

# Optical Detection of Magnetic Resonance of a Single Molecular Spin

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Historically, the standard methods of nuclear magnetic resonance and electron paramagnetic resonance have been limited in sensitivity to approximately  $10^8$  electron spins or  $10^{15}$  nuclear spins, respectively, due chiefly to the weak interaction between the individual spins and the rf electromagnetic fields used to excite the transition. Optical detection of magnetic resonance (also called ODMR) provides the possibility of higher sensitivity, since the spin transition is effectively coupled to a much stronger optical transition with oscillator strength near unity, and a wealth of information about the magnetic properties of photo-excited molecules and ions in the condensed phase has been obtained in this fashion.<sup>1</sup> In general, ODMR spectroscopy is performed by monitoring the intensity of optical emission (either phosphorescence or fluorescence) as the frequency of a microwave signal is scanned. Crucial to the method is the presence of metastable states in the optical pumping cycle whose lifetimes or populations can be affected by the microwave radiation. For example, when the microwave frequency is resonant with a transition among the metastable states, the optical emission rate can be altered. The use of the ODMR method improves the spin sensitivity of magnetic resonance by some orders of magnitude, but until recently single-spin sensitivity had not been achieved.

In the past few years, it has become possible to optically probe individual single molecules in solids by both absorption and fluorescence excitation spectroscopy<sup>2,3</sup> when the molecules are trapped (doped) in solids and the samples are cooled to liquid helium temperatures to reduce phonon vibrations. Under these conditions, properly chosen impurity molecules, such as the planar, rigid aromatic molecule pentacene, show an inhomogeneously broadened optical absorption profile. This happens because the homogeneous width of the individual molecular absorption lines becomes much narrower than the overall inhomogeneous linewidth caused by local strains and other imperfections in the host matrix. With sufficiently low concentration of impurity molecules, a narrowband, single-frequency laser can select and probe exactly one impurity molecule. To avoid laser shot noise, the highest signal-to-noise ratio is achieved with fluorescence excitation methods where the total Stokes-shifted emission is measured as a function of the wavelength of the pumping laser radiation.<sup>3</sup> These ideas have allowed detailed study of optical lineshapes, spectral diffusion, photon bunching and antibunching, Stark effects, amorphous system physics, and many other properties at the single-molecule level.<sup>4</sup>

Using a combination of single-molecule optical spectroscopy and ODMR, two groups have independently ob-

served the magnetic resonance transition of a single molecular spin for the first time. One group was composed of researchers at the University of Leiden, The Netherlands, and at the IBM Almaden Research Center, San Jose, Calif.,<sup>5</sup> and the other group was composed of scientists at the Free University of Berlin, Germany, and at the University of Bordeaux, France.<sup>6</sup> Both efforts used the useful model system composed of pentacene molecular impurities in a crystal of p-terphenyl.

To understand the experiment, it is useful to summarize the properties of the electronic energy levels of pentacene. Optical radiation strongly pumps the allowed transition between the ground singlet (spin 0) state  $S_0$  and the first excited singlet state,  $S_1$ . From  $S_1$ , the molecule often emits a fluorescent photon; however, about 0.5% percent of the time, a spin flip occurs so that the molecule enters the triplet state  $T_1$  which has spin 1. (The triplet state is formed by two electrons with spin parallel to each other leading to a net spin of the molecule and consequently to a magnetic moment.) After a time of some microseconds, the metastable triplet state decays back to the nonmagnetic singlet ground state  $S_0$ . Because  $T_1$  forms a bottleneck in the optical pumping cycle of the molecule (a dark state), the emission rate of fluorescent photons from  $S_1$  is affected by the lifetime of  $T_1$ . In addition, due to the anisotropy of the molecule itself and of the local crystalline environment, the triple degeneracy of  $T_1$  is lifted and three spin sublevels are formed:  $T_x$ ,  $T_y$ , and  $T_z$ . Thus, even with zero external magnetic field, various magnetic dipole transitions can occur between the triplet sublevels.

By using a single-frequency dye laser near 593 nm to select a single pentacene molecule and simultaneously irradiating with tunable microwave radiation, both groups observed the (zero field) 1480 MHz magnetic resonance transition among the  $T_x$  and  $T_z$  triplet spin sublevels at 1.5 K for a single molecular spin. The figure (see next page) shows examples of some of the spectra, where the signal plotted is the change in the fluorescence emission rate as a function of the applied microwave frequency. Traces (a) and (b) show the lineshapes when many pentacene molecules are pumped by the laser, where  $O_1$  and  $O_2$  refer to two of the possible substitutional sites for pentacene in the p-terphenyl crystal. Traces (c)-(g) show the single-molecule lineshapes for four different single molecules. An interesting observation is that the onset of the transition varies from single molecule to single molecule, in a fashion similar to the difference in onsets for the two inhomogeneously broadened origins  $O_1$  and  $O_2$ . However, the location in frequency space suggests that some molecules with an  $O_2$  local magnetic environment are located in the long-wavelength edge of the  $O_1$  site.

As is the case for large  $N$ , the lineshape of the microwave transition for a single spin is broadened by hyperfine interactions induced by the large number of different configurations possible for the nearby proton nuclear spins. This is in accordance with the ergodic theorem, as many different configurations of the proton nuclear spins in the molecule are sampled on the time scale of the measurement of the triplet state transition. In contrast, in the large  $N$  experiment, an ensemble average is measured rather than a

T<sub>x</sub>—T<sub>z</sub> transition of pentacene in *p*-terphenyl detected with Fluorescence Detected Magnetic Resonance under various experimental conditions. **(a), (b)** Conventional FDMR spectra at large N with excitation in the O<sub>1</sub> and O<sub>2</sub> sites, respectively. **(c)** to **(g)** Single-molecule FDMR spectra for a thin sublimed crystal with different excitation wavelengths of the laser  $\lambda = 592.447$  nm **(c)**,  $\lambda = 592.370$  nm **(d)**,  $\lambda = 592.404$  nm **(e)**,  $\lambda = 592.065$  nm **(f,g)**. Traces **(c)** and **(e)** are averages of three; traces **(f)** of eight and trace **(g)** of four individual scans, respectively. Spectra **(a)** and **(b)** are given in arbitrary units. (See Fig. 3 of Ref. 5)

time average. These observations open the way for a variety of new studies of magnetic interactions in solids at the level of a single molecular spin. In particular, the properties of various amorphous organic materials may be able to be studied in greater detail, as the selection of a single molecular spin removes all orientational anisotropy as well as all inhomogeneous broadening. The power of magnetic resonance in general in the study of fine and hyperfine interactions, local structure, and molecular bonding can now be enhanced with these first demonstrations of useful sensitivity in the single-spin regime.

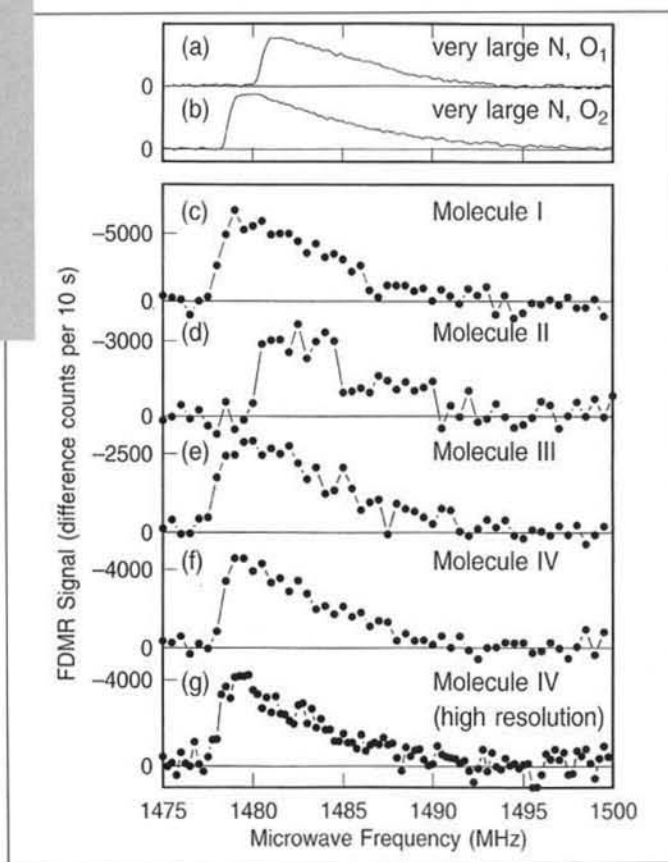
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## Toward Ultrafast Movies of Moving Atoms

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By combining ultrashort laser pulses techniques with scanning tunneling microscopy (STM), we have developed an instrument that obtains simultaneous 2 psec time resolution and 50 Å spatial resolution. This is a nine orders of magnitude improvement over the time resolution previously attainable with STM. We have used this instrument to measure the response of the tunneling gap to excitation by a subpicosecond electrical pulse. Our technique is not limited to STM, and can be implemented in a variety of scanning probe microscopies, allowing the observation of ultrafast dynamics on the atomic scale.



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The basic idea behind this demonstration is the use of a nonlinear tip-sample interaction to obtain the ultrafast time resolution.<sup>1</sup> This is achieved by modulating both the sample and the tip responses with two short optical pulses. By scanning the time delay between the two pulses and integrating the signal, a cross-correlation of the tip-sample response is obtained. To demonstrate the technique, we used an external nonlinearity, an ultrafast photoconductive switch, photolithographically introduced into the STM tip assembly, rather than the intrinsic nonlinearity of the tunneling gap.

In the experiment (see Figure 1(a)),<sup>2,3</sup> 100 fsec pulses from a modelocked Ti:sapphire laser excited ~650 fsec wide voltage pulses on the sample transmission line. As those voltage pulses passed under the STM tip, a second laser beam gated the switch on the tip assembly. The average tunnel current was recorded as a function of time delay between the two laser pulses. In Figure 1(b), we show a series of time-resolved tunnel current correlations, taken at different tip-sample separations. For clarity, only the changes relative to the average tunnel current are shown. The height of the correlation peak in each trace is approximately proportional to the average tunnel current. Moreover, when the