

11. External field effects

The homogeneous width of a single-molecule line at low temperatures (typically 30 MHz or 10^{-3} cm^{-1}) is 5 to 6 orders of magnitude lower than the inhomogeneous width of a frozen solution ($3 \times 10^2 \text{ cm}^{-1}$) or at least 3 orders of magnitude narrower than lines of spectroscopic sites in ordinary molecular crystals (a few cm^{-1}). Such narrow resonances offer a very sensitive way to probe the effect of external perturbations, applied either as homogeneous fields from large sources in the laboratory, or from micro- or nanoscopic sources in the environment of the molecule. The information that a single molecule can relay about its environment is of high interest in physical chemistry and in nanoscience. In the present section, we discuss some external field effects that have been or could be applied to single molecules.

11.1. Stark effect

An applied electric field perturbs the wavefunctions of atoms and molecules, and shifts their electronic levels. The Stark effect is the shift of the transition frequency, i.e., the difference in the shifts of the excited and ground electronic states. Applied fields are usually much weaker (they are limited by dielectric breakdown to about 10-100 MV/m in the « strongest » insulators) than the internal fields in molecules, by a factor of about 1000. Therefore, the quadratic Stark effect is much weaker than the linear one, except when the latter is zero for symmetry reasons. The third and higher-order Stark effects are negligible under usual conditions (dc voltage and macroscopic samples). The Stark shift can therefore be written as a function of the electric field \vec{E} :

$$h\delta\nu = -\delta\vec{\mu} \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot \delta\vec{\alpha} \cdot \vec{E},$$

where $\delta\vec{\mu}$ and $\delta\vec{\alpha}$ are the changes in molecular dipole moment and molecular polarizability tensor upon excitation. The linear and quadratic shifts depend on the direction of the electric field with respect to the molecular axes. The field responsible for the shifts is the local field, i.e. the part of the true microscopic field which is linear in the applied external field. The local field depends not only on the matrix, but also on the polarizability of the guest molecule itself, as there is a coupling between the matrix polarization induced by the molecular dipole, and polarization of the molecule induced by the matrix charges. If this polarizability is the same as that of the matrix,

and for a continuous and isotropic medium, the local field is given by the Lorentz correction factor, $(\epsilon + 2)/3$. A discussion of this polarizability contribution can be found in Aubret et al., *ChemPhysChem* **20** (2019) 345.

Most of the aromatic hydrocarbons used in single-molecule spectroscopy are centrosymmetric. If they occupy a centrosymmetric insertion site which conserves their inversion symmetry, as is the case in many molecular crystals (pentacene or terrylene in p-terphenyl, DBATT in naphthalene, etc.), there is no permanent dipole moments in first approximation and the Stark effect is mainly quadratic [Wild et al. *Chem. Phys. Lett.* **193** (1992) 451]. Polarizability changes upon excitation are of the order of 2×10^{-39} Fm², or 20 Å³, corresponding to quadratic Stark shifts of about 4 MHz/(MV/m)². In reality, crystal defects slightly break the central symmetry of the site, leading to linear Stark shifts of about 1 MHz/(MV/m), corresponding to dipole moments of a few tens of micro-Debye (1 D = 3.34×10^{-30} C×m).

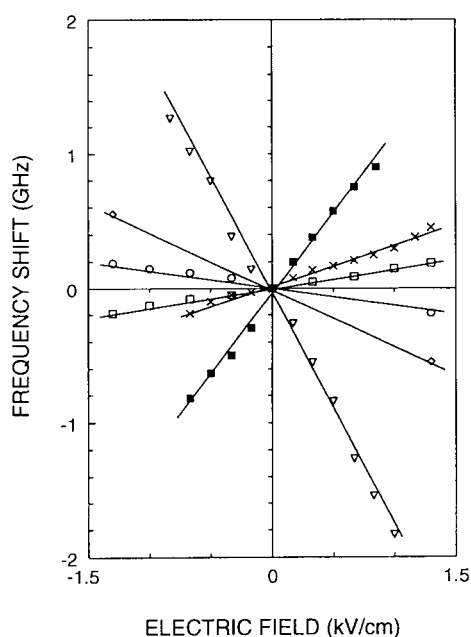


Figure 11.1 : Linear Stark shifts of single terrylene molecules in polyethylene [M. Orrit et al., *Chem. Phys. Lett.* **196** (1992) 595].

On the contrary, if the insertion site breaks the molecular symmetry, the matrix induces a linear Stark effect in the guest. This is notably the case for dibenzoterrylene in a di-bromonaphthalene crystal, where each of the 8 host molecules in the host crystal's unit cell give rise to 8 distinct insertion sites and thus to 8 different linear Stark effect coefficients (see Moradi et al., *ChemPhysChem* **20** (2019) 55). Another case of a broken inversion symmetry is that of a disordered matrix, such as a polymer,

where the linear Stark shift dominates for all fields. Figure 11.1 shows a plot of the Stark shifts of some single terrylene molecule lines in polyethylene. The dipole moment changes are of the order of 1 D. In a hole-burning measurement, the hole would broaden dramatically with applied field, and would very soon become too shallow to observe. A single-molecule line remains narrow at all fields, which makes it possible to investigate the Stark effect at high applied fields.

In Shpol'skii matrices, two types of inserted molecules coexist. For one population, the linear shift is very weak, and linear and quadratic contributions are comparable (see Figure 11.2). Presumably, those are molecules imbedded in centrosymmetric sites. For the other population, much larger dipole moments and linear shifts are observed.

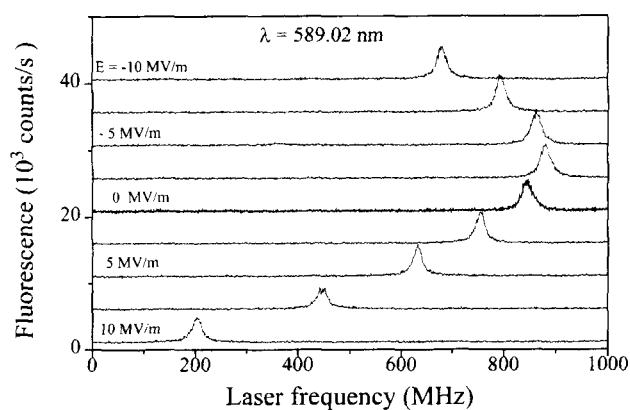


Figure 11.2 : Linear and quadratic Stark effect of the line of a single DBATT molecule in *n*-hexadecane [Brunel et al. *J. Phys. Chem. A* 103 (1999)2429].

The Stark effect can be used to test the symmetry of an insertion site. As we will see later in the case of terrylene in *p*-terphenyl, this symmetry can become lower after a spectral jump, which indicates that the rearrangement has broken the point symmetry of the molecule. In other cases, the Stark effect can be used to monitor a local field, or to shift a single molecule's line by as much as several GHz at very high rates of tens of MHz. As long as charge carriers are immobile in the material, the electronic polarization of atomic and molecular wavefunctions is mainly responsible for the shift. Therefore, the Stark effect has a nearly instantaneous response, and high rates of shifting can be achieved. If charge reorganizations take place, they usually occur via tunneling at low temperatures and are therefore very slow and present stretched kinetics. In this case, the Stark effect will have a much slower response.

11.2. Pressure and strain

The electronic levels of a molecule are also sensitive to pressure or strain in the surrounding matrix. Forces exerted by nearby molecules slightly deform the electronic cloud and displace the nuclei, again leading to changes in wavefunctions and energies. Similar effects take place when the molecule is brought from vacuum to the site it occupies in the matrix, and lead to the “solvent shift” of the electronic transition. Therefore, pressure shifts can be seen as small variations of the solvent shift. Calculations of the solvent shift and of the pressure shift are very difficult. Yet, a simple phenomenological model gives a qualitative understanding of the effect. We assume the Van der Waals interactions to dominate the solvent shift. Since this shift varies as R^{-6} , its variation can be related to those of the volume, which varies as R^3 . Therefore, for low pressures, the pressure shift coefficient writes :

$$\frac{\delta\nu}{\delta p} = 2\kappa \Delta\nu_S$$

where $\Delta\nu_S$ is the solvent shift and $\kappa = -\frac{1}{V} \frac{\partial V}{\partial p}$ is the compressibility of the matrix.

The pressure shift of pentacene [M. Croci et al., Chem. Phys. Lett. 212 (1993) 71] and terrylene [A. Müller et al., Chem. Phys. Lett. 241 (1995) 547] in p-terphenyl crystals have been measured with single molecules. In both cases, the shifts were linear, of the order of 1 MHz/hPa (or 1 GHz/atm. ; the shift was slightly larger for terrylene). Important variations (up to $\pm 30\%$) from molecule to molecule were found in the case of terrylene.

Anisotropic deformations of the matrix by a macroscopic stress field or by a localized deformation, e.g. induced by a tip, would lead to shifts of single molecule lines. Due to their difficulty, such experiments have not been published yet.

11.3. Zeeman effect

A magnetic field can also induce a weak shift of single-molecule lines. Due to the absence of a permanent magnetic moment, the Zeeman shift of a singlet-singlet transition is quadratic, and corresponds to the magnetic energy of diamagnetic materials. The quadratic Zeeman effect has been measured by hole-burning for porphyrins, molecules whose disk-like geometry enhances the diamagnetic

coefficient. Nevertheless, very high fields of several T had to be applied to observe the deformation of the spectral hole. The Zeeman coefficients in the case of porphine were of 60 MHz/T². Measurements on single terrylene molecules by the group of L. Kador in Bayreuth have given a value of up to about -8 MHz/T², i.e., considerably weaker than for porphine [Bauer and Kador, Chem. Phys. Lett. **407** (2005) 450].

11.4. Other external perturbations

Other external perturbations can be applied to the sharp lines of single molecules. For example, a rise in temperature causes a broadening and a shift of the line, which can be modeled with electron-phonon interactions. Another possible perturbation is a change in the bulk properties of a half-space in the vicinity of which single molecules are placed. For example, single molecules close to a surface might be used to sense the deposition of a thin gas layer on the surface, or the replacement of vacuum by liquid helium. No such experiments have been published yet.

A convenient way to change the properties of a material is to apply a voltage or current. This experiment has been performed with single terrylene molecules on a thin indium-tin oxide (ITO) semiconducting film. Moderate currents gave rise to very strong shifts of single molecules, as illustrated in Figure 11.3. The shift was attributed to a change in dielectric permittivity of the semiconductor under the applied current. Although the lattice temperature remained low, it is likely that the electron gas and/or shallow donor impurities were strongly perturbed by the field. The change in permittivity modifies the interaction of the molecular dipole with its electrostatic image in the interface, thereby shifting the transition.

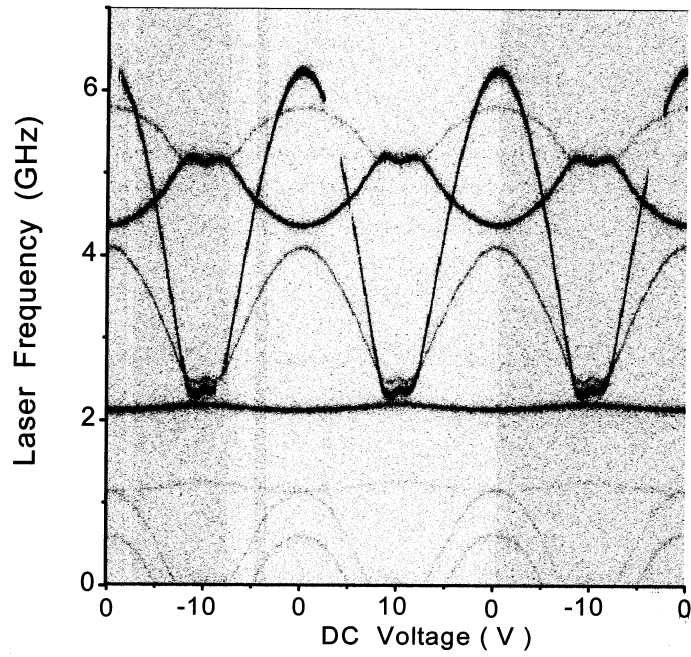


Figure 11.3 : Shifts of single terrylene molecules in hexadecane on an ITO layer, under the influence of a saw-tooth voltage. The lines shift without broadening because of modifications in the properties of the underlying semiconductor under the applied current [J.-M. Caruge et al., Phys. Rev. B 64 (2001) 205202].

Exercise 11.1: A molecule in a polarizable matrix is modelled as a point dipole placed at the center of a spherical cavity in an isotropic dielectric medium. A uniform electric field is applied from faraway electrodes and acts on the whole system, inducing polarization charges in the dipole and in the matrix. Write the most general solution of the Poisson equation corresponding to a polarizable dipole placed at the center of a sphere of dielectric permittivity ϵ_2 , itself surrounded by an infinite dielectric medium with a different permittivity, ϵ_1 , in presence of an applied field.

Examine and solve in the following cases:

- i) sphere of the dielectric with ϵ_2 in vacuum, no dipole in the center;
- ii) empty cavity in dielectric with ϵ_1 with and without a dipole in the center;
- iii) cavity containing a sphere with the same permittivity. From this case, derive the Lorentz-Lorenz correction factor:

$$L_L = (\epsilon + 2)/3$$

- iv) Take into account the polarizability α of the dipole in the empty cavity model.

Repeat the derivation when the dipole has a different polarizability α' than that of the surrounding matrix.

Exercise 11.2: Estimate the Zeeman shift of a single-molecule line based on the diamagnetic susceptibility χ of a typical organic material, with the magnetization

density $\vec{M} = \chi \frac{\vec{B}}{\mu_0}$. ($\chi \approx -10^{-9}$ m³/mol).