

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 (Heisenberg). 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 nuclear wavefunctions in the excited states are different, exciting the electron modifies the nuclear movement, i.e., it can bring about vibrations in the molecule. Fortunately, one does not have to consider all possible vibration modes to understand the absorption and fluorescence spectra. 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 responsible for most of the coupling. We further assume that only the equilibrium position of the nuclei along the associated vibration coordinate is modified (linear vibronic coupling).

We therefore consider a harmonic potential $E_g(R)$ in the ground state $|g\rangle$, which is displaced by ΔR in the excited state $|e\rangle$ (potential $E_e(R)$), without a change in the curvature. In the crude Born-Oppenheimer approximation, we can write the wave functions 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 \tilde{n} means n quanta in the excited well potential, and 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. It can be shown easily (see Exc. 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

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

is the harmonic oscillator displacement in reduced (dimensionless) units of the spatial spread of the ground state, 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 [vibronic] states). The intensities of these absorptions are proportional to the Franck-Condon factors (Fig. 1.3). 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 symmetric with respect to the zero-phonon line (mirror images).

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). Neglecting the 0-2 transitions (this approximation is not always a good one: indeed these transitions are weak, but their number is very large, of order N^2 , with N the number of modes), we find a broad band on the blue side of the 0-0 absorption line. The 0-0 line, which is common to all modes, is called zero-phonon line (ZPL), and the broad band is called phonon wing (PW). The intensity of the ZPL is called its 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 Moessbauer spectroscopy. This strength decreases rapidly with temperature. One often uses the following approximated formula for the oscillator strength of the ZPL at non-zero temperature:

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

The intensity of the ZPL therefore decreases exponentially with temperature. In most organic materials, the intensity of the ZPL becomes negligible at temperatures higher than 30 K. In diamond, which is a much harder material with a high Ω_0 (the Debye temperature is about 1000 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 (quadratic coupling: the 1-1 transition occurs at a different frequency than the 0-0 transition);
- 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 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 (often called "decoherence" in quantum optics), arising from interactions with phonons and other dynamical modes activated at finite temperatures. Any process in which some change of state in a bath takes place will lead to decoherence of the electronic ZPL. One therefore 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 "pure dephasing" time, i.e. the lifetime of the coherence between the two electronic levels, determined by bath fluctuations at relatively low frequencies (phonons, etc.). At very low temperatures, the pure dephasing rate tends to zero, since no degrees of freedom of any bath are activated any more. In many molecular crystals, this limit is reached already at 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} .

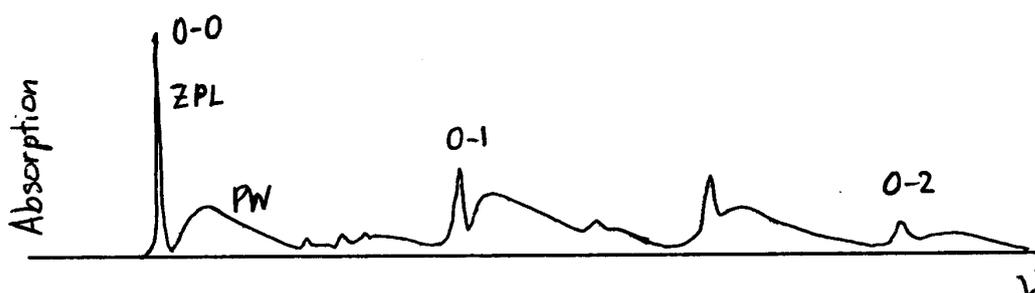


Figure 8.1 : Schematic absorption spectrum of a single molecule at low temperature. Several vibration modes contribute their own 0-1, 0-2, ... transitions.

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 of the width of the vibrational levels (homogeneous contribution; in ensemble experiments, there is an inhomogeneous contribution as well). Each intramolecular vibration mode gives rise to its own vibronic progression, ZPL's and PW's, but the pure electronic ZPL is common to all modes.

8.2. Inhomogeneous broadening

In usual samples, 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. This phenomenon is called inhomogeneous broadening. It is nearly independent of temperature, because it is determined by structure, and structure is nearly frozen at low temperatures (at least as long as the matrix is solid). The size of this broadening depends strongly on the quality of the sample 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 or in 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 for substitutional impurities in a low-quality molecular crystal is about 10 cm^{-1} . Therefore, in all cases, the inhomogeneous width is several orders of magnitude broader than the linewidth of a single molecule at low temperature. Broad absorption profiles are constituted of the superposition of many randomly shifted narrow lines (see Fig. 8.2).

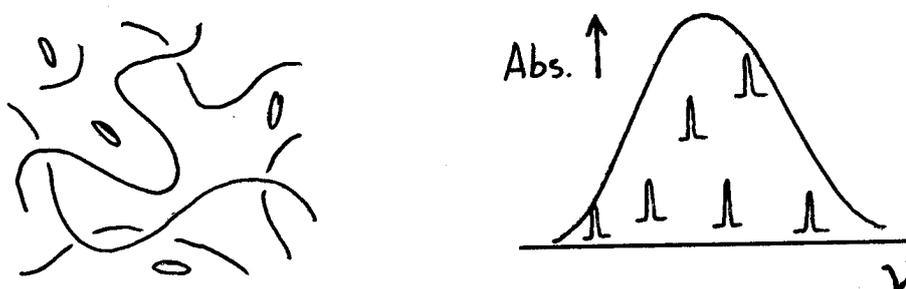


Figure 8.2 : Different environments in a disordered matrix shift the ZPL's of single molecules at random. The resulting ensemble spectrum is inhomogeneously broadened. It results from a superposition of the many narrow lines of individual molecules.

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

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 or in fluorescence spectra recorded with broad excitation, or excited at high energies

(several thousands wavenumbers) above the 0-0 transition. Each one of these sites corresponds to molecules with slightly different structures, giving rise to slightly different vibrational spectra, lifetimes, etc. A particularly important case is that of Shpol'skii matrices, which are crystals of linear n-alkanes. Their crystal structure is layered with the long axis of the molecules nearly perpendicular to the layer. Narrow Shpol'skii lines are often obtained when the guest molecule matches the holes left in the crystal when removing one or a few host molecules. Shpol'skii systems are very current and useful in 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 absorb light. The other ones 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 the 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).

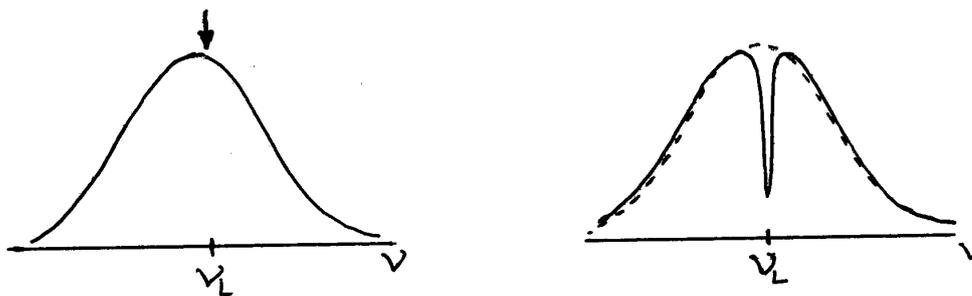


Figure 8.3 : Inhomogeneous absorption spectrum of an ensemble of molecules before (left) and after (right) illumination at the laser frequency ν_L . The sharp spectral hole appears because the narrow lines of the excited molecules have been shifted to new frequencies, in the present case within the inhomogeneous profile (photophysical hole-burning).

Molecules in solid matrices at low temperatures can undergo a number of different photochemical and photophysical processes. Photochemistry may involve electron, proton transfers, or large 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.

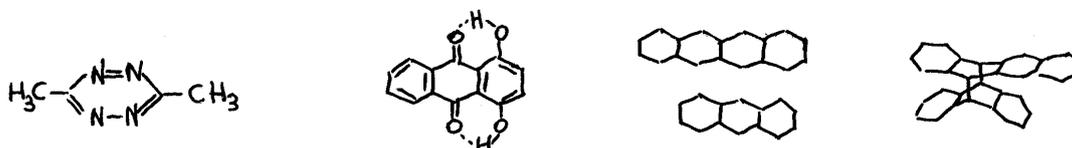


Figure 8.4 : Dimethyl-*s*-tetrazine (1st left) may decompose upon illumination, producing the very stable nitrogen molecule. Other processes involve rearrangements of hydrogen bonds, between molecules or within the probe molecule, as in the case of quinizarine (2nd left). Right : Tetracene and anthracene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

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).

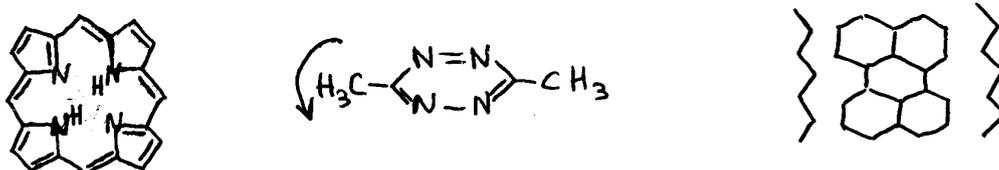


Figure 8.5 : Photophysical hole-burning proceeds from slight molecular rearrangements, and in general leads to photoproducts within the inhomogenous profile. Free-base porphine may tautomerize by a correlated jump of the two protons to neighboring nitrogens. Although it can be considered as chemical, the result amounts to a rotation of the molecule, i.e. to 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.

The experimental method to burn persistent holes is rather simple, since 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 hole. Contrast enhancement methods can be used to detect narrow holes, for example by holography, polarization, or lock-in detection methods.

The hole-burning method is very useful in molecular spectroscopy (determination of lifetimes, 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 aims at using such media in optical information analyzers and processors, which could 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.

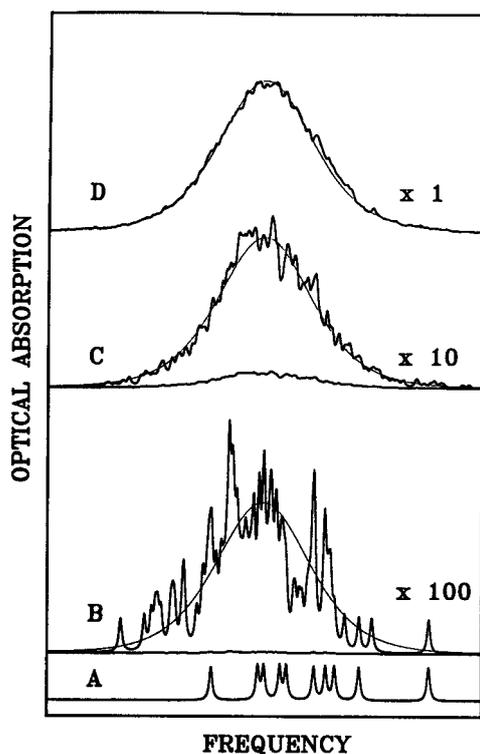


Figure 8.6 : resolution of the inhomogeneous profile into a set of single-molecule lines.

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 (laser frequency *and* molecular resonance frequency were modulated at different frequencies) of 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).

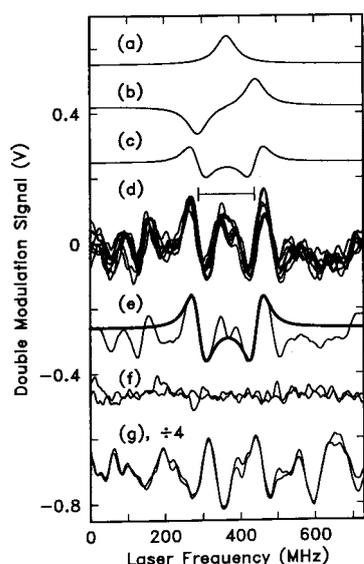


Figure 8.7 : The first optical detection of a single molecule, via absorption (Reproduced with permission from W. E. Moerner and L. Kador, *Phys. Rev. Lett.* 62 (1989) 2535. Copyright 1989 by the American Physical Society).

The absorption signal is 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 is 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 (second part of this course), then for microscopy at room temperature, which we have discussed in the first part of this course.

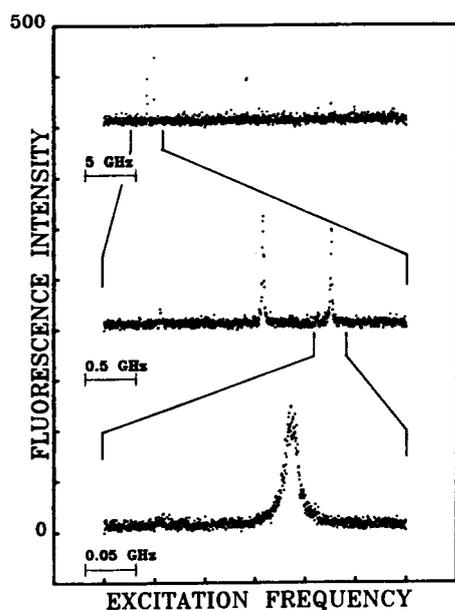


Figure 8.8 : Detection of single molecules by fluorescence excitation (M. Orrit and J. Bernard, *Phys. Rev. Lett.* 65 (1990) 2716).

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 $(b - b^+)$. Relate the translation operator to the momentum operator of the vibration, and derive the expression of ξ given in the course .

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 prove the equation given above.

Exercise 8.2: 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 .