Molecular Spectroscopy Cheat Sheet by Patrick Wang, Page 1 of 2

1 Introduction

This sheet is based on the lecture notes of Dr J. Olof Johansson of the University of Edinburgh in his Chemistry 3A: Molecular Spectroscopy course.

Transition Dipole Moments

The basis of all spectroscopy is a change in the dipole moment. For a spectroscopic transition to occur, there needs to be a time-dependent dipole moment in the molecule. The intensity of the spectroscopic transition depends on the magnitude squared of the transition dipole moment integral:

$$\mu_{\rm fi} = \int {\rm d}\tau \, \Psi_f^* \hat{\mu} \Psi_i$$

(1)

(3)

(4)

(5)

Term Values

It is important to note that spectroscopy examines the difference in energies of two levels. In general, the wavenumber \tilde{v} is given by the difference between two terms. The term ϵ for a given state is as follows:

$$\epsilon = \frac{E}{hc} = T_e + G(v) + F_v(J)$$
(2)

where T_e , G(v), and $F_v(J)$ correspond to electronic, vibrational and rotational transitions respectively.

2 Rotational Spectroscopy

Rotational spectroscopy is carried out using microwaves and have peaks in the region $10 - 100 \text{ cm}^{-1}$. In order for a molecule to be rotational spectroscopically active, it needs to have a dipole moment, as this is the mechanism in which the molecule interacts with EM radiation.

Moment of Inertia

The moment of inertia of a diatomic molecule can coefficient *D* is defined as follows: be calculated using their reduced mass:

$$u = \frac{m_1 m_2}{m_1 + m_2}$$
$$I = \mu r_0^2$$

where r_0 is the equilibrium bond length. Solving the Schrödinger equation, the energy of a level with rotational quantum number *I* is given by:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$
$$F_J = \frac{h}{8\pi^2 I c} J(J+1)$$

to simplify the above equation, we define a rotational constant, which is unique for every molecule:

$$B_{v} = \frac{h}{8\pi^{2}Ic}$$

Rotational Spectroscopy Selection Rule

For a allowed transition to be observed, $\Delta I = \pm 1$. Thusly, we can find B_{ν} using two adjacent peaks,

$$2B_{\nu} = \tilde{\nu}_{J+1} - \tilde{\nu}_{J}$$

Rotational Spectroscopy Line Intensity

Each J energy value will have an associated number of rotational states. The degeneracy of a value *I* is given by:

$$g_I = 2J + 1 \tag{7}$$

in combination with the Boltzmann distribution. we can find the ratio of populations to the ground state:

$$\frac{N_J}{N_0} = (2J+1)\exp\left(-\frac{hcB_v J(J+1)}{k_B T}\right)$$
(8)

The *J* level with the maximum population is given by:

$$J_{\max} = \sqrt{\frac{k_B T}{2hcB_v}} - \frac{1}{2} \tag{9}$$

Isotopic Substitution

Isotopic substitution will not change the internuclear distance r_0 , but however will change the moment of inertia I, and consequently B_{ν} . In general, a substitution of a heavier isotope will lead to a smaller B_{ν} and hence smaller peak separation. It is notes that this can be exploited to calculate precise atomic masses.

Centrifugal Distortion

As molecules rotate faster (J > 10), the centrifugal distortion becomes appreciable. The distortion

$$D = \frac{2B_v^3}{\omega_e^2}$$

(10)

where ω_{e} is the vibrational frequency of the bond. Values calculated this way will differ from ones obtained from vibrational spectroscopy due to the lack of correction for anharmonicity. This gives:

(6)From a given set of data with the wavenumber of rotational lines and their corresponding J values, linear regression of the following will give *D* and B_v :

$$\frac{\tilde{\nu}_J}{(J+1)} = 2B_\nu - 4D(J+1)^2 \tag{11}$$

Polyatomic Molecules

The moment of inertia of the entire molecule is given by:

$$I = \sum_{i} m_i \times x_i^2 \tag{12}$$

where x_i is the distance of the atom i from the ro- where D_e parametrises the depth of the potential We can define 3 rotational axes I_a , I_b , and I_c . By convention, we select axes such that $I_c \ge I_b \ge I_a$. Here are four classes based on the values of I_i :

- 1. Linear rotors have two equal I values and a third that is 0. $I_c = I_b = I$, and $I_a = 0$, e.g. HCl, OCS, HC≡CCl
- 2. Symmetric rotors have two moments of inertia that are equal and a third that is non-zero, and this can have two forms:

oblate (pancake shaped, *i.e.* Benzene) $I_b = I_a < I_c;$

prolate (cigar shaped, i.e. CH₃I, NH₃), $I_c = I_b > I_o;$

3. Spherical rotors have three equal moments of inertia, $I_c = I_h = I_a = I$, *i.e.* CH₄, SiH₄, SF₆

Linear Molecules

Linear molecules will show peak separation of magnitude $2B_v$ reduced by distortion constant. Due to the moment of inertia about B or C axis is much greater, B_v will be much smaller (approx 1 cm⁻ for triatomics compared to 10 cm^{-1} for diatomics.

3 Vibrational Spectroscopy Harmonic Oscillator

By modelling a bond as a spring, the potential energy U for the system is given by Hooke's Law:

$$U = \frac{1}{2}k(r - r_{\rm eq})^2$$
(13)

(14)

(16)

where k is the spring constant with units N m⁻¹. The frequency in Hz for the oscillator is given by:

$$\omega_{\rm osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_{\rm eff}}}$$

note that we have divided by *c* to give $\omega_{\rm osc}$ in cm⁻¹. The term G(v) for a simple harmonic oscillator is given by:

$$G(v) = \left(v + \frac{1}{2}\right)\omega_{\rm osc} \tag{15}$$

Consequently, for v = 0, this gives the zero-point energy:

$$G(0) = \frac{1}{2}\omega_{\rm osc}$$

Anharmonic Oscillator

It is not true that atoms obey exactly Hooke's Law, a more accurate approximation would be the Morse potential, given as follows:

$$U = D_e \left\{ 1 - \exp\left[a(r_{\rm eq} - r)\right] \right\}$$
(17)

tational axis passing through the centre of mass. well, and \hat{a} is a constant unique to each molecule.



By solving the Schrödinger equation with the Morse potential, we find:

$$G(v) = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e \qquad (18)$$

where $\omega_e x_e$ is the anharmonicity constant $\approx 1\%$ of ω_{e} . By solving for two adjacent terms, we find:

$$\Delta G = \omega_e - \omega_e x_e (2\nu + 2) \tag{19}$$

the above equation indicates the transition energy decreases with increasing v, due to a decrease in the oscillation frequency, hence the subscript *e* for ω_e to indicate the equilibrium oscillation frequency. The zero-point energy for the anharmonic oscillator is give by:

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$$
(20)

3.1 Population of Vibrational Levels

At room temperature (300 K), approximately 1% of the population is in the state v = 1. There are four transitions of importance:

- 1. Fundamental: $v = 0 \rightarrow 1$, high intensity, $\Delta G = \omega_e - 2\omega_e x_e$
- 2. First Overtone: $v = \rightarrow 2$, low intensity, $\Delta G =$ $2(\omega_{e}-3\omega_{e}x_{e})$
- 3. Second Overtone: $v = 0 \rightarrow 3$, negligible, $\Delta G = 3(\omega_e - 4\omega_e x_e)$
- 4. Hot band: $v = 1 \rightarrow 2$, low intensity, $\Delta G =$ $\omega_e - 4\omega_e x_e$.

Birge-Sponer Plot

The Birge-Sponer plot allows for extrapolation of the disassociation energy of a bond. By plotting each successive ΔG against v + 1/2, and summing the area under the curve, we can find D_0 . This will lead to an over estimation of D_0 , as the plot does not model the fall-off of the true curve.

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Polyatomic Molecules

Each vibrational mode that is IR active can be thought of as an independent harmonic oscillator, for each mode *q*, the energy is described by:

$$G_q = \left(v_q + \frac{1}{2}\right)\omega_q$$
$$\omega_q = \frac{1}{2\pi c}\sqrt{\frac{k_q}{m_q}}$$

4 Rotational-Vibrational Spectroscopy

The term that describes a rotational-vibrational transition S is defined as follows:

$$S(v,J) = G(v) + F(J)$$
⁽²³⁾

Neglecting the centrifugal distortion, the explicit form of S is:

$$S(v,J) = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e + B_v J(J+1)$$
(24)

Rotational quantum number *I* is denoted " for those in v = 0, and ' for those in v = 1. This gives three branches:

- 1. P branch:, $\Delta J = -1$, transitions such as J'' = $1 \rightarrow J' = 0$. These transitions decrease in energy by incremental amounts of 2B.
- 2. R branch: $\Delta I = +1$, transition such as I'' = $0 \rightarrow J' = 1$. These transitions increase in energy by incremental amounts of 2B.
- 3. Q branch: $\Delta I = 0$, this is a forbidden transition due to the selection rule $\Delta I \neq 0$.

Interpretation of Rotational-Vibrational Spectrum

For a transition from $v = 0, J'' \rightarrow v = 1, J'$, the energy is given by:

$$\Delta S = \omega_e - 2\omega_e x_e B_1 J'(J'+1) - B_0 J''(J''+1)$$
(25)
= $\omega_0 + B_1 J'(J'+1) + B_0 J''(J''+1)$ (26)

Transitions for P, Q, and R Branches

The energies of the three branches are as follow:

$$\tilde{v}_{R}(J) = \omega_{0} + B_{1}(J+1)(J+2) - B_{0}J(J+1)$$
(27)
$$\tilde{v}_{P}(J) = \omega_{0} + B_{1}J(J-1) - B_{0}J(J+1)$$
(28)
$$\tilde{v}_{Q}(J) = \omega_{0} + J(J+1)(B_{1} - B_{0})$$
(29)

Deducing B_0 and B_1 from differences

Starting at the same level I, B_1 can be calculated:

$$\tilde{\nu}_{\mathrm{R}}(J) - \tilde{\nu}_{\mathrm{P}}(J) = 4B_1\left(J + \frac{1}{2}\right)$$

 B_0 can be calculated by looking at two transitions v_{max} is obtained: in the P and R branch that end on the same level J:

$$\tilde{\nu}_{\rm R}(J) - \tilde{\nu}_{\rm P}(J+2) = 4B_0 \left(J + \frac{3}{2}\right)$$
 (31)

The above two equations can be used in linear regression to determine B_1 and B_0 .

Radius of Bond (21)

(22)

The radius of the bond is given by:

$$r_v = \sqrt{\frac{h}{8c\pi^2 m_{\rm eff} B_v}} \tag{32}$$

As vibrational level increases so does r, hence B_{ν} decreases. The deviation of B_{ν} from the equilibrium B_{e} is given by:

$$B_{v} = B_{e} - \alpha \left(v + \frac{1}{2} \right) \tag{33}$$

5 Electronic Absorption Spectroscopy

Electronic spectroscopy transitions in molecules involve the promotion of an electron from a lower energy M.O. to a higher unoccupied or partially occupied M.O.

Born-Oppenheimer Approximation

The total of energy of a transition can be described by the following sum:

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \tag{34}$$

This is possible as the energies are completely independent of each other. This is the Born-Óppenheimer approximation.

Franck-Condon Principle

The Franck-Condon principle states: An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

The electronic transitions will give rise to rapid electron re-distribution from one region of the molecule to the other. This takes place without change in nuclear geometry. Thus the most intense transitions are ones where the wavefunctions of the initial and final states overlap the most.

Disassociation Energy

Once the molecule is excited to an energy that exceeds the bond energy, the bond will break. As a consequence of this, a continuum of non-quantized transitions are observed. This limit is given by:

$$\tilde{\nu}_{\text{continuum}} = D_0'' + E_{\text{ex}} \tag{35}$$

where E_{ex} is the excitation energy, which is the energy gap between the disassociation energies of the ground state and the excited state. By taking (30) eq. (19) and in the continuum limit of $\Delta G \rightarrow 0$,

$$v_{\max} = \frac{\omega_e}{2\omega_e x_e} - 1 \tag{36}$$

this is the maximum number of vibrational states. $v_{\rm max} \sim 50$

6 Raman Spectroscopy

Raman spectroscopy involved shining a sample with an incident light. There are three forms of scattering processes that occur. The light that is scattered is of the same frequency is called *Rayleigh* scattering, slightly lower frequency is called Stokes scattering, and higher frequency being anti-Stokes. In order for a molecule to be Raman-active, the molecule must be anistropically polarizable.

Rotational Raman Spectroscopy

Distortion constant does not need to be included as Raman techniques are not sensitive enough to detect it. The selection rule for rotational Raman spectroscopy is:

$$\Delta J = 0, \ \pm 2$$

(37)

where $\Delta I = 0$ gives rise to the Rayleigh line, $\Delta I = +2$ gives Stokes lines, and conversely anti-Stokes lines for -2.

The energy difference in a pure rotational transition in Raman spectroscopy is given by:

$$\Delta F = B_v (4J + 6) \tag{38}$$

Vibrational Raman Spectroscopy

The analysis is mostly restricted to the fundamental absorption due to weaker intensities in higher energy states. Thus, the energy gaps is again:

$$\Delta G = \omega_e - 2\omega_e x_e$$

IR and Raman Spectra

The principle of mutual exclusion states: If a molecule has a centre of symmetry, then Raman active vibration bands are not infrared active and vice versa. If there is no centre of symmetry, then some (but not necessarily all) vibration may be both Raman and infrared active.

Vibrational-Rotational Raman Spectra

Unlike the normal vibrational-rotational spectroscopy, $\Delta I = 0$ is an allowed transition and corresponds to the Q branch, where $\Delta I = -2$ is the O branch, and $\Delta I = +2$ is the S branch. The sequence of branches runs energetically: O,P,Q,R, and S.

7 Electronic Emission Spectroscopy

The process of absorption is outlined as follows:

- 1. Molecule absorbs light and electrons undergo ($S^* \leftarrow S$).
- 2. The S* undergoes vibrational relaxation and the electrons move to the lowest vibrational level of S*

- 3. The molecule dissipates energy by internal conversion. The electron moves to lowest excited state S_1 . This is a horizontal transition from an overlapping excited state to a lower energy excited state. This process does not give off a photon.
- 4. Another vibrational relaxation occurs and is a photophysical process. Kasha's rule states: photophysical processes happen from the lowest vibrational state of the lowest excited state. The electron can under go the following three processes:

fluorescence, giving off a photon,

internal conversion,

or intersystem crossong to a triplet state, at which point the molecule can undergo phosphorescence or deactivation.

The Jablonski diagram, akin to the potential energy surfaces, describe these transitions pictorially. Fluorescence

Emission is always at a longer wavelength than absorption. This shift is called Stokes shift. The emission spectroscopy is typically a mirror image of the absorption spectrum. Emission spectroscopy has two advantages over its absorption counterpart:

- 1. Not all species emit or show appreciable emission. This allows for the studying of complex mixtures where there may only be one emitting species. Useful in biophysical chemistry.
- 2. Emission is especially sensitive to the environment, *i.e.* pH and solvent... and can be a useful characterisation tool. This is useful to study quenchers in analytical chemistry.

Emission Quenching: Stern-Volmer Equation

(39)The two competing pathways for excited state deactivation is as follows:

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$
 (emission) (40)

$$S_1 \xrightarrow{k_d} S_0 + heat$$
 (non-radiative) (41)

$$S_1 + Q \longrightarrow S_0 + Q^*$$
 (quenching) (42)

The Stern-Volmer equation gives the ratio of quantum yields Φ , the number of molecules that undergo the process as a fraction of the number of photons absorbed by the sample, and Φ_f^0 is the quantum yield of fluorescence in the absence of a quencher:

$$\frac{\Phi_f^0}{\Phi_f} = \frac{I_f^0}{I_f} = 1 + k_q \tau_0[Q]$$
(43)

This can be related to the emission intensity and given either one of τ of k_a, the other quantity can be found through linear regression.