

8. Optical spectroscopy at low temperatures

8.1. Zero-phonon line and phonon wing

Before discussing single-molecule experiments at low temperature, we need some basic knowledge of the optical spectroscopy of impurities in solids. We start with the simple case of only one molecule in a solid at zero temperature. If there was no coupling to vibrations, the absorption spectrum would consist of a single line, with a width given by the excited state lifetime, according to Heisenberg's relation. However, the electronic system of a molecule is in principle coupled to all possible vibration modes in the molecule and in the solid matrix around it. This coupling arises from the change in vibrational potential between ground and excited electronic states: Because the vibrational potential and the associated nuclear wavefunctions in an excited state are different from those in the ground state, exciting the electron modifies the nuclear movement, i.e., it can change the number of vibrational quanta, i.e., it can modify the vibrations of the molecule. This action of an optical excitation on the nuclear degrees of freedom takes place although the electronic dipole moment does not directly act on nuclear variables. Fortunately, one does not have to consider all possible vibration modes to understand the absorption and fluorescence spectra qualitatively. Usually only a few of these modes are coupled strongly to the optical transition, which simplifies the analysis considerably. We first consider coupling of the electron to a single *harmonic* vibration mode. Often, a totally symmetric C-C stretching mode (breathing mode) is coupled most strongly and is responsible for the most striking features of the optical spectra. For simplicity's sake, we further assume here that only the equilibrium position of the nuclei along the associated vibration coordinate is modified: this is the approximation of a *linear* vibronic coupling.

We therefore consider a harmonic potential $E_g(R)$ in the ground state $|g\rangle$, which is displaced by ΔR_e in the excited state $|e\rangle$ (potential $E_e(R)$), without any change in its curvature (such a change would give rise to quadratic coupling and be responsible for additional broadening processes that we neglect here). In the crude Born-Oppenheimer approximation, we can write the wavefunctions as products :

$$\begin{aligned} |e, n\rangle &\equiv |e\rangle |\tilde{n}\rangle \\ |g, m\rangle &\equiv |g\rangle |m\rangle \end{aligned} \quad , \quad [8.1]$$

where n and m are integers and the above notation \tilde{n} means n quanta in the excited well potential, whereas m means m quanta in the ground state potential. One usually calls Franck-Condon amplitude the overlap amplitude :

$$f_m^n = \langle \tilde{n} | m \rangle \quad , \quad [8.2]$$

and Franck-Condon factor the square modulus of this overlap :

$$F_m^n = |f_m^n|^2 = |\langle \tilde{n} | m \rangle|^2 \quad . \quad [8.3]$$

The Franck-Condon amplitudes can be expressed analytically from the overlap of harmonic oscillator wavefunctions. The special case where one of the wavefunctions is the ground vibrational state is very important, as this is the only populated state at low temperature. It can be shown easily (see Ex. 8.1) that the Franck-Condon factors have the following form:

$$F_0^n = |\langle \tilde{n} | 0 \rangle|^2 = \frac{\xi^{2n}}{n!} e^{-\xi^2} \quad , \quad [8.4]$$

where

$$\xi = \Delta R_e \sqrt{\frac{M\Omega_0}{2\hbar}} = \frac{\Delta R_e}{2\Delta x} \quad , \quad [8.5]$$

is half the harmonic oscillator displacement in reduced (dimensionless) units of the spatial spread of the ground state Δx , M is the mass and Ω_0 the angular frequency of the oscillator.

The absorption spectra of a molecule at low enough temperature are recorded starting from the ground vibrational state of the ground electronic state, and going to all vibrational states of the excited electronic state (these states are called vibronic [vibrational)-(electronic] states). The intensities of these absorptions are proportional to the Franck-Condon factors (see the schematic absorption and fluorescence spectra in Chap. 1). A similar argument applies to the emission or fluorescence spectrum, starting from the ground vibrational state of the excited electronic state, and going to all vibrational states of the ground electronic state. For linear vibronic coupling, the intensity distributions of the absorption and emission spectra are perfectly symmetric with respect to the zero-phonon line. They are mirror images of each other. Quadratic vibronic coupling and anharmonic terms introduce deviations from the mirror symmetry.

We now consider the coupling of a molecule to a large number of modes, for example to a branch of acoustic phonons. Each mode is now weakly coupled (weak ξ), and contributes a weak 0-1 absorption sideband shifted to the blue of the main absorption line (which corresponds to the 0-0 transition). Let us neglect the 0-2 transitions. Although the weakness of ξ suggests that this approximation should be a good one, this is not necessarily so. Indeed, these transitions are very weak, but their number is very large, of order N^2 , with N the number of modes. Considering only 0-1 transitions, we find a broad band on the blue side of the 0-0 absorption line, composed of many 0-1 transitions corresponding to each of the many vibration modes. The 0-0 line, however, is common to all modes and therefore remains very sharp. It is called the zero-phonon line (ZPL) because it corresponds to a purely electronic transition, where no vibrational quantum has been created, or destroyed if there were some vibrations present before photon absorption. The broad absorption band at higher energy is called the phonon wing (PW). The intensity of the ZPL with respect to the total absorption strength is called Debye-Waller factor, and is analogous to the intensity of spots in X-ray diffraction, or to the intensity of the recoil-free structure in Mössbauer spectroscopy. This Debye-Waller factor decreases rapidly with temperature. For a single oscillator with purely linear vibronic coupling, one can show (see Ex. 8.2) that the oscillator strength of the ZPL at non-zero temperature is proportional to:

$$I_{ZPL} = \exp \left[-\xi^2 \left(\tanh \frac{\hbar\Omega_0}{2k_B T} \right)^{-1} \right]. \quad [8.6]$$

Note that the overlap is less than 1, even at zero temperature, and that the ZPL intensity decreases exponentially with temperature as soon as this temperature exceeds the vibrational quantum. The ZPL is a quantum effect arising from a direct quantum overlap of the wavefunctions of electronic ground and excited states. It can be considered as the collapse of the ground state wavefunction by an optical “measurement” in the excited state (cf. Collapse or Measurement postulate of quantum mechanics). When the molecule is coupled to several oscillators, the Debye-Waller factor is obviously the product of the factors corresponding to each particular mode. The exponential decrease of the ZPL is therefore very sensitive to low-frequency modes such as acoustic phonons if they are not very weakly coupled. In

most organic materials, the intensity of the ZPL becomes negligible at temperatures higher than 30 K. In diamond, which is a very hard and light material with a high Ω_0 (the Debye temperature of diamond is about 2,000 K), the ZPL of certain impurities can still be observed at room temperature.

In the preceding model, the ZPL is a narrow line (with a linewidth given by the excited state lifetime). However, several processes contribute to its broadening:

- higher-order coupling to phonons, notably via the change in curvature of the potential. The latter effect, called quadratic coupling, shifts the 1-1 transition with respect to the 0-0 transition, in effect broadening the ZPL;
- anharmonicity of the vibrations; vibrational states are broadened by decay to modes with lower frequencies, thereby broadening the electronic transitions involving those vibrations;
- slower processes, called spectral diffusion, which will be discussed later in more detail.

If spectral diffusion is neglected, the homogeneous linewidth of a molecule is composed of two contributions, one from the lifetime T_1 of the excited state, the other one from "pure dephasing" processes, and called "decoherence" in quantum optics. Decoherence arises from interactions with phonons and other fast dynamical modes activated at finite temperatures. A process in which any other system coupled to the molecule changes state, in particular the thermal bath of the surrounding matrix, will lead to decoherence of the electronic ZPL. Taking both sources of broadening into account (see Ch. 9), one writes the full width at half maximum of the optical line, measured in units of angular frequencies ω , as:

$$\gamma_{\text{hom}} = \frac{1}{T_1} + \frac{2}{T_2^*}, \quad [8.7]$$

where T_2^* represents the "decoherence" time, i.e. the lifetime of the coherence between the two electronic levels, determined by bath fluctuations at relatively low frequencies such as acoustic phonons, etc.. At very low temperatures, the decoherence rate vanishes, since no degrees of freedom of any bath are activated any more. In many molecular crystals, this limit is reached already below a few K, which means that the optical width is limited by the lifetime of the excited state only. For an

allowed transition, the lifetime is of the order of a few ns, corresponding to a width of 30 MHz, or one-thousandth of a cm^{-1} .

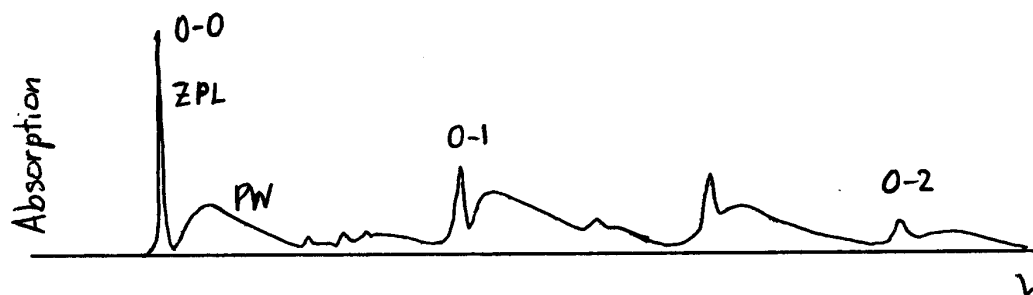


Figure 8.1 : Schematic absorption spectrum of a single molecule at low temperature. Several vibration modes contribute their own 0-1, 0-2, ... transitions. Note the sharp transitions due to an intramolecular vibration mode and the much broader phonon wings due to continua of lattice modes, such as acoustic and optical phonons.

Figure 8.1 illustrates the absorption spectrum of a molecule when coupling to phonons and intramolecular vibrations is considered. Note that the vibronic ZPL's are much broader than the pure electronic ZPL because vibrational levels have short lifetimes, on the order of picoseconds, and contribute their own width to the optical vibronic transition's width. In addition to this homogeneous contribution, there is an inhomogeneous contribution as well in ensemble experiments, which doesn't appear in single-molecule experiments. Each intramolecular vibration mode gives rise to its own vibronic progression, complete with ZPL's and PW's. However, the pure electronic ZPL is common to all modes, no matter how many modes are coupled to the molecule. Because of their large widths, one-phonon and multiphonon contributions to the phonon wing PW cannot be readily distinguished.

8.2. Inhomogeneous broadening

In usual experiments on ensembles, billions of molecules are observed at the same time. Because of defects and disorder, the electronic transition of each individual molecule is shifted with respect to the average value of the ensemble. This phenomenon is called inhomogeneous broadening. It is nearly independent of temperature, because it is essentially determined by structure, and structure is nearly frozen at low temperatures, at least as long as the matrix is solid. The extent of this broadening depends strongly on the nature of the sample, its purity, its

crystallographic quality, whether it is amorphous or microcrystalline, etc., and on the way the impurity molecules are embedded in the matrix. For optical transitions of molecules, the inhomogeneous width varies from about 300 cm^{-1} (10 THz) in a polymer, an amorphous glass, or a frozen solution, to less than $3 \times 10^{-2} \text{ cm}^{-1}$ (1 GHz) in unstressed sublimation-grown crystals, the best molecular crystals one can grow. A typical value of the inhomogeneous width for substitutional impurities in a low-quality molecular crystal is about $1\text{-}10 \text{ cm}^{-1}$. Therefore, in all cases, the inhomogeneous width is from one to several orders of magnitude broader than the linewidth of a single molecule at low temperature, typically 10^{-3} cm^{-1} (30 MHz) for an excited-state lifetime of 4 ns. In ensemble experiments, broad absorption profiles are constituted of the superposition of many narrow but randomly shifted single-molecule lines (see Fig. 8.2).

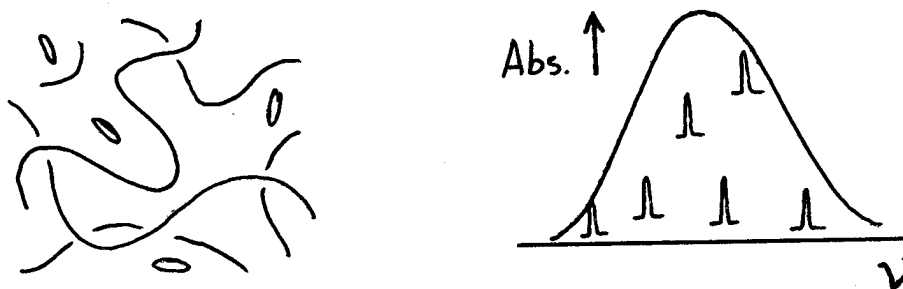


Figure 8.2 : Different environments in a disordered matrix shift the ZPL's of single molecules at random. The resulting ensemble spectrum is inhomogeneously broadened. It results from a superposition of the many narrow lines of individual molecules.

Comparatively little is known about the inhomogeneous distributions and lineshapes. They are determined by the local structure around the impurity, which is not known in any detail, only from ensemble statistical properties. In many cases, the local structure is relatively well defined, and can be considered as perturbed by many independent defects, such as vacancies, grain boundaries or dislocations in crystals. Assuming the contributions of such defects to be approximately equal, and applying the central limit theorem, we then expect a Gaussian inhomogeneous lineshape. However, other models give different shapes, for example, a uniform random three-dimensional distribution of defects interacting with an inverse cubic dependence on distance (dipole-dipole interaction) gives rise to a Lorentzian lineshape (see Ex. 8.3). In

general, the inhomogeneous distribution is neither Gaussian nor Lorentzian, and it is asymmetrical or skewed.

In crystals, a guest molecule often may occupy several imbedding positions, called insertion sites. They give rise to multiplets of zero-phonon lines in absorption spectra, called spectroscopic sites. Distinct insertion sites generally give rise to distinct spectroscopic sites, but distinct insertion sites related by a crystal symmetry will obviously give rise to the same spectroscopic site. Multiplets of sites also appear in fluorescence spectra, provided they are recorded with broad excitation, or excited at high energies (several thousands wavenumbers) above the 0-0 transition, where many combinations of transitions contribute to the absorption and all sites are excited with similar probabilities. Each one of these sites corresponds to molecules with slightly distorted structures, giving rise to slightly different vibrational spectra, lifetimes, etc. A particularly important case of multiplet spectra is found in Shpol'skii matrices, which are crystals of linear n-alkanes consisting of stacks of horizontal lattice layers where the molecules are packed nearly vertically. Narrow Shpol'skii lines are often obtained when the guest molecule matches the holes left in the crystal when one or a few host molecules have been removed. Shpol'skii systems are very convenient and useful in high-resolution molecular spectroscopy.

8.3. Hole-burning

Transient or persistent spectral hole-burning results from a modification by light of the optical properties of a material. It is therefore a nonlinear optical effect, which can be seen as a two-photon process. Let us consider an ideal hole-burning experiment at zero temperature. An ensemble of molecules absorbing with very narrow homogeneous lines (ZPL's) is irradiated with a monochromatic (or very narrow) laser. In first approximation, if the laser intensity is not too high, only the resonant molecules will efficiently absorb laser light through their ZPL. In first approximation, the other molecules don't see the laser. Now, an excited molecule may undergo a number of possible photophysical and photochemical processes. For example, it can be temporarily stored in its triplet state, with a different (usually lower or zero) absorption. During the lifetime of the triplet, the sample will absorb less at the frequency of the illuminating laser. If an absorption spectrum of the sample is measured, it will show a hole—a transient spectral hole—at the frequency of the laser

(see Fig. 8.3). But a molecule can also enter a much longer-lived dark state. Some of these product states may have very long (for all practical purposes infinite) lifetimes, in particular if the molecule undergoes a (photo-)chemical reaction. In that case, the spectral hole is permanent: one calls the process *persistent spectral hole burning* (PSHB).

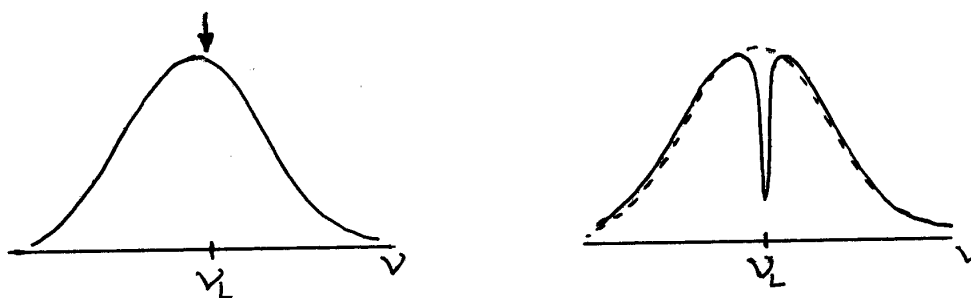


Figure 8.3 : Inhomogeneous absorption spectrum of an ensemble of molecules before (left) and after (right) illumination at the laser frequency ν_L . The sharp spectral hole appears because the narrow ZPLs of the excited molecules have been shifted to new frequencies. In the present case of a photophysical hole-burning process, these lines still appear within the inhomogeneous profile, leading to a small increase of the absorption at different frequencies (the total oscillator strength is conserved).

Molecules in solid matrices at low temperatures can undergo a number of different photochemical and photophysical processes. Photochemistry may involve electron or proton transfer, or larger rearrangements of atoms. Photochemical hole-burning generally leads to very large shifts of the photoproducts, which means that antiholes cannot be found in the spectrum. Figure 8.4 shows a few examples of photochemical processes.

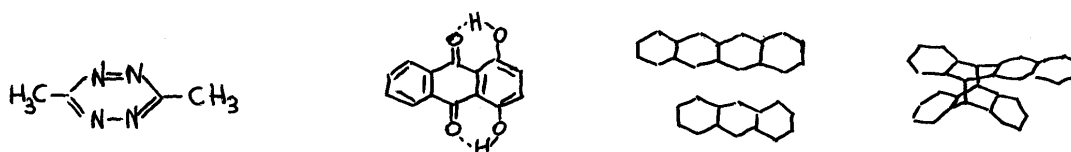


Figure 8.4 : Dimethyl-*s*-tetrazine (1st left) may decompose upon absorption of two photons, producing the very stable nitrogen molecule and radicals. Other processes involve rearrangements of hydrogen bonds, between molecules or within the probe molecule, as in the case of quinizarine (2nd left). Right : Tetracene and anthracene may react upon excitation of tetracene to form a photodimer (structure last right), whose absorption spectrum is shifted to the UV because of the loss of aromatic conjugation.

In photophysical processes, the conformation of neighboring atoms or groups of atoms is modified by illumination, leading to a shift of the absorption line, much larger than the homogeneous width, but usually smaller than the inhomogeneous bandwidth. The resulting antihole is much broader than the hole, and can only be measured after very deep and broad holes have been burned. Figure 8.5 illustrates some possible photophysical processes. Photophysical hole-burning is called ‘light-induced spectral diffusion’ in the context of single-molecule spectroscopy (see a later lecture on this subject).

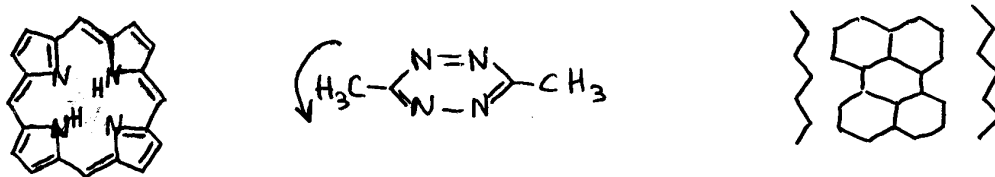


Figure 8.5 : Photophysical hole-burning proceeds from slight molecular rearrangements, and in general leads to photoproducts absorbing within the inhomogeneous profile. Free-base porphine may tautomerize by a correlated jump of the two protons to neighboring nitrogens. Although it arises from a photochemical process (two N-H bonds are broken and two new ones are established), the result amounts to a rotation of the molecule, i.e. may be considered as a physical process. Dimethyl-s-tetrazine (center) may also hole-burn due to tunneling of the methyl groups. Perylene in heptane Shpol'skii matrix presents several insertion sites between which the molecule may jump upon irradiation, leading to photophysical hole-burning between spectroscopic sites.

The experimental method to burn persistent holes is rather simple, inasmuch as the holes are long-lived. A single tunable narrow-band laser suffices. It is first used to irradiate the sample somewhere in the inhomogeneous bandwidth. Then, the laser is scanned to record an absorption spectrum, revealing the spectral hole. Contrast enhancement methods can be used to detect narrow holes, for example by holography, polarization analysis, or lock-in detection methods.

The hole-burning method is very useful in molecular spectroscopy, for the determination of lifetimes, or for vibrational spectroscopy, in the spectroscopy of molecules or ions with spin-multiplet states via the analysis of satellite holes, for the study of dynamical degrees of freedom in solids at low temperatures notably glasses, for the effect of external perturbations such as electric and magnetic fields, pressure and stress. A hole being very narrow, it enhances the sensitivity of these experiments by several orders of magnitude as compared to bulk experiments. More than 20 years

ago, hole-burning materials have been proposed as optical memories. A hole-burning sample can be seen as a photographic plate sensitive to several millions of different colors! However, practical difficulties, such as the low temperature and the problem of burning while reading, have limited their applications so far. Current research with rare-earth ions as optically active centers, aims at using such media in optical information analyzers and processors, which can treat many different wavelengths in a massively parallel way.

8.4. Single-molecule spectroscopy

We now consider a system in which molecules are very stable (hole-burning is inefficient or unlikely). If we focus our laser on a very small volume of sample, we will start to see statistical fluctuations of the number of molecules in resonance with the laser. If we scan our laser, we will see characteristic fluctuations of the optical absorption, or of the total fluorescence of the sample. These fluctuations have been first detected by Moerner in 1987 and are called statistical fine structure. Their analysis provides the homogeneous width of the molecules. In the same way that FCS reveals the average diffusion time in an ensemble of molecules, the autocorrelation of the statistical fine structure provides a peak whose width is related to the homogeneous linewidth.

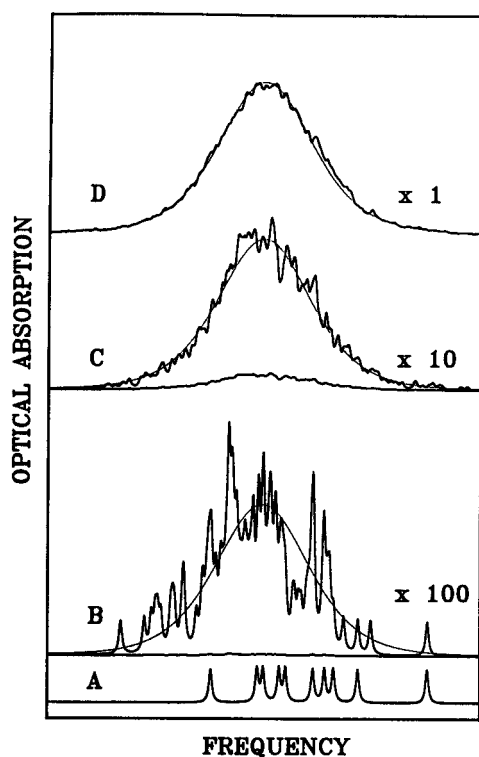


Figure 8.6 : resolution of the inhomogeneous profile into a set of single-molecule lines.

If we further reduce the focal volume and/or the concentration, the relative amplitude of the statistical fine structure increases (it scales like the inverse square root of the average number of molecules in the focus). In the regime where the average number of molecules is less than unity, the spectrum ideally consists of a set of resolved sharp lines on a low background (see Fig. 8.6). Each single peak corresponds to the absorption line of a single molecule.

The first optical signal of a single molecule has been detected in 1989 by W. E. Moerner and L. Kador with a complex method, involving a double frequency modulation, in which laser frequency *and* molecular resonance frequency were modulated at different frequencies. They applied this method to the absorption of a thin sample of pentacene in a para-terphenyl crystal. Although this method is very sensitive, it does not give very good results in the case of a single molecule because of optical saturation (see next lecture).

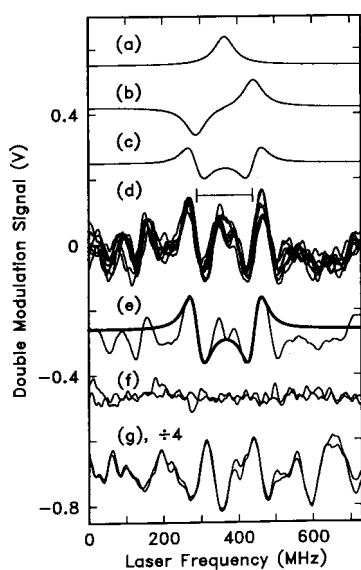


Figure 8.7 : The first optical detection of a single molecule, via absorption (Reproduced with permission from W. E. Moerner and L. Kador, *Phys. Rev. Lett.* **62** (1989) 2535. Copyright 1989 by the American Physical Society).

In the absorption experiment, the signal was measured as a weak variation of the intensity of the transmitted beam. In order to reduce the relative photon noise on that beam, the intensity has to be large, and as a consequence, the molecular signal saturates; in other words, the absorption cross-section of the molecule decreases. That was the main source limiting the signal/noise ratio in this first experiment (see Fig. 8.7). M. Orrit and J. Bernard showed in 1990 that a fluorescence excitation method provided a much better signal/noise ratio, as illustrated in Fig.8.8 by the line of a

single molecule for the same system. Since then, the fluorescence excitation method has been improved and generalized. It was first used for low-temperature spectroscopy, as detailed in this second part of the course, then for microscopy at room temperature, which we have discussed in the first part of this course.

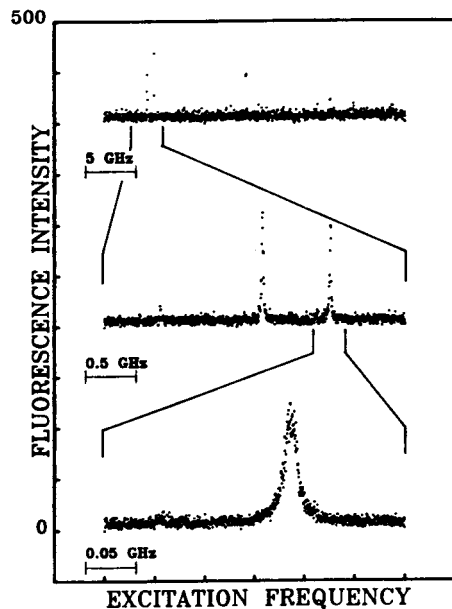


Figure 8.8 : Detection of single molecules by fluorescence excitation (M. Orrit and J. Bernard, *Phys. Rev. Lett.* **65** (1990) 2716).

Exercise 8.1: The wave functions of the nuclear harmonic oscillator in the electronic excited state are obtained from those in the electronic ground state by action of a translation operator,

$$U = \exp[-\xi(b - b^+)]$$

where ξ is a parameter proportional to the translation length and the operator parameter $(b - b^+)$ is proportional to the momentum operator of the vibrating particle.

i) Relate the translation operator to the momentum operator of the vibration, and derive the expression of ξ given in the course .

ii) Make use of the Glauber identity:

$$U = \exp(\xi b^+) \exp(-\xi b) \exp(-\xi^2 / 2)$$

to find the overlap $f_0^n = \langle \tilde{n} | 0 \rangle$ between the functions with n quanta in the excited state and the one with 0 quantum in the ground state, and derive the form of the Franck-Condon amplitudes given in the course.

Exercise 8.2: It can be shown that the distribution of the position for a harmonic oscillator (mass m , frequency ω) in thermal equilibrium at temperature T is Gaussian. A similar relation holds for the thermal distribution of momentum p , which obeys, $\lambda(T)$ being some function of temperature :

$$\rho_{th}(p) = \frac{1}{m\omega\lambda\sqrt{\pi}} \exp(-p^2 / m^2\omega^2\lambda^2).$$

For such a distribution, one can show the following relation:

$$\langle \exp(i\xi P) \rangle_{th} = \exp\left(-\frac{\xi^2}{2} \langle P^2 \rangle_{th}\right).$$

i) Using the expression of the momentum operator with creation and annihilation operators, show that $\langle P^2 \rangle_{th} = m\hbar\omega[\langle n \rangle_{th} + 1/2]$. Reminder: for a harmonic oscillator at temperature T , $\langle n \rangle_{th} = \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right]^{-1}$.

Calculate the same thermal average from the distribution $\rho_{th}(p)$, using the definite

$$\text{integral } \int_{-\infty}^{+\infty} \exp(-x^2) x^2 dx = \sqrt{\pi} / 2.$$

Deduce $\lambda(T)$ from the condition that these expectation values must be equal. What is the expectation value of the kinetic energy at temperature T ?

ii) Express the Debye-Waller factor as a sum of intensities of all transitions where no vibrational quanta are created or destroyed, and show that it can be expressed as the thermal average of the translation operator $U = \exp[-\xi(b - b^+)]$ (see Ex. 8.1 above), ξ being the coordinate displacement of the harmonic oscillator in reduced units (see Eq. 8.2).

From the expression of the above thermal average $\langle \exp(i\xi P) \rangle_{th}$, deduce the expression of the Debye-Waller factor given in the lecture.

Exercise 8.3: We study a simple model of inhomogeneous broadening, where a molecule's transition is shifted by interaction with point-like impurities distributed

randomly in space within a large volume V . The interaction varies as a power law of distance, $w(r) = W \left(\frac{r}{a} \right)^{-\alpha}$.

i) For one impurity, find the probability distribution $p_1(w)$.

ii) Assuming the probability distribution for N impurities $p_N(w)$ to be known, express $p_{N+1}(w)$ with $p_1(w)$ and $p_N(w)$.

iii) Introducing $\Pi_N(t)$, the Fourier transform of the probability distribution $p_N(w)$, show that it can be expressed as $[\Pi_1(t)]^N$.

iv) Study the real part of this Fourier transform in the case $\alpha = 3$, and show that it decays as $\exp(-\pi c v t / 2)$, where c is the concentration of impurities and v is an effective volume. Deduce the lineshape of its inverse Fourier transform, i.e., of the inhomogeneous profile.

Hint: note that $\Pi_1(t) = 1 + \varepsilon$ differs very little from unity because the integration volume is very large, and develop the N -th power as an exponential of the small difference ε (a similar argument was used in Exercise 6.4).