

# Chapter 6

## Spectroscopy with light

### 6.1 Terahertz spectroscopy

The Terahertz domain lies at the upper end of frequencies that can be generated electronically and includes the frequencies relevant for rotational spectroscopy of small and medium-sized molecules. Here, we will only cover a novel development of Fourier Transform Microwave (FTMW) Rotational Spectroscopy, which may have the potential to characterize biomolecular structure via high-resolution rotational spectroscopy in the time domain.

#### 6.1.1 Rotational states

The energy  $E_{rot}$  of a rotating body in classical physics can be determined via its moment of inertia and the angular velocity or rotational frequency 6.1. However, the masses should be substituted with the reduced masses  $\nu_i$ .

rotational energy	$E_{rot}$	angular velocity:	$\omega = 2\pi \cdot \nu_{rot}$	
particle i mass	$m_i$	moment of inertia:	$I = \sum m_i r_i^2$	(6.1)
particle i position	$r_i$	rotational energy:	$E_{rot} = \frac{1}{2} I \omega^2$	
rotational frequency	$\nu_{rot}$			

In the quantum physical formulation, the energy levels of a rigid rotor are spaced proportionally to  $J(J+1)$  with  $J$  being the rotational quantum number (1). Here, we want to continue to consider a quasi-classical case, but in the presence of an external electrical field. Fig 6.1 illustrates the potential which is felt by molecules with a dipole moment. The molecules feel a force orienting their dipole moments in the external field and instead of vibrating, they can only librate within the potential. However, this is only true if the field is turned on slowly (adiabatically), so the molecules will not obtain an additional angular momentum from the field. The adiabatic condition is fulfilled if the field is turned on slowly compared to the rotational period, so the molecules will feel a time-integrated force of zero (because the molecules continue to rotate, and later librate, the force is directed half the time to the positive, and half the time to the negative direction).

If the field is turned on suddenly, then the molecules will retain their original rotational energy and will obtain additional rotationally energy in the new potential. Depending on their orientation when the field was turned on, the molecules can be caught in the potential minimum and librate, or will sit on the potential maximum and continue to rotate with higher momentum. In this nonadiabatic field (field turned on faster than the timescale of rotation), we therefore find no trapping of the molecules in oriented states, but see an impulsive increase or decrease of the rotational energy as a function of the molecular orientation. If the field is turned off again, the molecules will be have different rotational momenta, i.e. we impulsively excited rotational states (see Fig. 6.2).

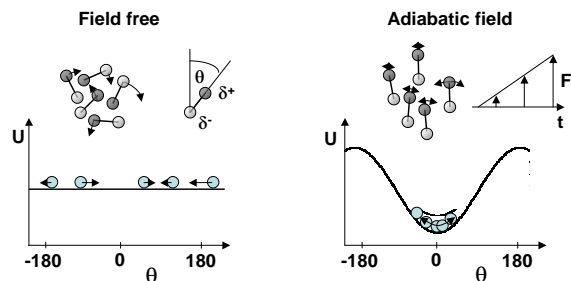


Figure 6.1: Adiabatic alignment of molecules in an external electric field: in absence of a field, molecules rotate freely with a rotational frequency corresponding to their rotational state (left). In presence of a strong field, the molecules feel a sinusoidal potential which forces them to align their dipole moments.

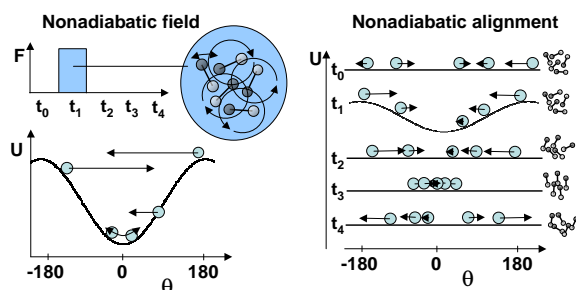


Figure 6.2: Nonadiabatic alignment of molecules in an external electric field. Left: If a strong field is turned on suddenly, the molecules feel a sudden sinusoidal potential which traps some molecules in librational states, but increases the rotational energy of others which will continue to rotate. Right: If the field is suddenly turned off, the molecules continue to rotate with the momentum they picked up in the strong field. This leads to temporary "nonadiabatic alignment" of the rotating molecules, e.g. at  $t_3$ .

Because all molecules feels the field at the same time, they get excited in a coherent fashion. In the right side of fig. 6.2 we see what can happen if the duration of the pulsed field was shorter than a rotational period, but long enough to dominate the rotational motion of the molecules: the molecules have new rotational impulses which point towards the potential minimum of the pulsed field. If we wait for some time, the molecules can meet in the rotational phase space, e.g. we have a transient orientation of the molecules (Fig. 6.2,  $t_3$ ).

### 6.1.2 Rotational spectroscopy

In Terahertz spectroscopy, the molecules are rotationally excited by AC fields. If the frequency of the exciting wave corresponds to a transition frequency for an allowed transition ( $\delta J = \pm 1$ ), the field can drive this transition. To connect this excitation with the alignment concepts we just covered, you may think about the AC field like a DC field for molecules rotating with the AC field frequency. If the pulse is long, it is possible to scan the frequency and observe rotational transitions, hence perform rotational spectroscopy in the frequency domain. To produce the corresponding far-IR pulses is a challenge which was recently mastered by generating the difference frequency between two infrared laser pulses with nonlinear optical media (usually crystals with different refractive index along two crystal axes).

If the excitation pulse is short, then the bandwidth of the excitation pulse is large (remember the uncertainty principle:  $\Delta E \cdot \Delta t \geq \hbar$ ) and many states are excited simultaneously. In this case, the excitation is

impulsive (similar to the nonadiabatic alignment) and the molecules rotate with well-defined phase. Large molecules have higher moments of inertia, hence they rotate slower and the corresponding transition frequencies are lower. The transition frequencies for larger molecules falls into the microwave regime and can be excited using technology corresponding to electron spin resonance spectroscopy. The short pulse excitation scheme is used for fourier transform microwave spectroscopy (FTMW), where molecules are excited in phase.

### 6.1.3 Fourier Transform Microwave Spectroscopy

For FTMW spectroscopy, a molecular gas is expanded into vacuum through a pulsed valve. Often an inert carrier gas (typically a noble gas) at atmospheric or higher pressure is used to improve the expansion conditions. The expansion creates a supersonic jet, in which the molecules cool drastically. The cooling is due to the fact, that the molecules in the expansion collide until they have the same velocity ( $T_{kin} \rightarrow 0K$ ) and every collision redistributes energy between the internal rotational and vibrational degrees of freedom and the kinetic degree of freedom ( $T_{rot,vib} \rightarrow T_{kin}$ ). The rotationally cold molecules are excited coherently (in phase) with a short Terahertz pulse. The rotating dipoles of the molecules in vacuum induce currents into a detector antenna and the rotational frequencies are determined via this time domain signal (very similar to FT-NMR/ESR). A fourier transformation of the time domain signal yields the rotational frequencies with a resolution limited only by the observation time, because the molecules in vacuum rotate freely. Recent experiments reach a resolution in the kHz regime. This spectroscopy requires very cold molecules because the signal is only proportional to the initial population in the molecular ground state.

## 6.2 Visible and Ultraviolet Spectroscopy

Optical spectroscopy detects absorption or emission of visible light. This radiation interacts with vibrational and electronic degrees of freedom in atoms and molecules. Spectroscopy of rotational states and low-energy vibrational states falls into the near and far infrared regime, and will only be discussed as they are relevant for the discussion of electronic transitions. Fluorescence spectroscopy is most relevant for biology: It allows imaging and detection of a small number or even single particles. The number of biomolecules (e.g. proteins) in a cell may range from single molecules to  $10^4$  molecules and the high sensitivity is therefore of large importance.

## 6.3 Molecular States

To describe optical transitions, we often think in concepts derived from the mathematical description of Eigenstates. To discuss concepts like absorption and emission or the Franck-Condon principle, it is useful to quickly recapitulate the quantum mechanical description of matter.

Mathematically, Eigenstates are found by defining a molecular wavefunction  $\Phi(x, t)$  which describes the positions and momenta of all particles. To jump to the wavefunction formalism is a leap of imagination, but is in line with the observation of the wave-particle dualism described earlier. Lets consider a periodic wavefunction with wavelength  $\lambda = \frac{1}{k}$  in space (x) and with the frequency  $\omega$  in time (t):

$$\Psi(x, t) = a \cdot e^{i(kx - \omega t)} \quad (6.2)$$

Lets consider the derivative of the wavefunction versus time. We know that the energy of a particle wave is  $E = h\nu = \hbar\omega$ , and by substitution we can directly relate the temporal derivative of the wavefunction to its energy:

$$\frac{\partial \Psi}{\partial t} = (-i\omega)\Psi(x, t) = (-i\frac{E}{\hbar})\Psi(x, t) \quad (6.3)$$

Next, lets consider the second derivative versus space. Here we can relate the wavelength  $\frac{1}{k}$  to the impulse using the deBroglie wavelength  $p = \frac{h}{\lambda}$ :

$$\frac{\partial^2 \Psi}{\partial x^2} = (-k^2) \Psi(x, t) = \left(\frac{p^2}{\hbar^2}\right) \Psi(x, t) \quad (6.4)$$

So the wavefunction formalism usefully relates some abstract wave properties to observables like energy and impulse according to the wave-particle dualism. To describe useful Eigenstates of matter, we must assure that Energy conservation is obeyed:  $E_{const} = E_{kin} + E_{pot} = U(x) + \frac{p^2}{2m}$ . Multiplication with the wavefunction allows us to substitute the terms for energy and impulse described above and leads to the famous Schrödinger equation:

$$E\Psi(x, t) = U(x)\Psi(x, t) + \frac{p^2}{2m}\Psi(x, t) \quad (6.5)$$

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = U(x)\Psi(x, t) - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \quad (6.6)$$

The Schrödinger can be used to find time-independent (stable) states which correspond to standing waves. If we want to describe a molecule, we have many particles interacting and we must find a solution for each particle in the electric potential of all other particles. Fortunately, the wavefunction can be assembled by using the sum of (partial) wavefunctions which correspond to standing waves ( $\Psi(x, t) = \sum a_n e^{i(k_n x - \omega_n t)}$ ). In ab initio calculation, the wavefunctions are often approximated by the sum of gaussian functions.

When it comes to calculate molecular Eigenstates, the Born Oppenheimer approximation helps to reduce the magnitude of the mathematical problem. Born and Oppenheimer suggested that the nuclear and electronic motion can be treated separately, because the electron move very rapidly as compared to nuclei. We can therefore consider the nuclei as frozen in space and optimize the electronic configurations independently. Mathematically, this corresponds to a separation of the wavefunction into an electrical and a nuclear part  $\Psi = \Psi_{el.} \cdot \Psi_{nuc.}$ . The resulting Eigenstate energies become  $E = E_{el.} + E_{nuc.}$ , hence the electronic and vibrational / rotational energy levels can be described independently. Once the electronic problem is solved, the forces on the nuclei, or the motion of the nuclei in the electronic field can be considered. By varying the nuclear positions until the lowest energy structure is found, it is possible to predict stable molecular structures.

## 6.4 Selection rules

For optical transitions, just as for non-optical transitions, the laws of energy conservation and momentum conservation must be observed. Energy conservation means, that in an optical transition the energy difference between initial and final state must correspond to the photon energy. Momentum conservation is harder to grasp, but it is clear that the photon momentum must be conserved. Hence, optical transitions between states of identical symmetry are forbidden. Less stringent selection rules can be derived from the assumption that optical processes are instantaneous processes ("sudden approximation"). For the vibrational states this leads to the expected conservation of positions and momenta, e.g. the Franck-Condon factors as shown in Fig. ???. This also forbids the simultaneous excitation of two particles, because there is no interaction time for the particles during the optical process. Hence we expect that electronic transitions allow only the excitation of a single active electron and the remaining electron configuration remains unperturbed ("Koopmanns' correlation").

The Frank-Condon approximation is a direct consequence of the Born-Oppenheimer approximation: If the wavefunction can be separated into an electronic and a nuclear part, then the same separation can be used for the calculation of transition probabilities. Hence it is possible to calculate electronic transition probabilities independently from vibrational ones. The vibrational probabilities reflect the nuclear positions and momenta in the initial and final state, whereas the electronic term is independent thereof. This leads to very intuitive considerations when we want to understand the dominant vibrational transitions in an electronic excitation: The nuclear wavefunction in initial and final state must overlap (remember: the wavefunction describes the position and momenta of the particles).

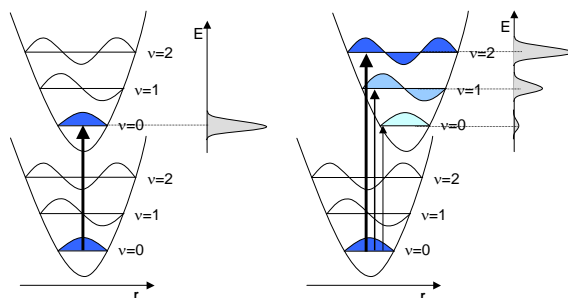


Figure 6.3: Franck Condon factors describe the vibrational selection rules via a probability matrix  $FC_{n,m}$  for transitions from each initial vibrational state  $\nu_n$  (lower potential) to each final vibrational state  $\nu_m$  (higher potential). The positions and moments of the nuclei are not allowed to move during the excitation process, this is equivalent to the statement, that the vibrational wavefunctions must overlap. Hence the excitation in the potential energy scheme shown here must be exactly vertical and the probability to access a final state is directly proportional to the waverfunction overlap.

The Frank-Condon approximation can also be considered as a instantaneous approximation for electronic transitions: if electronic transitions occur faster than the timescale of motion for the nuclei, then the nuclei have no time to change their position or momentum during the excitation process.

## 6.5 Good Fluorophores

Good fluorophores are chromophores which show large fluorescence quantum yields and are stable against photodegradation. Lets consider what determines the excited state lifetime. There are a number of relaxation processes open to a photoexcited molecule: (1) Fluorescence is the transition from a higher to a lower electronic state by emission of a photon and often occurs on a nanosecond timescale. All considerations about selection rules discussed for absorption must apply. (2) Phosphorescence is also the emission from an excited electronic state, but involving an electron spin-flip, e.g. transition from a triplet to a singlet state. This is a somewhat forbidden process and as a result the process occurs on a much longer timescale, e.g. milliseconds to seconds. (3) Internal conversion (IC) is an electronic transition without absorption or emission of a photon. The energy difference between initial and final electronic state is deposited into other molecular degrees of freedom, i.e. vibrational excitation. The probability for this process depends on the overlap between the wavefunctions of initial and final state. Here, Frank-Condon considerations are helpful to consider the nuclear overlap, which will be large for similar structures and small energy gaps (–, similar states can overlap). Hence we expect fast IC for states with small energy gaps. But there are cases when the overlap becomes large along one coordinate of motion, e.g. along an isomerization coordinate, and IC is notoriously difficult to predict and can occur on the femtosecond to nanosecond timescale. (4) Intersystem crossing (ISC) is a radiationless transition involving a spin-flip. Due to the forbidden nature of a simultaneous spin flip and electronic transition, this process is typically slow (ns regime). (5) Isomerization or dissociation processes can occur directly from electronically excited states, the latter in particular when sigma-antibonding orbitals are occupied.

According to Kasha’s rule, higher electronically excited states quickly relax to the first excited state which determines the photochemical properties. This is a simple result of the small energy gap and resulting large state overlap and fast IC between higher excited states. The first excited state is usually much higher in energy than the electronic ground state (typically several eV) and here IC may be too slow allowing fluorescence to dominate. A large flexibility of the molecule can also lead to fast IC along some deformation coordinate, hence good fluorophores are usually rigid molecules (or, like the green fluorescent protein, encased into a rigid environment). ISC to triplet states can quench fluorescence, and due to the long lifetime of triplet states lead to chemical reactions which destroy the chromophore.



# Bibliography

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