Molecular Spectroscopy

I. OPTICAL TRANSITIONS IN MOLECULES: INTRODUCTION

The origin of spectral lines in molecular spectroscopy is the absorption, emission, and scattering of a proton when the energy of a molecule changes. In atomic spectroscopy, all transitions reflect changes in the configuration of electrons. In molecules, in addition, there are energy states corresponding to nuclei vibrations and rotations. In consequence, the molecular spectra are more complex than atomic spectra and contain information on the molecular structure and the bond strength. They also provide a way of determining a variety of molecular properties, like dipole and quadrupole moments and the quantum numbers characterizing all molecular degrees of freedom. The molecular spectroscopy is also important for astrophysical and environmental science, for investigation of chemical reactions, for biology, and in many other areas of science and technology which needs detailed investigation of properties of microscopic atomic and molecular objects.

In the Born-Oppenheimer approximation the energy of a molecule can be presented as sum of electronic energy E_{el}, vibrational energy E_{vib} and rotational energy E_{rot} energy.

$$E = E_{el} + E_{vib} + E_{rot} \tag{1}$$

The energy difference corresponding to the excitation of electrons $\Delta E_{el} = h\nu_{el}$ in this approximation is much larger that the energy difference corresponding to the molecular vibration $\Delta E_{vib} = h\nu_{vib}$ which is large that the energy difference corresponding to the molecular rotations $\Delta E_{rot} = h\nu_{rot}$:

$$h\nu_{el} \gg h\nu_{vib} \gg h\nu_{rot} \tag{2}$$

Usually, transitions within the rotation energy levels manifold belong to the far infrared and microwave spectral region, transitions within the vibrational energy levels manifold belong to the infrared spectral region, and the transitions between the electronic energy levels belong to the visible, or ultraviolet spectral region. In general, the vibrational transitions result in changes in the rotational mode and the electronic transitions result in changes in the rotational and vibrational modes as well. Selection rules determine whether transitions are allowed or not.

As discussed above the Time-Dependent Perturbation Theory shows that the probability of absorbing a light photon by a molecule is proportional to

$$W_{k\leftarrow 0} \propto |\langle k| \, \mu_Z \, |0\rangle|^2 \, E_z^2, \tag{3}$$

where $\langle k| \mu_Z |0 \rangle$ is the matrix element of the **transition dipole moment**:

$$\langle k| \mu_Z |0 \rangle = \int \Psi_k^* \mu_z \Psi_0 dq \tag{4}$$

and Ψ_0 and Ψ_k denote the wave functions of the molecular initial and excited states, respectively.

Absorbing the photon a molecule passes from its initial (ground) state to the excited state. Here we assume that the electric vector of light **E** (the light polarization vector) is parallel to the laboratory Z axis. As shown in eq. (3) the rate of the transition is proportional to E_Z^2, and therefore, to the intensity I of the incident radiation and is also proportional to the squire of the Z component of the dipole moment matrix element $\langle k| \mu_z |0 \rangle$. In general, the total molecular dipole moment is a vector which can be presented as

$$\vec{\mu} = \sum_i q_i \vec{r}_i, \tag{5}$$

where q_i is the charge of the i-th particle (electron, or nucleus), $\vec{r}_i$ is the radius-vector of the i-the particle, and summation is proceeded over all electrons and nuclei of the molecule.

This matrix element in eq. (4) depends on the symmetry of both molecular states which are indicated by the corresponding quantum numbers. For some particular quantum numbers of the initial and excited molecular states the matrix element $\langle k| \mu_Z |0 \rangle$ can be equal to zero, the corresponding optical transition is called **forbidden transition**. The relationship between the quantum numbers of the initial and excited molecular states for which the transition matrix element is not zero are known as **transition selection rules**.

II.   OPTICAL TRANSITIONS AND SPECTRAL LINES

A.   Einstein Coefficients

In **emission spectroscopy** a molecule undergoes a transition from a high energy state E_1 to a state of lower energy E_2 and emits the excess energy as a photon. In **absorption spectroscopy** the absorption of nearly monochromatic incident radiation is monitored as function of the radiation frequency. Anyway, the energy of the emitted, or absorbed photon $h\nu$ is given by the Bohr formula

$$h\nu = E_1 - E_2 \tag{6}$$

These are two convenient units which are often used by spectroscopists for characterizing a transition energy:

$$\lambda = \frac{c}{\nu} \quad \text{and} \quad \bar{\nu} = \frac{\nu}{c}, \tag{7}$$

where the wavelength λ is measured in nanometers, microns, or Angströms ($1\mathring{A} = 0,1nm$) and the units of wavenumber $\bar{\nu}$ are almost always chosen as **reciprocal centimeters** (cm^{-1}). It is easy to see that $\bar{\nu} = 1/\lambda$.

Emission and absorption spectroscopy give the same information about energy level separation and only practical considerations generally determine which technique is employed.

As known from the Einstein theory of radiation spontaneous decay of the excited state E_1 can be described by the equation

$$\frac{dN_1}{dt} = -A_{12} \cdot N_1 \tag{8}$$

where N_1 is population of the level 1 and A_{12} is the Einstein coefficient of **spontaneous emission**.

This equation has the evident solution

$$N_1(t) = N_1(t = 0) \cdot e^{-A_{12} \cdot t} \tag{9}$$

The **life time** τ of the state is defined as the time needed for a reduction of the level population by a factor of 1/e. Thus,

$$\tau = \frac{1}{A_{12}} \tag{10}$$

If the molecule is initially in its lower state 2 interacting with incident radiation the transition rate of the **stimulated absorption** from the state 2 to the state 1 is

$$w' = B_{21} \cdot \rho, \tag{11}$$

where $\rho d\nu$ is the radiation energy density and B_{21} is the Einstein coefficient of **stimulated absorption**.

If the molecule is initially in its upper state 1 interacting with incident radiation population of the state 2 through **stimulated emission transition** obeys the equation

$$w = B_{12} \cdot \rho, \tag{12}$$

where B_{12} is the Einstein coefficient of **stimulated emission**.

Relationship between all three Einstein coefficients is as follows

$$\frac{B_{21}}{B_{12}} = \frac{g_1}{g_2} \quad \text{and} \quad A_{12} = \left(\frac{8\pi h\nu^3}{c^3}\right) \cdot B_{12} \tag{13}$$

where g_1 and g_2 are the multiplicities of degeneracy of the corresponding states. If the degeneracy of both states is the same, we have

$$B_{21} = B_{12} \tag{14}$$

B. The Intensity of Spectral Lines: Absorption

In absorption spectroscopy the ratio of the transmitted light intensity to the incident light intensity at a given frequency is called **transmittance**, T of the sample:

$$T = \frac{I}{I_0} \tag{15}$$

According to the **Lambert-Beer** law, the transmitted light intensity varies with the sample length l as

$$I = I_0 e^{-\sigma N l}, \tag{16}$$

where σ is an absorption cross section and N is the number of molecules per volume (concentration). Adequate units are: cm^2 for σ, cm^{-3} for N, and and cm for l.

Another form of eq. (16) which is widely used in laboratory practice is

$$I = I_0 10^{-\epsilon c l}, \tag{17}$$

where ϵ is the **extinction coefficient** and c is a **molar concentration** :

$$c = \frac{n}{V} = \frac{\text{number of molecules}}{N_A V} = N/N_A, \tag{18}$$

where N_A is the Avogadro number, $N_A \approx 6.022\,10^{-23} mol^{-1}$. The appropriate units are mole/liter ($[mol L^{-1}]$) for c and $[L mol^{-1} cm^{-1}]$ for ϵ.

Each of the coefficient σ and ϵ can be determined from experimental data

$$\ln(\frac{I}{I_0}) = -\epsilon\,c\,l\ln(10) = -\sigma\,N\,l, \tag{19}$$

where the I, σ and ϵ are function of the light frequency ν.

In case if the exponent factor $\alpha = \sigma N l$ in eq.(16) is small compare to unity $\alpha \ll 1$ the exponential function can be expanded over α. Keeping in this expansion only first two terms

one comes to the important for practice particular case called **low optical density** of the sample:

$$I = I_0(1 - \sigma \, N \, l). \tag{20}$$

Integrating the expression in eq.(20) over the light frequency within the absorption peak, one obtains the integrated cross section $< \sigma >$

$$< \sigma >= \int \sigma d\nu = B_{mn} \frac{h\nu_0}{c}, \tag{21}$$

where B_{mn} is the Einstein absorption coefficient and ν_0 is the center of the molecular absorption line.

Thus the Einstein coefficient B_{mn} can be directly determined from experiment.

C. Spectral Line Shape

1. Lifetime Broadening

It is found that spectroscopic lines from gas-phase samples are not initially sharp. The same is true for the spectra from solid state and solutions. There are several reasons for the spectral line broadening. One them is due to quantum mechanical effects. Particularly, if the quantum mechanical system is changing with time it is impossible to specify the energy levels exactly. If the system survives in a quantum state for a time τ, the energy of the level in principle cannot be known with accuracy better than spontaneous decay spontaneous decay

$$\delta E \approx \frac{\hbar}{\tau} \tag{22}$$

This is fundamental **uncertainty relation for energy**. In principle, no excited state has infinite lifetime, thus all excited states are subject of the lifetime broadening and the shorter the lifetimes of the states involved in a transition, the broader the corresponding spectral lines. These are two main processes which are responsible to the finite lifetime of excited states.

Firstly, there is the spontaneous decay which is proportional to the corresponding Einstein coefficient A. The intensity the spontaneous decay is proportional to the square of the matrix element of interaction with **electromagnetic modes of vacuum** and in principle cannot be changed. However, for some particular pairs of the energy states these matrix elements

can be very small, the corresponding states are called **metastable states** Of cause, the transition intensity from these states is very small.

Secondly, there is interaction between the molecular quantum states and other particles. In the gas phase this interaction is just inelastic collisions with surrounding particles. In the condensed matter there can be interaction with phonons (vibration of the surrounding lattice). The collision frequency in the gas phase can be reduced by decreasing the number of molecules in the, or by decreasing their velocity (temperature).

In both cases the finite lifetime results in a specific spectral line shape which is called **Lorentz** line shape:

$$I(\nu) \propto \frac{1}{\pi} \frac{\gamma/2}{(\nu - \nu_0)^2 + \gamma^2/4}, \tag{23}$$

where γ is the excited state decay rate, $\gamma = 1/2\pi\tau$ and ν_0 is the line center.

The Lorentz line is a bell-shaped with characteristic linewidth of $\Delta\nu_L = \gamma$. The natural lifetimes of electronic transitions are very much shorter than that for vibrational and rotational transitions. For example, a typical electronic excited state at the energy of about several eV has a lifetime of about $10^{-8}s$, corresponding to a natural linewidth of about $15 MHz$ ($5 \cdot 10^{-4} cm^{-1}$). A typical rotational state lifetime is about 10^3 s, corresponding to a natural linewidth of 10^{-4} Hz ($5 \cdot 10^{-15} cm^{-1}$).

This broadening of the line due to collisions and the respective width is called the **homogenous line width** because the collisions are **isotropic**. Under atmospheric conditions, collisions occur within intervals of nanoseconds and we observe widths of a few GHz ($10^9 Hz$). This value decrease linearly with the gas pressure. In liquids the collisions are much more often resulting in collision times in the picosecond time scale. Therefore, the width of a single transition in liquid is usually about several THz, ($10^{12} Hz$) corresponding linewidth of a few nanometers for transitions in the ultraviolet spectral range of about 300 nm.

In contrast, the line width is said to be **inhomogeneous** if the **anisotropic** collisions or interactions occur. Particularly, **inhomogeneous** line broadening is typical for certain atoms in the lattice of a solid medium.

2. Doppler Broadening

Another example of the **inhomogeneous** line broadening is so called **Doppler broadening** which is typical in gaseous samples. As known, the Doppler effect results in light

frequency shift when the source is moving toward, or away from the observer. When a source emitting radiation with frequency ν_0 moves with a speed $\mathbf{v}$, the observer detects radiation with frequency:

$$\nu = \nu_0 \left(1 \pm \frac{v_z}{c} \right), \qquad (24)$$

where the sign $+$ and $-$ is related to an **approaching** and **receding** source, respectively.

Molecules in a gas chaotically move in all directions and the observer detects the corresponding Doppler-broadened spectral line profile. This profile reflects the distribution of molecular velocities along the line of detection, which we designate as Z axis. In case of the thermal equilibrium this velocity distribution is known as Maxwell-Boltzmann distribution:

$$n(v_z)dv_z = \sqrt{\frac{2\,k\,T}{\pi\,m}}\, exp\left(-\frac{m\,v_z^2}{2\,k\,T} \right) \qquad (25)$$

Here $n(v_z)dv_z$ is a relative number of atoms with the velocity component v_z parallel to the light beam, m is the particle mass, k is the Boltzmann constant, and T is the gas temperature.

Combining eqs.(25) and (24), we can get the expression for the light intensity as function of ν

$$I(\nu) = I_0 \sqrt{\frac{4\,ln2}{\pi}}\, \frac{1}{\Delta\nu_D}\, exp\left(-4\,ln2\frac{(\nu - \nu_0)^2}{\Delta\nu_D^2} \right) \quad \text{where} \quad \Delta\nu_D = \frac{2\,\nu_0}{c}\sqrt{\frac{2\,ln2\,k\,T}{m}} \qquad (26)$$

The value $\Delta\nu_D$ (**Doppler width**) is the linewidth of the distribution at the half-hight. The distribution (26) is of the Gaussian type and it is called the **Doppler profile**.

It is seen that the Doppler width ν_D is proportional to the transition frequency ν_0, to the square root of the gas temperature T, and inverse to the squire root of the particle mass. For transitions which belong to the visible or the near-UV spectral range when the gas temperature is around 300 K, the Doppler width is typically within one GHz. However, the hydrogen atoms and molecules has exceptionally high Doppler widths of around 30 GHz due to their low mass. For the visible part of the spectrum the Doppler line broadening is usually much larger than the lifetime broadening. Therefore, the experimentally obtained line profiles have usually the Gaussian shape. In contrast, for microwave transitions, or in conditions of high collisional broadening, the lifetime broadening becomes larger than the Doppler one resulting in the Lorentz-type line profiles.

In case $\delta\nu_L$ and $\delta\nu_D$ have have comparable amplitudes, the observed spectral line can be obtained by the convolution of the Gaussian and Lorentz profiles:

$$I(\nu) = C \int_0^\infty \frac{exp\left(-\frac{c}{v_p}\frac{(\nu_0-\nu')}{\nu_0}\right)^2}{(\nu-\nu')^2 + \gamma^2/4} \, d\nu' \quad \text{where} \quad v_p = \sqrt{\frac{2\,k\,T}{m}} \qquad (27)$$

This intensity profile is called the **Voigt** profile. For example, Voigt profiles play an important role in the spectroscopy of stellar atmospheres where accurate measurements of line wings allow the contributions of Doppler broadening, or natural linewidth of collision line broadening to be separated. From this measurements the temperature and pressure of the emitting or absorbing layers in the stellar atmospheres can be determined.

III. EXPERIMENTAL TECHNIQUES

A. Sources of Radiation

There are two important types of light sources used in spectroscopy: **polychromatic** and **monochromatic** sources. The polychromatic sources span a wide range of frequencies. For instance, many commercial spectrometers use light sources which emit radiation similar to black-body radiation from hot materials. For far-infrared spectral range within $35\,cm^{-1} < \bar\nu < 200\,cm^{-1}$, a typical source is a mercury arc inside a quartz envelope where most of the radiation is generated by the hot quartz. Either a **Nernst filament** (ceramic with ZrO, YtO, TlO, ets.), or a **globar** (SiC) is used as a source of mid-infrared radiation within $200\,cm^{-1} < \bar\nu < 4000\,cm^{-1}$. **Tungsten filaments** is used in the visible and near infrared spectral range $320\,nm < \lambda < 2500\,nm$.

Different types of **gas discharge lamps** are common light sources in ultraviolet and visible spectral region $180\,nm < \lambda < 800\,nm$. In a **xenon discharge lamp** an electrical discharge excites xenon atoms to excited states which then emit ultraviolet radiation. At high pressure (several kPa) the output of a xenon lamp consists of sharp lines superimposed on a board intense background due to emission from plasma. High pressure xenon lamps are widely used as a source of radiation which is similar to the black body radiation at 6000 K. There are also many other widely used lamps which use discharge in **deuterium**, **mercury**, **neon**, **krypton** and produce polychromatic many-line radiation at different wave lengths.

Very important modern source of radiation from IR till X-rays spectral range is **syn-**

chrotron radiation. A typical synchrotron storage ring consists of a high energy electron beam travelling in a circular path many meters in diameter. The electrons move around the circle under influence of a strong magnetic field which is perpendicular to the circle plane and generate radiation in very wide spectral range. The polychromatic beam is dispersed by a diffraction grating and quasi monochromatic radiation is separated by a slit. Except in the microwave region, synchrotron radiation is much more intense than can be obtained by most other conventional sources.

The **monochromatic** sources span a very narrow range of frequencies around a central value. Convenient monochromatic sources in the near IR-UV spectral range ($200 \, nm < \lambda < 800 \, nm$) are electrodeless lamps containing a small amount of a chemical element at the pressure of about $10^{-3} \, Pa$ and a few Pa of inert gas Ne. Radio frequency discharge in the lamp results in emission of extremely narrow bond **resonance** spectral lines of the element. There are large number of various chemical elements which can be used in these lamps, for instance $Cs, Rb, K, Na, Ag, Hg, Sn, Be, Sr$, and others. These monochromatic sources can be used for detection of many small amounts of elements and find wide application in the **atomic absorption spectroscopy**.

However, the most widely used monochromatic sources of radiation are **lasers** which revolutionary transformed the whole world. The basic principle of laser operation is **stimulated emission** from the sample with the **population inversion**. Independent from the construction in detail, lasers contain the following important components: **an active medium with an upper and a lower working energy levels, a pumping source, and a resonator**.

The population inversion between the upper and the lower working levels is necessary for obtaining the amplification of the stimulated emission in the sample. As shown in eq.(13) the Einstein coefficient of **spontaneous emission**, A_{mn} is proportional to the third order of the radiation frequency, ν^3. Therefore, in the visible and even in the UV spectral range intensity of spontaneous emission is much larger than the intensity of the stimulated emission. For instance, for the radiation wavelength of 500 nm (green light) and at a temperature of 300 K, the ratio between the intensities of the spontaneous and stimulated transitions becomes $F = e^9 6 = 5 \cdot 10^{41}$. Therefore, among the $5 \cdot 10^{41}$ transitions, only one is due to induced emission. In contrast, for the radiation frequency $\nu = 1 \, GHz$ (microwave spectral range) and the same temperature the ratio is $F = 1,6 \cdot 10^{-4}$. Therefore, nearly all transitions are

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induced. Thus, it is not astonishing that the first laser generated microwaves. It was called the **maser**.

The first laser system developed by Maiman in 1960 was a ruby laser based on the three level scheme. Nowadays, the four level laser scheme is used for almost all lasers systems because it provides more effective way for producing the population inversion.

1. *Properties of the Laser Radiation*

The main features of the laser radiation reflect the features of stimulated emitted photons.

(i) The laser light can be very monochromatic. In principle, the laser linewidth depends on the active medium and on the laser design. The best results have been obtained for the low pressure gas lasers (Hansch was able to reach a ratio $\Delta\lambda/\lambda \simeq 10^{-15}$). Therefore, lasers can be effectively used for high resolution spectroscopy.

(ii) The laser beam can be of very low divergent (spatial coherence), which means that its diameter is increased only slowly in space. In principle, with laser beams it is possible to reach the diffraction limit:

$$\Theta \approx \frac{2\lambda}{\pi d} \tag{28}$$

This means that using a lens, it is possible to focus a laser beam on a spot of the diameter:

$$d \approx \frac{2\lambda}{\pi} \frac{f}{D} \tag{29}$$

where, f denotes the focal distance of the lens.

As, for the best lenses, the ratio of focal lens to diameter is about 0.8, it is a rule of thumb that the half of the light wavelength is approximately equal to the lower limit of the diameter of the spot.

(iii) Short laser pulses can be produced. Using specific techniques for generating the laser pulses (Q-switching, modes locking, pulse compression), the extremely short pulse duration can be achieved. As short as several hundreds of atoseconds (10^{-18}) pulse duration has recently been obtained! The pulse duration in the nanosecond (10^{-9}), picosecond (10^{-12}), and femtosecond (10^{-15}) range are now available commercially.

Particularly, femtosecond laser pulses are of great importance, because they allow to investigate chemical reactions **in the real-time domain**.

(iv) High power output. The continuous CO_2 lasers are now can produce the high power output up to 100 kW. These technological lasers are now widely used in industry and for military aims. The pulsed lasers, especially those operating in the pico- and femtosecond time-domain can have extremely high pick power. Particularly, the pick powers from 10^9 to 10^{12} watts are now available. High power pulsed lasers are widely used for investigation of **multiple photon processes**.

2. *Practical Lasers*

IV. ROTATIONAL SPECTRA

In classical mechanics, the energy of an particle which rotates around an axis is given by $E = \frac{1}{2}I\omega^2$. Here ω is the angular velocity in radian per second and $I = mr^2$ is the moment of inertia, where m is the particle mass and r is the distances between the particle and the axis. For an arbitrary object the rotation energy can be written in the following form:

$$E = \frac{1}{2}I_A\omega_A^2 + \frac{1}{2}I_B\omega_B^2 + \frac{1}{2}I_C\omega_C^2, \tag{30}$$

where A, B, C are so-called **principal axes of rotation**.

Using $J_i = I_i\omega_i$, with $i = A, B, C$, where J_i is angular momentum, we get

$$E = \frac{1}{2}\frac{J_A^2}{I_A} + \frac{1}{2}\frac{J_B^2}{I_B} + \frac{1}{2}\frac{J_C^2}{I_C} \tag{31}$$

To begin with, we assume that the shape of the molecule does not depend on rotation, i.e. that the the bond lengths are not affected by centrifugal forces. This molecule is called **rigid rotor** in contrast to an **elastic rotor**. We will consider the following cases, see Table III:

TABLE I:

Spherical top	$I_A = I_B = I_C = I$	e.g. CH_4, CCl_4, SF_6
Symmetric top	$I_A = I_B = I_\perp$ and $I_C = I_\parallel$ $I_\perp < I_\parallel$ oblate $I_\perp > I_\parallel$ prolate	e.g. benzene CH_3I
Linear Rotor (a special case of symmetric top)	$I_A = 0, I_B = I_C$	all diatomic molecules and e.g., CO_2, N_2O, C_2H_2
Asymmetric top	$I_A \neq I_B \neq I_C$	e.g. H_2O

A. Spherical Top

Examples: CH_4, CCl_4, SF_6.

For this case ($I = I_A = I_B = I_C$) the rotational energy is given by:

$$E = \frac{J_A^2 + J_B^2 + J_C^2}{2I} = \frac{J^2}{2I} \tag{32}$$

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We corresponding quantum mechanical expression for the rotational energy is given by:

$$E_J = \frac{\hbar^2}{2I} \cdot J(J+1), \tag{33}$$

because the eigenvalues of the operator $\mathbf{J}^2$ are $\mathbf{J}^2\Psi = \hbar^2 J(J+1)\Psi$.

Usually in spectroscopy eq. (33) is presented in the form

$$E_J = hcB \cdot J(J+1), \tag{34}$$

where the rotational constant B measured in cm^{-1}. The product hcB in eq.(34) is equal to $\hbar^2/2I$. The rotational constant B is as

$$B = \frac{\hbar}{4\pi cI} \tag{35}$$

B. Symmetric Top

Examples: CH_3I, C_6H_6, NH_3.

Denoting $I_\parallel$ as the moment of inertia which is parallel and $I_\perp$ as the moment of inertia which is perpendicular to the molecular axis, we can consider two cases: $I_\parallel < I_\perp$ and $I_\parallel > I_\perp$. In the first case we have an **oblate top** and the second case a **prolate top** (which is like a cigar). Within the world of atoms and molecules, benzene is an example for the first, while methyliodide an example for the second. For both types, the rotational energy can be presented as sum of two terms:

$$E = \frac{J_A^2 + J_B^2}{2J_\perp} + \frac{J_C^2}{2I_\parallel} \tag{36}$$

Transition to quantum mechanics is eased by the fact that the energy values respective $\mathbf{J}^2$ and one selected axis obtained simultaneously. For $\mathbf{J}^2$, which is

$$\mathbf{J}^2 = J_A^2 + J_B^2 + J_C^2 \tag{37}$$

the energy values are defined by

$$E = \frac{J^2}{2I_\perp} + J_C^2 \cdot \left(\frac{1}{2I_\parallel} - \frac{1}{2I_\perp}\right) \tag{38}$$

We now replace the square of the angular momentum by the eigenvalues of the quantum mechanical angular momentum operator $\mathbf{J}^2 -> J(J+1)\hbar^2$ and use the quantum number

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K as projection of the momentum $\mathbf{J}$ onto the molecules axis (i.e. $J_C \Psi = K\hbar\Psi$). For the quantum mechanical energy levels, we finally obtain:

$$E_{JK} = B \cdot J(J+1) + (A-B)K^2, \text{ with } J = 0,1,2,\ldots \; K = 0, \pm 1, \ldots, \pm J, \quad (39)$$

where the rotational constants A and B are

$$A = \frac{\hbar^2}{4\pi c I_\parallel} \quad B = \frac{\hbar^2}{4\pi c I_\perp} \quad\quad (40)$$

Obviously, the sign of K does not affect the energy as it dependents on the square of K. Therefore, all levels are doubly degenerated. There are $2J+1$ projections of the angular momentum onto the external axis ($M_J = 0, \pm 1, \pm 2, \pm 3, \ldots \pm J$) and therefore, each energy level of the symmetric top is $2(2J+1)$-fold degenerated. For $K = 0$ we have $(2J+1)$-fold degeneracy. Though there is no definition for clockwise/anti-clockwise and $+/?$, the sign indicates two possibilities of rotation with the same energy.

We now consider two extreme cases of a rotating symmetric top: $|K| \simeq J$ and $K = 0$.

For the first case $|K| \simeq J$, when J has maximum projection onto the molecular axis, the rotation is mainly proceeds around this axis and the rotational constant A is decisive for the energy levels.

$$E_{J,K=J} = B \cdot J + AJ^2 \approx A \cdot J^2 \quad\quad (41)$$

For the other case $K = 0$ the molecule rotates perpendicular to its axis. Therefore, the projection of the angular momentum on the axis is zero and the rotational energy becomes

$$E_{J,K=0} = B \cdot J(J+1) \quad\quad (42)$$

C. Linear Top

All diatomic molecules and all linear molecules: $HCCH$, $NCCN$, CO_2.

Due to the small mass of electron, linear molecules show almost zero moment of inertia with respect to the molecular axis. Therefore, the considerations here are confined to a rotation around the two axes perpendicular to this axis ($K = 0$). For the rotational energy we obtain the important relation:

$$E_J = B \cdot J(J+1) \quad\quad (43)$$

This is the same equation as for spherical top. Nevertheless we should have in mind that for linear top the energy levels are $(2J + 1)$-fold degenerated according to the number of projections of J onto the external axis. In contrast, for a spherical top, there is no difference between rotational constants A and B and the quantum number K accepts one of the $(2J+1)$ arbitrary values that correspond to an orientation of the angular momentum to the molecular axis. Together with an $(2J + 1)$ degeneracy respective to a fixed external orientation of the angular momentum, we find for an energy level of a spherical top a $(2J+1)^2$-fold degeneracy.

For all known masses of a molecule and fixed distances between them, we are able to calculate its moment of inertia and even extend this theoretical approach to energy levels. Some useful formulas that deal with the types of molecules discussed so far can be found here and in Peter Atkins' text book.

D. Asymmetric Top

Examples: H_2O, $OClO$, NO_2.

The diagram below shows the eigenvalues of energy for the oblate and prolate case of an asymmetric top. In the prolate case, the energies decrease with increasing K, whereas in the oblate case, energies increase with increasing K. For values of I_B in between I_A and I_C, the diagram provides the energy of the asymmetric top. We here describe the asymmetric top by using a pair of projection quantum numbers K_a and K_c of the symmetric limiting cases. The rotational state is completely defined by the three quantum numbers $J\, K_a\, K_c$.

E. Elastic Rotator

So far, we assumed that rotation does not affect the shape of a molecule (rigid rotor). However, in general there are centrifugal forces that stretch the bonds of a rotating molecule. We will confine our treatment of this problem with the case of linear rotor.

An increased length of the bond corresponds to a higher moment of inertia ($I = r^2$). In turn, the rotational constant B decreases ($B \sim I^{-1}$), i.e. we would expect a rotational energy with a minor slope than in the case of $E_{rot} = B_{rigid}J(J + 1)$.

In this case we have no exact solution of the Schrodinger equation, however, we are can

attack the problem using a series expansion and write an expected rotational energy as:

$$E_J = B \cdot J(J+1) - D \cdot J^2(J+1)^2 + \cdots \qquad (44)$$

Here we assume that the coefficient D is a small correction, in other words, D is much smaller than B.

From the treatment above we should expect that the weaker the bond, the more pronounced the deviation from the rigid rotor becomes. A weak bond corresponds to a low vibrational energy: $E_{vib} = \hbar\omega(v + 1/2)$; $\omega = (k/\mu)^{1/2}$, where k is a force constant of the bond. The value of D can be either calculated, or derived from spectral data.

F.   Selection Rules for Pure Rotational Spectra

The rules are applied to the rotational spectra of polar molecules when the transitional dipole moment of the molecule is in resonance with an external electromagnetic field. Polar molecules have a permanent dipole moment and a transitional dipole moment within a pure rotational spectrum is not equal to zero.

In contrast, no rotational spectra exists for homonuclear diatomics; the same is true for spherical tops. Nevertheless, certain states of a such molecules allow unexpected interactions with the electromagnetic field; i.e. some vibrations, that introduce a time-dependent dipole moment high rotational speeds that cause some distortion of an originally spherical symmetry. A (weak) dipole moment emerges. The conservation of the angular momentum is fundamental for the selection rules that allow or prohibit transitions of a linear molecule:

$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1 \qquad (45)$$

For a symmetric top, an existing dipole moment is always parallel to the molecular axis. Thus, with respect to this axis, no changes of the rotational state occur:

$$\Delta K = 0 \qquad (46)$$

For energy difference corresponding to the transitions $J + 1 < -J$ can be presented as:

$$\nu(J) = B \cdot (J+1)(J+2) - B \cdot J(J+1) = 2B(J+1) \quad \text{with } J = 1, 2, \ldots, \qquad (47)$$

where the energy is measured in wave numbers, cm^{-1}.

It is easy to see that the frequency difference between two neighbor absorption lines is constant: $\Delta\nu = \nu(J) - \nu(J-1) = 2B$. Therefore, the constant B as well as the bond's length r can be directly determined from the absorption spectrum.

A more accurate expression for ν is

$$\begin{aligned}
\nu(J) &= B \cdot (J+1)(J+2) - D \cdot (J+1)^2(J+2)^2 - B \cdot J(J+1) + D \cdot J^2(J+1)^2 \\
&= 2B \cdot (J+1) - 4D \cdot (J+1)^3
\end{aligned} \tag{48}$$

That is the frequency difference between two neighbor absorption lines is

$$\Delta\nu = \nu(J) - \nu(J-1) = 2B - 4D(3J^2 + 9J + 7) \tag{49}$$

and decreases with J.

Thus, the centrifugal constant D for diatomic molecules is in connection with the wavenumber ν_S that corresponds with the molecule's vibration.

$$D = \frac{4B^3}{\nu_S^2} \tag{50}$$

Reversely, D provides information on ν_s. Of course, the intensity of an absorption is dependent on the transitional dipole moment and on the population of the initial and the final state.

V.   ROTATIONAL AND VIBRATIONAL-ROTATIONAL SPECTRA

VI. ELECTRONIC TRANSITIONS

In the Born-Oppenheimer approximation the energy of a molecule can be presented as sum of electronic energy E_{el}, vibrational energy E_{vib} and rotational energy E_{rot} energy.

$$E = E_{el} + E_{vib} + E_{rot} \tag{51}$$

As a first approximation, we describe the energy $E = \hbar\omega$ of a diatomic molecule as a sum of electronic, vibrational and rotational energies

$$\omega = T_e + \omega_e \left(v + \frac{1}{2}\right) + B_e J(J+1), \tag{52}$$

where T_e is the minimum of the potential curve. Each of the three terms in eq. (52) may be different for the lower and higher energy states and may be changes during an optical transition. The total transition frequency can be written as

$$\begin{aligned}\Delta\omega &= T_e' - T_e'' + \omega_e'\left(v' + \frac{1}{2}\right) - \omega_e''\left(v'' + \frac{1}{2}\right) + B_e' J'(J'+1) - B_e'' J''(J''+1)\\ &= \omega_{el} + \omega_{vib} + \omega_{rot},\end{aligned} \tag{53}$$

where the lower energy state is denoted by a double prime (”), while the higher energy state is denoted by prime (’).

Note, that the energy difference corresponding to the excitation of electrons $\Delta E_{el} = \hbar\omega_{el}$ in this approximation is much larger that the energy difference corresponding to the molecular vibration $\Delta E_{vib} = \hbar\omega_{vib}$ which is large that the energy difference corresponding to the molecular rotations $\Delta E_{rot} = \hbar\omega_{rot}$:

$$\omega_{el} \gg \omega_{vib} \gg \omega_{rot} \tag{54}$$

A. Selection Rules for Electronic Transitions in Diatomic Molecules

The selection rules for optical transitions between different electronic states of a diatomic molecule are shown in Table II.

If we consider the rotational states as well, it is required that the total angular momentum of photon and molecule remains constant. In general, the selection rules for the total angular momentum J are as follows: $\Delta J = 0, \pm 1$ however, for $\Sigma \leftrightarrow \Sigma$ transitions the $\Delta J = 0$ transition is forbidden. These rules are summarized in table III below.

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TABLE II: **Selection Rules for Electronic Transitions in Diatomic Molecules**

Allowed Transitions	Examples
$\Delta\Lambda = 0, \pm1$	$\Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Pi, \Sigma \leftrightarrow \Pi, \Delta \leftrightarrow \Pi$
$\Delta S = 0$	${}^1\Sigma \leftrightarrow {}^1\Sigma, {}^3\Pi \leftrightarrow {}^3\Pi, {}^1\Sigma \leftrightarrow {}^1\Pi, {}^3\Sigma \leftrightarrow {}^3\Pi$
$+ \leftrightarrow +$	$\Sigma^+ \leftrightarrow \Sigma^+$
$- \leftrightarrow -$	$\Sigma^- \leftrightarrow \Sigma^-$
$g \leftrightarrow u$	$\Sigma_g^+ \leftrightarrow \Sigma_u^+, \Sigma_g \leftrightarrow \Pi_u$

TABLE III: **Selection Rules for rotational quantum number J in Electronic Transitions**

Electron Transition	Allowed transitions	Name
$\Sigma \leftrightarrow \Sigma$	$\Delta J = -1$	P branch
	$\Delta J = 1$	R branch
all others	$\Delta J = -1$	P branch
	$\Delta J = 1$	R branch
	$\Delta J = 0$	Q branch

B. Rotational Structure of Electronic Transitions

In general, rotational transitions accompany the excitation of the vibrational structure levels that accompany electronic excitation. We should expect P, Q, and R branches for each vibrational transition (but for $\Sigma \rightarrow \Sigma$ transitions, see section VI A) and therefore, electronic transitions have very reach structure. Let us consider the rotational structure for a given vibrational transition $v' \leftarrow v''$, where v'' belongs to the molecular ground state and v' belongs to the molecular excited state. Denoting

$$\tilde{\nu}_0 = E'_{el} - E''_{el} + \omega'_e \left(v' + \frac{1}{2} \right) - \omega''_e \left(v'' + \frac{1}{2} \right), \tag{55}$$

where $\tilde{\nu}_0$ is measured in the **wave numbers**, cm^{-1}, we can write the expressions for the P, Q, and R branches as

$$P \text{ branch} \, (\Delta J = -1): \quad \nu_P = \tilde{\nu}_0 + (\tilde{B}_e' - \tilde{B}_e'')J^2 - (\tilde{B}_e' + \tilde{B}_e'')J; \;\; J = 1, 2, \ldots$$

$$Q \text{ branch } (\Delta J = 0): \quad \nu_Q = \tilde{\nu}_0 + (\tilde{B}_e{}' - \tilde{B}_e{}'')J(J+1); \quad J = 0, 1, 2, \ldots \tag{56}$$

$$R \text{ branch } (\Delta J = 1): \quad \nu_R = \tilde{\nu}_0 + (\tilde{B}_e{}' - \tilde{B}_e{}'')(J+1)^2 + (\tilde{B}_e{}' + \tilde{B}_e{}'')(J+1); \quad J = 0, 1, 2, \ldots$$

Normally, the rotation constant $\tilde{B}_e$ is smaller for the excited state that for the ground state, $\tilde{B}_e{}' - \tilde{B}_e{}'' < 0$. This is because the electron excitation usually increases the bond length. Note, that $\tilde{B}_e = 1/(8\pi^2 c I_e)$ and $I_e = \mu R_0^2$, where the sign tilde ($\tilde{\ }$) reminds that $\tilde{B}_e$ is measured in the wave numbers. In this case one can see from eq. (56) that the lines of the R branch converge with increasing J, that is the line frequency increases at small J values till $(\tilde{B}_e{}'' - \tilde{B}_e{}')(J+1) = (\tilde{B}_e{}' + \tilde{B}_e{}'')$ and then decreases at larger J values. That is, the branch R has a **band head** at $(\tilde{B}_e{}'' - \tilde{B}_e{}')(J+1) = (\tilde{B}_e{}' + \tilde{B}_e{}'')$ and is said to be **red shadowed**.

In more rare case when the electron excitation decreases the bond length $\tilde{B}_e{}' - \tilde{B}_e{}'' > 0$. Then, the lines of the P branch begin to converge and go through a **head** at $(\tilde{B}_e{}' - \tilde{B}_e{}'')J = (\tilde{B}_e{}' + \tilde{B}_e{}'')$. This means that the line frequency decreases at low J values before the band head and increases at higher J values. In this case the branch ia said to be **blue shadowed**.

C.   Franck-Condon Principle

Using the Franck-Condon principle, we are able to calculate the intensities of transitions between vibrational states of the electronic energy levels. Due to their low mass, electron movement is fast compare with the nuclear movement and we can consider these two movements separately. Particularly, the position of nucleus can be considered as fixed during the electron transition. This means that the electron transition can be drawn as a vertical line on the potential curve diagram. However, after the electron transition took place, the nuclear vibrations move the nucleus toward the position of a new equilibrium distance with respect to the new potential energy curve.

In terms of quantum mechanics, the probability of an electron transition is proportional to the squire of the overlap integral between the vibrational wavefunction $\Psi_{v''}(R)$ and $\Psi_{v'}(R$ before and after the electronic transition.

To treat the problem quantitatively, the complete molecular wavefunction of the initial and the final state are needed. Fortunately, it is often possible to present this wavefunction as a product of the electronic wave function Ψ_{el} with depends on the coordinates of all

electrons $\mathbf{r}_i$ and the vibrational wavefunction $\Psi_v(R)$ which is a solution of the Schrödinger equation for nuclei and depend on the internuclear distance R. This approach is based on the Born-Oppenheimer approximation which argues with large difference in mass for nuclei and electrons. In the Born-Oppenheimer approximation the probability of a radiative transition is written as (see eq. (3)):

$$W_{k \leftarrow 0} \propto |\langle k| \, \mu_Z |0\rangle|^2 \, E_z^2, \tag{57}$$

where $\langle k| \, \mu_Z |0\rangle$ is the matrix element of the **transition dipole moment**:

$$\langle k| \, \mu_Z |0\rangle = q_{v''v'} \int \Psi_{el_k}{}^*(\mathbf{r}_i) \mu_z \Psi_{el_0}(\mathbf{r}_i) d\mathbf{r}_i \tag{58}$$

$$q_{v''v'} = \int \Psi_{v''}^*(R) \Psi_{v'}(R) dR \tag{59}$$

The integral over the electron coordinates $\mathbf{r}_i$ does not dependent on the vibration of nuclei and it is identical for all pairs of v', v". The integral over R represents overlap of the vibrational wave functions.

The quantities $|q_{v''v'}|^2$ are called **Franck-Condon factors**. No selection rules exist for changes of the vibrational quantum number v. This is because the vibrational wave functions of the initial and final states are in general not orthogonal to each other being the subject of Scrödinger equation with two different potentials $V'(R)$ and $V''(R)$. Apart from that, the **Franck-Condon-principle** allows to calculate the probability of a transition from some vibrational level v' of the initial state to another vibrational level v'' of the final state.

D.   Dissociation and Predissociation

If excitation transfers a molecule in a state containing more energy than the separated components (atoms, or molecules), **dissociation** takes place. Above the dissociation limit the energy is not quantized and energy continuum appears instead of discrete energy levels. The **dissociative state** is not stable, which means that the molecule disassembled into the separated components very quickly (approximately during the time of one vibration).

In some spectra the discrete energy level structure disappears already for energies which are below the dissociation limit but reappears again at some higher energies. This phenomenon is called **predissociation**.

Predissociation can be usually explained as a result of internal conversion from an excited state A into a dissociative state B. We assume relationship between the vibrational states closely above the level of intersection and the translational motion during dissociation. These circumstances allow a separation of a molecule via state B without supplying the energy of dissociation for state A. Note that, in the range beyond the blurred caused by predissociation, discrete lines are found. An interpretation would be that for higher vibrational states, a conversion towards state B is excluded again.

Sometimes, predissociation is a result of some additional external factors. For example, we can imagine a molecule to be pushed from state A to state B due to collision with another atom, or molecule. Alternatively, an external electric, or magnetic field can cause to the predissociation of an initially stable molecule. In such cases, we speak of **collision-** or **field-induced predissociation**.