (x,y)$
$A_2'' \leftrightarrow z$

3 rotations $A_2' \leftrightarrow R_z$
$E'' \leftrightarrow (R_x, R_y)$

This leaves 6 vibrations

$\chi^{VIB} = \chi^{A_1'} + 2\chi^{E'} + \chi^{A_2''}$ (total of 6)
(four normal modes, two are doubly degenerate)

We can go further - to figure out bend vs. stretch or mixed character of the 4 normal modes (especially when there is only 1 mode in a symmetry class)

Γ^{RED} from 

(stretches only)

$$\chi^{red} = (3 \quad 0 \quad 1 \quad 3 \quad 0 \quad 1) = \chi^{A_1'} + \chi^{E'}$$

pure stretch (only A'_1)

mixed bend and stretch (there is another E′)

Thus
A_1' pure symmetric stretch
A_2'' pure bend (out of plane – because $\chi(\sigma_h) = -1$)
$2E'$ mixed bend and stretch

scissors ↑↓ pseudo rotation

one out, two in
also pseudo rotation

(compression of one angle rotates around either clockwise or counterclockwise, but no real rotation)

Now we are ready to work out selection rules for vibration-rotation spectra

$$\Gamma^{(v_1,v_2,v_3,v_4)} = \left[\chi^1\right]^{v_1} \otimes \left[\chi^2\right]^{v_2} \otimes \left[\chi^3\right]^{v_3} \otimes \left[\chi^4\right]^{v_4}$$

$$\Gamma^{(0,0,0,0)} = A_1'$$

fundamentals			overtones		
	$\Gamma^{(1\,0\,0\,0)}$	A_1'		$\Gamma^{(2\,0\,0\,0)}$	A_1'
	$\Gamma^{(0\,1\,0\,0)}$	A_2''		$\Gamma^{(0\,2\,0\,0)}$	A_1'
	$\Gamma^{(0\,0\,1\,0)}$	E'		$\Gamma^{(0\,0\,2\,0)}$	$A_1' + A_2' + E'$
	$\Gamma^{(0\,0\,0\,1)}$	E'		$\Gamma^{(0\,0\,0\,2)}$	$A_1' + A_2' + E'$

$E' \otimes E' = (4 \quad 1 \quad 0 \quad 4 \quad 1 \quad 0) = (A_1' + A_2' + E')$ (all $'$)

Selection rules for fundamental bands

$\Gamma' \otimes \Gamma'' =$

$(1\,0\,0\,0) \leftarrow (0\,0\,0\,0)$	A_1'
$(0\,1\,0\,0)$	A_2''
$(0\,0\,1\,0)$	E'
$(0\,0\,0\,1)$	E'

in order for transition integral to be nonzero, need $\Gamma^{x,\,y,\,\text{or}\,z} = \Gamma' \otimes \Gamma''$

mode				
	#1	A_1'	IR	forbidden
	#2	A_2''	z	IR allowed
	#3 or 4	E'	(x, y)	IR allowed

But how will the rotational transitions behave?

inertial axes unit vectors

$Q_e \equiv 0$

$$\text{Recall } \vec{M}_j(\underset{\sim}{Q}) = \hat{a}\left[M_{j,a}(0) + \sum_i \left(\frac{\partial M_{j,a}}{\partial Q_i}\right)_e Q_i + \ldots\right]$$
$$+\hat{b}\left[M_{j,b}(0) + \sum_i \left(\frac{\partial M_{j,b}}{\partial Q_i}\right)_e Q_i + \ldots\right]$$
$$+\hat{c}\left[M_{j,c}(0) + \sum_i \left(\frac{\partial M_{j,c}}{\partial Q_i}\right)_e Q_i + \ldots\right]$$

rotational selection rules

pure rotation spectrum

rotational selection rule in vibration-rotation-band

vibrational selection rules

$\psi(r_{elect}; \mathbf{Q})$

$\Gamma^{(abc)}$

$$\left(\frac{\partial M_{j,abc}}{\partial Q_i}\right)_e = \int \frac{\partial}{\partial Q_i}\left(\psi_j^* \begin{bmatrix} a \\ b \\ c \end{bmatrix} \psi_j\right) d\tau$$

Γ^{Q_i}

totally symmetric

be careful if ψ_j^{elect} is degenerate

So mode #1 A_1' $\frac{\partial M_{j,abc}}{\partial Q_1} = 0$

#2 A_2'' $\frac{\partial M_{j,z}}{\partial Q_2} \neq 0$

#3 E' $\frac{\partial M_{j,x \text{ or } y}}{\partial Q_{3 \text{ or } 4}} \neq 0$

for BCl_3 an oblate symmetric top

z = c x,y = (a,b)

mode #2 fundamental is c type (||)

mode #3,4 fundamentals are a,b type ($\perp$)

$\parallel$	$\Delta K = 0$	weak Q
$\perp$	$\Delta K = \pm 1$	strong Q

General procedure

3N dimensional χ^{RED}

find (and classify) all normal mode symmetries

(x,y,z) $\leftrightarrow$ (a,b,c)

$\uparrow$ highest order C_n

activity and rotational type of each vibrational fundamental

Raman

Figures from Bernath:

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The E-A_1 energy level diagram is given in **Figure 7.51**. The energy level structure of an E vibrational state is complicated by the presence of a first order Coriolis interaction between the two components. The selection rules are $\Delta K = \pm 1$ and $\Delta J = 0, \pm 1$. Note also that for $\Delta K = +1$ the transitions connect to the $(+\ell)$ stack while for $\Delta K = -1$ they connect with the $(-\ell)$ stack. The transition can again be represented by a superposition of sub-bands. Notice how the sub-bands do not line up as they do for a parallel transition, but they spread out (**Figure 7.52**). Each sub-band is separated by approximately $2[A(1-\zeta)-B]$. This gives rise to a characteristic pattern of nearly equally spaced Q branches (**Figure 7.53**).

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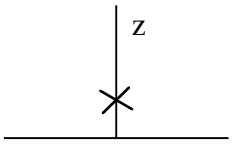
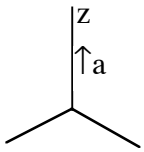
What if BCl_3 were not D_{3h} (planar)?

C_{3v} (like NH_3) prolate or oblate, depending on apex angle

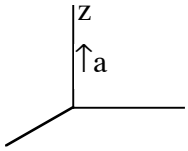


C_{2v} planar (near oblate) tee



planar (near prolate) wye

C_s



planar (3 different bond lengths or 3 different angles)

Truth table

point group	# of normal modes	pure rotational spectrum type	# of IR active fundamentals	Rotational type of IR fundamentals	Raman active fundamentals
D_{3h}	4	—	3	1-c, 2-a,b	
C_{3v}	4	c-oblate a-prolate	4	2-c, 2-a,b	
C_{2v}	6	asymmetric hybrid a,b or b,c	6	3-a, 2-b, 1-c	

For D_{3h} here will be **two** $\perp$ polarized (E′) fundamentals

There will be **one** || polarized (A_2'') fundamental

There will be **one** forbidden (i.e. not observable by IR) fundamental (A_1')

(a,b)-type $\perp$ polarized (i.e. $\Delta K = \pm 1$) oblate top vibrational spectrum (the two E′ modes in BCl_3

$$E_{JK}^{ROT} = BJ(J+1) + (C-B)K^2 \qquad C - B < 0$$

Strong Q branches. Q branch "spikes" dominate band profile.

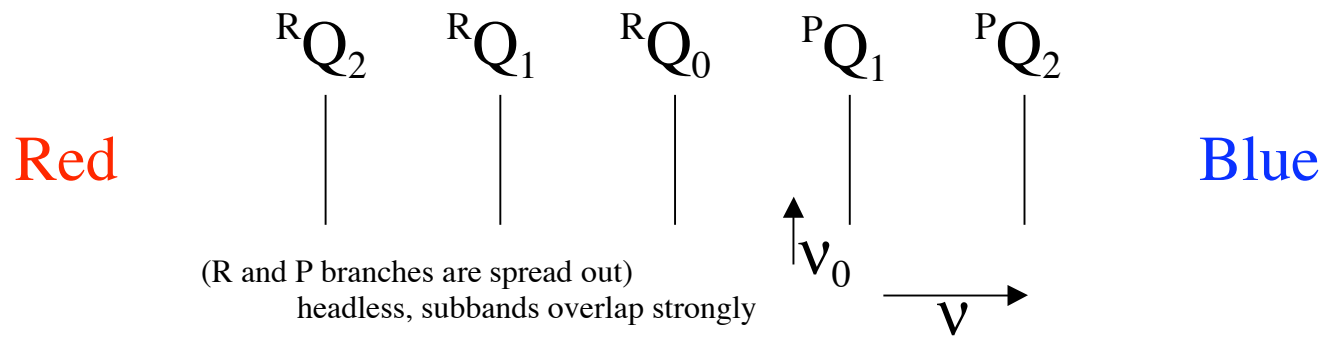
$$K' - K''$$

$$^{R}Q_0(J) \approx (C-B)[1^2 - 0^2] \quad \text{(since } \Delta B \text{ is small)}$$

$$^{R}Q_1(J) \approx (C-B)[2^2 - 1^2]$$

$$^{P}Q_1(J) \approx (C-B)[0^2 - 1^2]$$

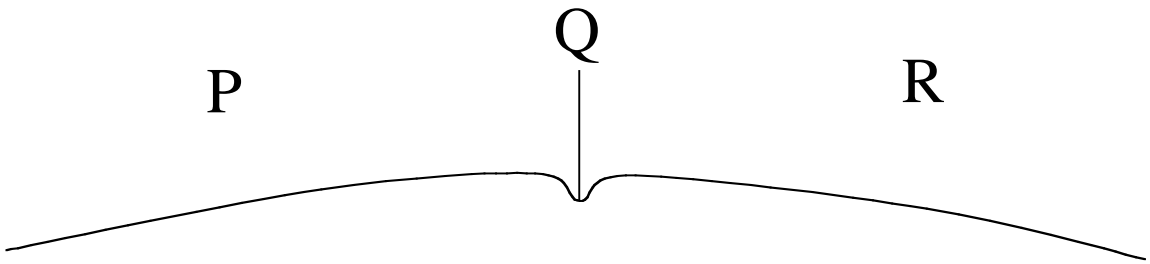
etc.



(R and P branches are spread out)
headless, subbands overlap strongly

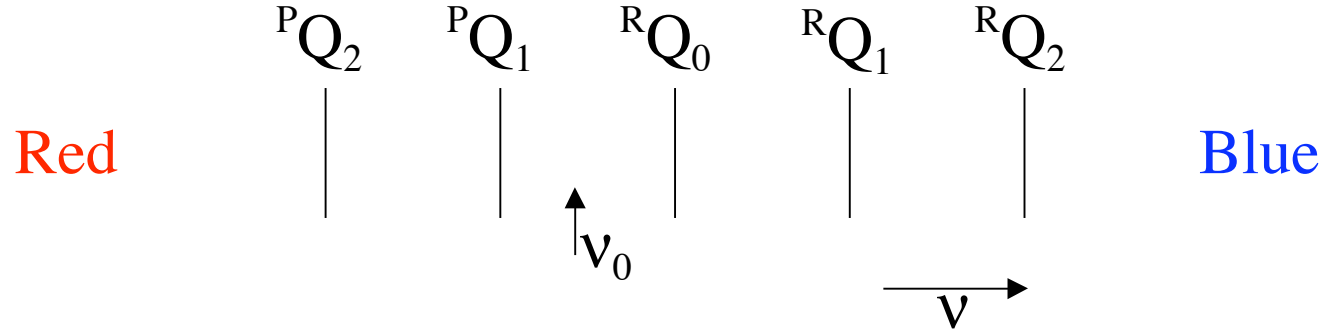
(c)-type || polarized (i.e. $\Delta K = 0$) <u>oblate top</u> vibrational spectrum. (the one A_2'' out-of plane bend from BCl_3)

weak Q branches, except at $J \approx K$ and high K
$\Delta K = 0$ only. All $^{Q}Q_K(J)$ tend to pile up as spike at band origin.



(b,c)-type ⊥ <u>prolate top</u> bands (x,y,z)↔(b,c,a)

Strong Q branches
$^{R}Q_0$ (A – B) 1
$^{R}Q_1$ (A – B) 3



Looks very similar to ⊥ type oblate band except that branches are labeled in reverse order and more spread out (less overlap of K sub-bands) because usually $|A - B|_{prolate} \gg |B - C|_{oblate}$

a-type (||) prolate $\Delta K = 0$, weak Q except at low $J \approx K$

Asymmetric tops: Resemble symmetric top when $J \approx K$
More complicated because $E_{J_{K_a K_c}}$ can't be separated into J-dependent and K-dependent additive terms.

Special simplification for linear molecules.

zero-point level has only $\ell = 0$ vibrational angular momentum.

There is no K projection of J.

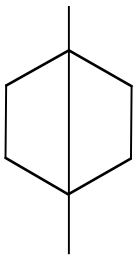
Bending mode is $\pi \leftrightarrow \ell = 1$.

$\parallel$ type $\Delta\ell = 0$ (anti-symmetric stretch), $\perp$ type $\Delta\ell = \pm 1$ (bend)

Benzene

				thru atoms ↓	thru bonds ↓		h = 24				
E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
36	0	0	0	–4	0	0	0	0	12	0	+4

D_{6h}	D_6
$A_{1g}\ \frac{1}{24}(\underline{-12}+12+12+36)=2$	$\frac{1}{12}[36-12]=2$
$A_{2g}=\frac{1}{24}(36+12+12-\underline{12})=2$	$\frac{1}{12}[36+12]=4$
$B_{1g}=\frac{1}{24}(36-12-12-12)=0$	$\frac{1}{12}[36-12]=2$
$B_{2g}=\frac{1}{24}(36+12-\underline{12}+12)=2$	$\frac{1}{12}(36+12)=4$
$E_{1g}=\frac{1}{24}[72-24]=2$	$\frac{1}{12}[72]=6$
$E_{2g}=\frac{1}{24}[72+24]=4$	$\frac{1}{12}[72]=6$
$E_{2u}=\frac{1}{24}[72+-24]=2$	
$A_{1u}=\frac{1}{24}(36-12-12-12)=0$	
$A_{2u}=\frac{1}{24}(36+12-\underline{12}+12)\ =2$	



symmetries and numbers of normal modes

$2A_1$	2g – 1	0u
$4A_2$	2g	2u – 1
$2B_1$	0g	2u
$4B_2$	2g	2u
$6E_1$	2g – 1	4u – 1
$6E_2$	4g	2u
	18	18
	–3	–3
	15	15

translation: $A_{2u}(z)$, $E_{1u}(x,y)$

rotation: $A_{2g}(R_z)$, E_{1g} (R_x, R_y)