Statistical Fine Structure of Inhomogeneously Broadened Absorption Lines

W. E. Moerner and T. P. Carter[a]

IBM Almaden Research Center, San Jose, California 95120

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Using laser frequency-modulation spectroscopy, we have observed statistical fine structure (SFS) in the inhomogeneously broadened optical absorption of pentacene in *p*-terphenyl at liquid-helium temperatures. SFS is time-independent structure on the inhomogeneous line profile caused by statistical variations in the spectral density of absorbers in each frequency interval. The size of the SFS varies as the square root of the number of centers, and the autocorrelation of the SFS yields an estimate of the homogeneous linewidth without the requirement of spectral hole burning or coherent transients.

Inhomogeneous broadening[1,2] is a common feature of the low-temperature spectra of impurity centers in solids that can appear in optical spectroscopy[3] as well as in NMR, ESR, and Mössbauer absorption. For zero-phonon transitions in crystals, the inhomogeneous profile (for a particular orientation or site) is composed of many narrow homogeneous absorption lines with a distribution of center frequencies caused by dislocations, point defects, or random internal electric fields and field gradients. In an amorphous host, it is principally the large multiplicity of available sites that leads to inhomogeneous broadening.

Inhomogeneously broadened absorption lines are generally regarded as smooth, Gaussian profiles. In this paper we demonstrate the surprising fact that significant fine structure is a fundamental property of such lines. Consider a fixed frequency interval Δv within the inhomogeneous lines that satisfies $\Gamma \gg \Delta v \gg \gamma$, where γ is the homogeneous linewidth (full width at half-maximum absorption, or FWHM and Γ is the FWHM of the inhomogeneous line. The variations in the absorption coefficient we observe in a given interval Δv are due to statistical changes in the absorber spectra density over Δv. The phrase "statistical fine structure" (SFS) is used to refer to this static, time-independent, frequency-dependent structure. We show that SFS can be detected in a *high*-concentration sample by means of a zero-background technique, laser frequency-modulation (FM) spectroscopy.[4] Information about the statistics of the centers and about the underlying homogeneous linewidth γ can be derived from the SFS spectra, without the requirement of spectral hole burning or coherent transients.

The SFS measurements were performed on the inhomogeneously broadened optical absorption of pentacene molecules in *p*-terphenyl crystals and polycrystals at liquid-helium temperatures. Samples were prepared from mixtures of sublimed pentacene and zone-refined *p*-terphenyl which were either (i) heated between glass cover slips at $\approx 220\,°C$ and then cooled to form a 10–20-μm-thick polycrystalline thin film with $\approx 50 \times 50$-μm^2 crystalline regions, or (ii) grown into single crystals

with Bridgman techniques and cleaved into samples 200–300 μm in thickness. Concentrations ranged between 1×10^{-5} and 2×10^{-7} mol/mol, yielding low-temperature optical densities at the peak of the O_1-site absorption[5] between 0.01 and 0.15.

Standard FM techniques[6] employing a deuterated–ammonium-dihydrogen-phosphate electro-optic phase modulator and a Si avalanche photodiode were used to phase-sensitively detect the SFS signal. Complete details of the apparatus will be presented elsewhere.[7] The crucial feature of the FM technique is that the detected signal varying as $\cos(2\pi v_m t)$, $F(v)$, is proportional to

$$F(v) \sim -MP_0 e^{-a_0 L}[a(v+v_m) - a(v-v_m)]L, \quad (1)$$

where v is the laser frequency, v_m is the rf modulation frequency, P_0 is the laser power on the sample, M is the modulation index, $a(v)$ is the absorption coefficient, L is the sample length, and a_0 is the background value of a. [The component of the photocurrent varying as $\sin(2\pi v_m t)$ measures dispersion and will be discussed separately.[7]] Thus the FM signal measures the difference in aL at the two sideband frequencies. $F(v)$ has two well defined limits depending upon the ratio of v_m to the linewidth of the spectral features.[6] Let $L_\gamma(v) = (\gamma/2\pi)/[v^2 + (\gamma/2)^2]$ signify a single Lorentzian absorption of FWHM γ. When $v_m > \gamma$, $F(v)$ consists of two replicas of the Lorentzian line, one positive and one negative, separated by $2v_m$. In this regime $F(v)$ is maximal and independent of v_m. However, if $v_m < \gamma$, $F(v)$ approaches the derivative of a Lorentzian, with amplitude approaching zero with decreasing v_m.

A simple analysis helps in understanding the influence of various material parameters on the size of the SFS signals. We define the spectral density of absorbers in the probed volume n_v by requiring that $n_v dv$ be the number of absorbers with center frequencies in dv at v. Then the number of centers per homogeneous linewidth is $N_H = \int_{(\gamma)} n_v dv$, and the variations in this quantity (or in n_v) with frequency are the underlying source of SFS. Let $\Delta N_H, \bar{N}_H$ and $\Delta a, a_0$ signify the RMS amplitude and mean value of N_H and a, respectively, over the larger in-

terval Δv, then $(\Delta a)/a_0 = (\Delta N_H)/\bar{N}_H \cong (\bar{N}_H)^{-1/2}$, where the last relation follows by basic statistical physics and the assumed independence of the contributions from the individual absorbers. Therefore, small-$\bar{N}_H$ samples ($\bar{N}_H < 10$, for example) would be expected to be optimal for the observation of SFS. However, the detection of such a small number of centers in the presence of considerable background from the host matrix is quite difficult.[8]

Zero-background techniques like FM spectroscopy provide a way around this problem. When $v_m > \gamma$, it is easy to see that $F(v)$ measures the size of $(\Delta a)L$ directly and with maximum amplitude. One may show that $(\Delta a)L = \sigma(\bar{N}_H)^{1/2}/A = \sigma(\rho L/A)^{1/2}$, where σ is the peak absorption cross section, A is the beam area, and the volume density per homogeneous linewidth is $\rho = \bar{N}_H/AL$. Therefore, $F(v)$ increases if the concentration of absorbers or the sample length increases, and increases for smaller laser spots. Further, centers with higher cross sections lead to larger FM signals.

Figure 1 shows FM spectra of SFS (with $v_m = 58.1$ MHz) under varying conditions for pentacene in a single crystal of p-terphenyl. These spectra were acquired by our repetitively scanning a rhodamine-6G single-frequency dye laser (2.8-MHz linewidth) over the desired frequency range and averaging 64 scans. Unless stated otherwise, the laser was focused to a 20-μm-diam spot, and the sample was immersed in superfluid helium at 1.4 K. Trace a in Fig. 1 shows the amplifier noise floor. For trace b, the laser was tuned 50 cm^{-1} away from the 2-cm^{-1}-FWHM O_1-site absorption to show the laser noise (shot plus avalanche). For trace c, the laser wavelength was set near the peak of the O_1 line where $\bar{N}_H \cong 5 \times 10^5$. The striking frequency-dependent structure is SFS, i.e., the superposition of a larger number of individual homogeneous line shapes with a distribution of center frequencies. We emphasize that at a fixed spot in the sample and for a fixed spectral range, the SFS signals are static and repeatable, as evidenced by trace d (overlaid with trace c) acquired under identical conditions. In trace e, the focused laser spot has been moved to another location in the crystal; the SFS has changed, reflecting the different statistical sample of the shape of the n_v distribution. In trace f, the center frequency of the laser scan has been shifted by 50 MHz from that for trace e.

Trace g in Fig. 1 shows that the amplitude of the SFS indeed drops for a larger laser spot. Trace h (overlaid with trace g) shows another interesting effect: A persistent spectral hole can be formed if the unmodulated laser beam is held fixed at the frequency corresponding to the center of the trace for 30 s with the power increased to 11 mW. Because of this low-efficiency hole burning, the total laser intensity at the sample during probing was kept below 0.5 W/cm^2 to minimize the for-

FIG. 1. FM spectra in the cosine phase for a single crystal of pentacene in p-terphenyl. Trace a, no light on the detector. Trace b, 3 μW on the detector at a wavelength not in resonance with the O_1-site absorption. Traces c and d, FM spectra at 1.4 K near the peak of the O_1 absorption at 592.3 nm with a focused spot. Trace e, a new spot on the sample, same spectral range as for trace c. Trace f, laser center frequency offset by 50 MHz from that for trace e. Trace g, larger laser spot (0.75 mm diam). Trace h, persistent hole burned in the spectral range of trace g. Trace i, 1.4 K, focused spot. Trace j, 5.6 K, same location. Trace k, 7 K. The vertical scale is exact for traces c and d; all the other traces have the same scale but are offset vertically for clarity. 1 V corresponds to a change in aL of 1.1×10^{-3}. The detection bandwidth was 0.1 to 300 Hz and $v_m = 58.1$ MHz with $M = 0.16$. The frequency scale was calibrated by optical observation of the rf sideband spacing.

mation of hole trenches[9] that could alter the structure of the SFS. The hole in trace h is power broadened (43 MHz FWHM); with the use of an unfocused (3 mm diam) laser beam and 2 μW burn power, the hole width at the detection
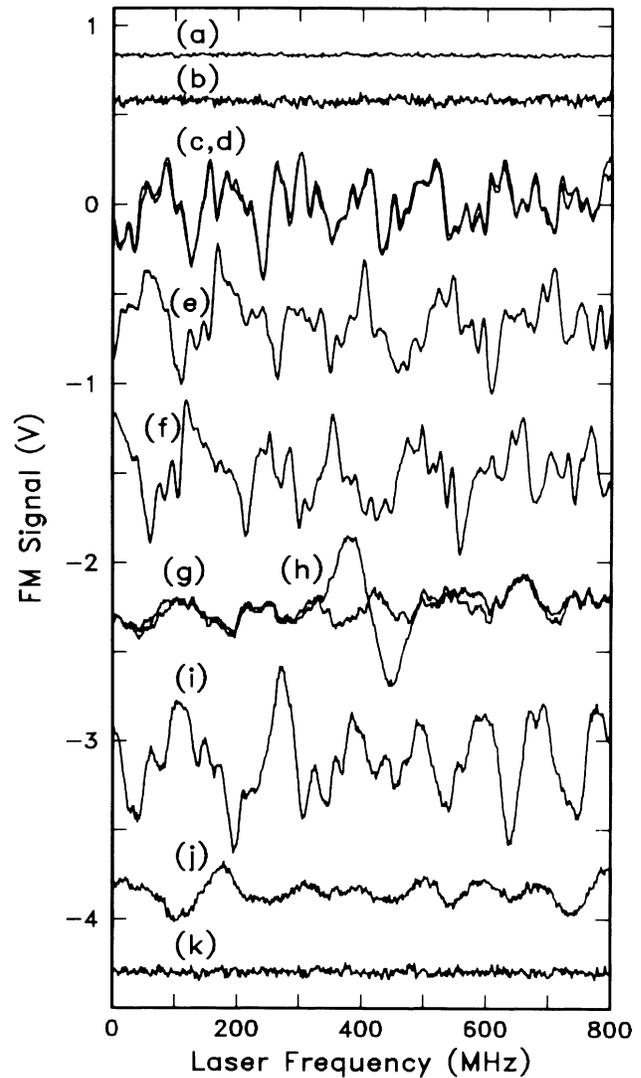
limit was measured to be 19.6 ± 0.5 MHz FWHM. This is the first reported observation of persistent spectral hole formation for the pentacene–p-terphenyl system. Since the guest is photostable and the host is crystalline, the hole formation process may involve reorientation of the pentacene in the hose as has been observed in other crystals containing photostable guests.[10]

The finest structure on the SFS signal is related to γ. For pentacene in p-terphenyl at 1.4 K, γ has been reported to be 7.8 ± 0.6 MHz.[11] Thus for traces c–h, in Fig. 1, the $v_m > \gamma$ limit applies and the SFS signals are maximal. Since the homogeneous linewidth of pentacene in p-terphenyl grows exponentially with temperature,[12] the small-v_m limit can be reached by a warming of the sample, and the SFS signal should disappear when $\gamma > v_m$. This is illustrated by traces i–k which are in-focus scans taken at 1.4, 5.6, and 7 K, respectively, corresponding to homogeneous linewidths of 7.8, 68, and 250 MHz.

Results similar to those in Fig. 1 were obtained for the O_2 site where $\gamma = 7.3 \pm 0.5$ MHz, but the O_3 and O_4 sites show smaller and broader SFS because γ is larger for O_3 and O_4. In addition, as the laser frequency is moved away from the center of the inhomogeneous line, the amplitude of the SFS continuously decreases, as expected.

SFS provides a new window on inhomogeneously broadened lines with intrinsic detail and complexity. For example, recording of SFS spectra over a larger fraction of the inhomogeneous profile may provide new information about the distribution of optical absorption energies available to the impurity centers. Furthermore, the scaling of the rms amplitude of the SFS spectra should reflect $\overline{N}_H$, and the spectral content of the SFS signal can be used to estimate γ. To demonstrate the scaling, Fig. 2 shows the rms amplitude of a larger number of FM spectra versus $\overline{N}_H$, for a sequence of seven polycrystalline thin-film samples. The samples were all prepared from a single concentration with different thicknesses. $\overline{N}_H$ was determined from the room-temperature optical density, the extinction coefficient, and the low-temper-
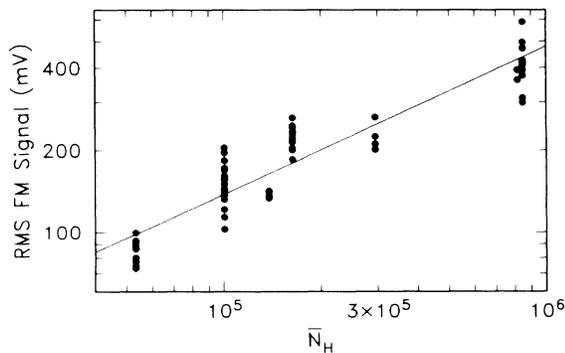
ature inhomogeneous broadening factor, $\Gamma/\gamma = 1.1 \times 10^4$. The straight line is a least-squares fit to the data showing that the rms amplitude of $F(v)$ grows as $(\overline{N}_H)^{0.54 \pm 0.05}$ which is consistent with the expected $(\overline{N}_H)^{1/2}$ dependence. The vertical scatter in the points is to be expected, because each FM spectrum was acquired over a different spectral range and therefore may be viewed as an independent statistical sample.

Estimates of γ can be extracted from the SFS spectra by exploitation of the properties of autocorrelation functions. The absorption coefficient may be written

$$\alpha(v) = c \int_{-\infty}^{+\infty} n_x L_\gamma(v-x) dx, \tag{2}$$

where c is the integrated absorption strength per molecule. We consider the ensemble-averaged autocorrelation of Eq. (2):

$$\langle a * a \rangle(v) = \left\langle \int_{-\infty}^{+\infty} \alpha(v') \alpha(v'+v) dv' \right\rangle, \tag{3}$$

where the angular brackets signify the expectation value over many spectral density functions n_x. To calculate $\langle a * a \rangle$, we note that the cross terms in this integral when $v \neq 0$ yield broad contributions with width on the order of the width of the n_v distribution. The result near $v = 0$ is

$$\langle a * a \rangle(v) \simeq c^2 L_{2\gamma}(v), \tag{4}$$

which is also a Lorentzian profile with FWHM equal to 2γ.

Equation (4) applies for the actual absorption, whereas the SFS spectra are related to $a(v)$ by the FM transformation, Eq. (1). It is a nontrivial problem to invert the FM operation for SFS spectra. Hence we consider the expected autocorrelation of the FM signals, $\langle F * F \rangle(v)$. We further limit ourselves to the case $v_m > \gamma$, although similar results can also be derived for the opposite limit.[7] The result is

$$\langle F * F \rangle(v) \simeq -L_{2\gamma}(v+2v_m) + 2L_{2\gamma}(v)$$
$$-L_{2\gamma}(v-2v_m). \tag{5}$$

Thus an estimate for γ can be derived from the FWHM or second derivative of $\langle F * F \rangle$ at the origin; i.e., the expectation value of the autocorrelation of the FM signal has a FWHM equal to twice that for the underlying homogeneous absorption lines. For a single-crystal sample with concentration 3×10^{-7} mol/mol, we find $\gamma = 7.9 \pm 0.8$ MHz for the O_1 site at 1.4 K by analyzing the autocorrelations of six SFS spectra over a 4.8-GHz spectral range using $v_m = 150$ MHz. This value is consistent with the previously reported value[11] of 7.8 ± 0.6 MHz.

The central result of this work is that the spectral density of absorbers for an inhomogeneously broadened line, n_v, is not a smooth Gaussian profile; rather, n_v contains significant statistical fine structure, even for high-concentration samples. SFS should be a general feature of all inhomogeneously broadened lines in solids, and

FIG. 2. rms amplitude of FM signal vs $\overline{N}_H$, with use of in-focus spectra similar to trace c in Fig. 1 with $v_m = 50$ MHz. The solid line is a least-squares fit with slope 0.54 ± 0.05.

even in gases if measurements are performed on a time scale shorter than the collision time. We expect that SFS should be observable for color centers, ions, and molecular vibrational modes in crystals as well as in amorphous media. We note that SFS imposes a fundamental limit on the detectability of shallow spectral features in inhomogeneous lines.

(a)IBM visiting scientist.

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