

## Vibrational Energy Levels for H<sub>2</sub>O

The vibration QNs of each modes are given in parentheses ( $\nu_1, \nu_2, \dots, \nu_{3N-6}$ )

In water we have ( $\nu_1, \nu_2, \nu_3$ )

Fundamental levels : are levels with one  $\nu_i = 1$  and all other  $\nu_i$ 's = 0

e.g. (1, 0, 0) fundamental sym. str.

Overtone levels : are levels with one  $\nu_i > 1$  and all other  $\nu_i$ 's = 0

e.g. (0, 0, 2) 1st overtone antisym. str. level.

Combination levels : are levels with more than  $\nu_i \neq 0$

Although combination levels exist, transitions among them is governed by symmetry rules.

The ground level (0, 0, 0) has the energy of:

$$\bar{E} = \sum_i^{3N-6} \frac{1}{2} h\nu_i \quad (\text{zero-point energy})$$

$$= (3900 + 3800 + 1600) \text{ cm}^{-1} / 2$$

$$= 4650 \text{ cm}^{-1}$$

① In the case of water molecule, vibrational energy levels are non degenerate.

However, if some normal modes are degenerate, like bending vibration in CO<sub>2</sub>, there is going to be a degeneracy in such a level.

For example:

In CO<sub>2</sub>

(0, 0, 0) ground level is degenerate as  $\nu_2$  is degenerate and two possible combinations are there ( $\nu_2$  and  $\bar{\nu}_2$  are of the same energy).

② Water molecule can represent "accidental degeneracy".

This happens when two vibrational levels have exactly the same energy.

for example:

If  $\nu_1 = 3\nu_2$  then:

(1, 0, 0, ..., 0) and (0, 3, 0, 0, ..., 0) are of the same energy.

③ A very common observation is "near-degeneracy".

This can be seen in vibrational levels of H<sub>2</sub>O.

for example:

\* (0, 0, 1) and (1, 0, 0)

\* (0, 0, 2), (1, 0, 1) and (2, 0, 0)

Near degeneracy gives rise to a commonly observed property in IR and Raman spectra, that is called "Fermi Resonance".

(A) Symmetry of vibrational levels can be assigned by using group theory.

For a given level, symmetry characters are multiplied to yield the symmetry species assigned to that level.

In  $H_2O$  molecule:

- $\nu_1$  and  $\nu_2$  belong to  $A_1$  species.
- $\nu_3$  belongs to  $B_2$  species.

The vibrational ground level is always having the highest symmetry.

Thus,  $(0,0,0)$  is  $A_1$

For the three fundamental levels in  $H_2O$ :

- Ground level  
↓
- $(1,0,0) : A_1 \times A_1 = A_1 \quad \nu_1$
  - $(0,1,0) : A_1 \times A_1 = A_1 \quad \nu_2$
  - $(0,0,1) : A_1 \times B_2 = B_2 \quad \nu_3$

For the three 1st overtone levels in  $H_2O$

- $(2,0,0) : A_1 \times A_1 = A_1 \quad 2\nu_1 \quad (\nu_1 + \nu_1)$
- $(0,2,0) : A_1 \times A_1 = A_1 \quad 2\nu_2 \quad (\nu_2 + \nu_2)$
- $(0,0,2) : B_2 \times B_2 = A_1 \quad 2\nu_3 \quad (\nu_3 + \nu_3)$

5) Transitions between non-degenerate vibrational states are governed by the general formula:

$$\Gamma(\Psi') \times \Gamma(\Psi'') = \Gamma(\bar{T}_x) \text{ and/or } \Gamma(\bar{T}_y) \text{ and/or } \Gamma(\bar{T}_z)$$

- $\Gamma$  is the irreducible representation of a given species.
- $\Gamma(\bar{T}_x)$  and  $y$  and  $z$  are the irreducible representations corresponding to a translational motion.

Those in general are equivalent to the change in the dipole moment along  $x, y$  or  $z$  axis.

$\Psi''$  (lower state)  
 $\Psi'$  (upper state)

### 5.1. Fundamental and overtone transitions

$$\Gamma(\Psi') \times A = \Gamma(\bar{T}_e) \quad e = x, y \text{ and/or } z$$

$A = \text{totally symmetric species.}$

Thus, allowed transitions are those given below:

$$\begin{aligned} \Gamma(\bar{T}_x) &\leftarrow A \\ \Gamma(\bar{T}_y) &\leftarrow A \\ \Gamma(\bar{T}_z) &\leftarrow A \end{aligned} \quad A : \text{totally symmetric species.}$$

These three transitions are polarized "experiencing a net change in the dipole moment of the molecule" along one or more axes.

Example:

→ In  $H_2O$ , transitions  $\left\{ \begin{array}{l} A_1 \leftarrow A_1 \\ B_2 \leftarrow A_1 \end{array} \right.$  are allowed.

Polarized along the  $z$ -axis (pointing to  $A_1 \leftarrow A_1$ )

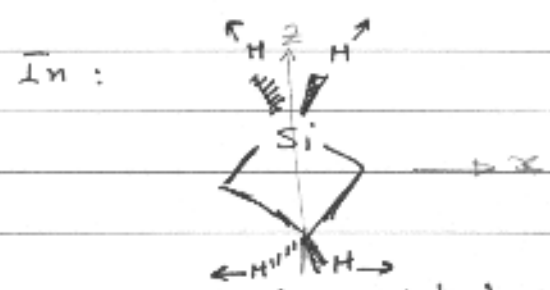
Polarized along the  $y$ -axis (pointing to  $B_2 \leftarrow A_1$ )

\* Generally for a  $C_{2v}$  symmetric molecule:

Allowed transitions

$A_1 \leftarrow A_1$
$B_1 \leftarrow A_1$
$B_2 \leftarrow A_1$

Forbidden transition  $A_2 \leftarrow A_1$



$SiH_2$  symmetric stretch has  $A_1$  symmetry and thus its transition fundamental is allowed.

$SiH_2$  twist has  $A_2$  symmetry and its fundamental transition is symmetry forbidden.

5.2 More general transitions (hot and combination bands)

$$\Gamma(\psi') \times \Gamma(\psi'') = \Gamma(\Gamma_e) \quad \text{where } \Gamma = x, y, \text{ and/or } z$$

Example: (for  $C_{2v}$  symmetry)

\* If  $\Gamma(\psi'') = B_2$   
 $\Gamma(\psi') = B_1$

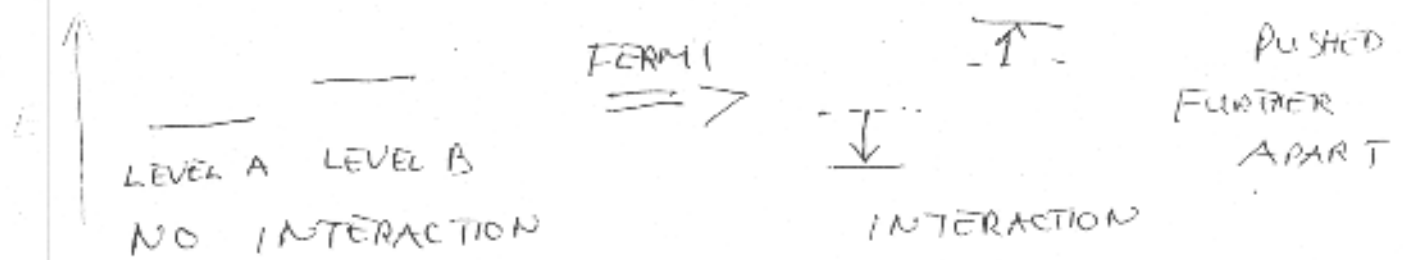
Then  $B_1 \times B_2 = A_2$  (Transition is symmetry forbidden)

\* if  $\Gamma(\psi'') = A_2$   
 $\Gamma(\psi') = B_1$

Then  $B_1 \times A_2 = B_2$  (Transition is symmetry allowed)

FERMI + RESONANCE:

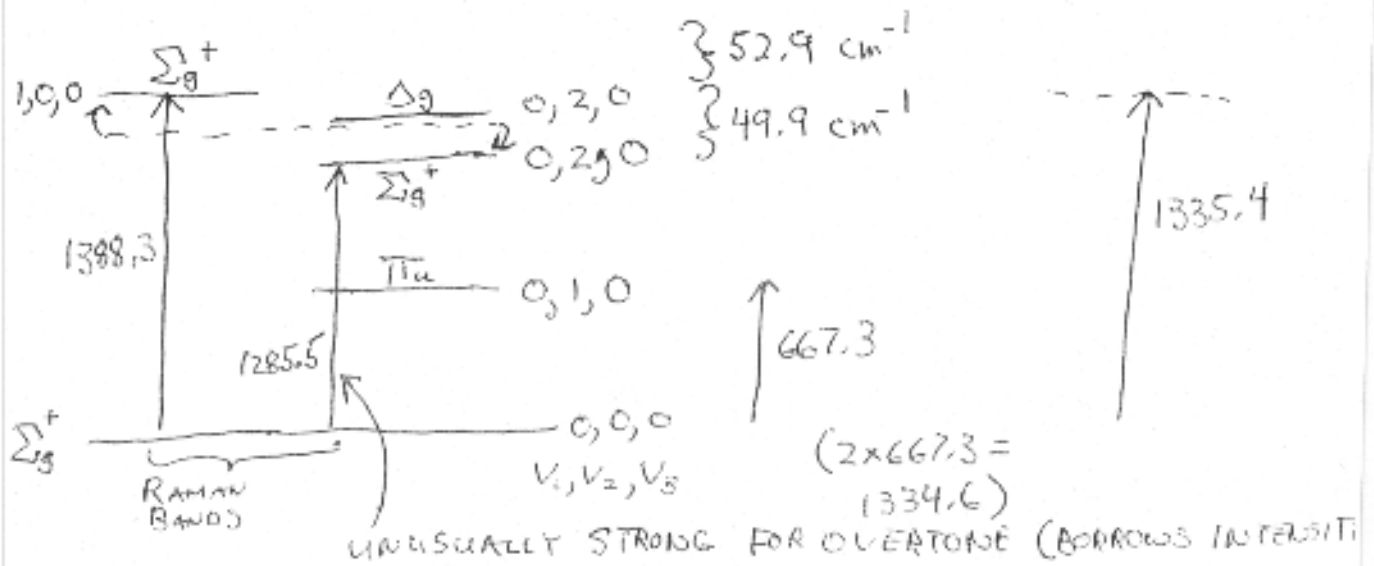
WHEN TWO VIBRATIONAL STATES, BELONGING TO THE SAME SYMMETRY SPECIES, HAVE ALMOST THE SAME ENERGIES SO THAT THEY ARE ACCIDENTALLY DEGENERATE, THEN THE PERTURBATION (ON ACCOUNT OF THE ANHARMONICITY) OF THE LEVELS CAN BE LARGE. THIS IS FERMI RESONANCE



AFTER INTERACTION THE LEVELS ARE "MIXED" AND CONTAIN CONTRIBUTIONS FROM BOTH A and B

THE INTERACTION IS PROPORTIONAL TO PROXIMITY OF LEVELS

EXAMPLE: CO<sub>2</sub> WHERE 2ν<sub>2</sub> ≈ ν<sub>1</sub>



$\Pi_u \times \Pi_u = (\Pi_u)^2 = \Sigma_g^+ + \Delta_g$  (using trigonometry)

ALMOST ALL ORGANIC MOLECULES  
SHOW FERMI RESONANCE IN THE  
C-H STRETCHING REGION

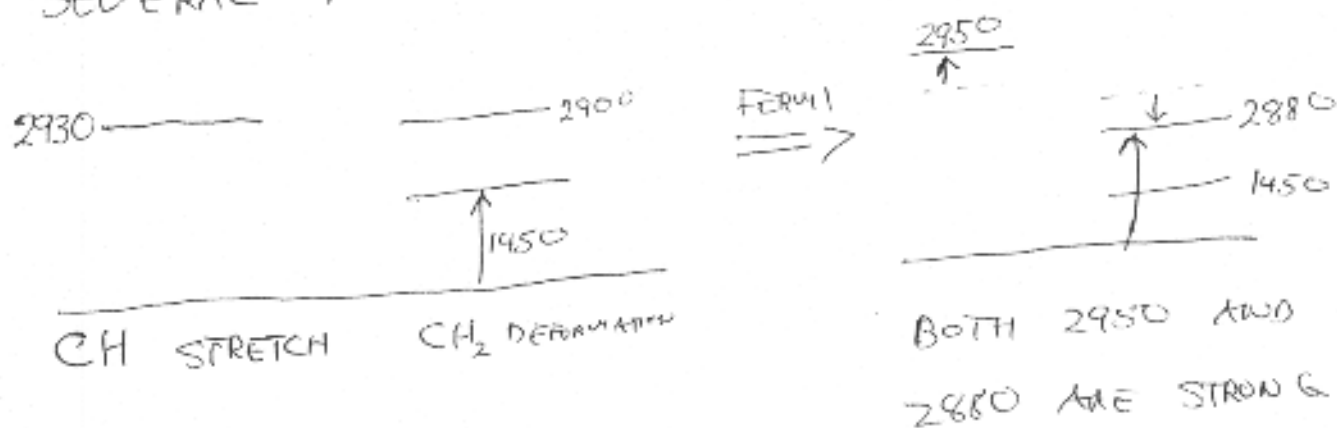
VR-2

C-H STRETCH:  $2850 - 3000 \text{ cm}^{-1}$

$\text{CH}_2$  DEFORMATION (S):  $1400 - 1450 \text{ cm}^{-1}$

2S:  $2800 - 2900 \text{ cm}^{-1}$

TYPICALLY THE C-H STRETCH REGION SHOWS  
SEVERAL MORE BANDS THAN C-H BONDS



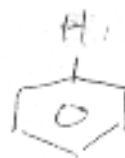
### TELLER-REDLICH PRODUCT RULE

UPON ISOTOPIC SUBSTITUTION, FREQUENCY  
SHIFTS OCCUR FOR A NUMBER OF  
VIBRATIONS

EXAMPLE:



COMPARED  
TO



IN PRINCIPLE, EXPECT 3 SHIFTS:

C-H (OR C-D)  
STRETCH

C-H IN-PLANE  
WAG

C-H OUT-OF-PLANE  
WAG