

phase variation onto the signal, leading in the time domain to a nonsymmetric pulse distortion (a) characteristic of that experienced by ultrashort pulses propagating in fibers near the zero-dispersion wavelength. Parts (b) and (c) show measurements of reconstructed pulses read-out in the real and time-reversed experimental geometries, respectively. Parts (d) and (e) show examples of correlation and [a time-reversed] convolution, respectively, achieved by using a shaped test pulse identical to the signal. In the case of correlation, the output is a short, featureless femtosecond pulse resembling the original reference; the holographic process automatically generates a matched filter appropriate for removing unwanted phase modulations from the signal. Such matched filtering could be used for dispersion compensation and pulse compression and for decoding of information transmitted in an encrypted format on ultrafast optical waveforms.

In summary, well known principles of holographic processing, used extensively for pattern recognition and filtering of two-dimensional spatial signals, have been extended to the femtosecond time domain. This makes possible signal processing operations, such as time reversal, correlation, and convolution, which are otherwise difficult to achieve for ultrafast optical waveforms.

SPECTROSCOPY

Quantum Optics of a Single Molecule in a Solid

By W. E. Moerner, IBM Research Division, Almaden Research Center, San Jose, Calif.

Trapping of single atomic ions in a radio-frequency trap by photon-recoil cooling and detection of the emitted fluorescence has proven to be a successful way to investigate the fundamental interaction of light and matter and to test our understanding of quantum physics.¹ The extension of these studies to molecules has failed so far, because all molecules—even diatomic species—possess several internal degrees of freedom that prevent laser cooling

In the past few years, it has become possible to optically probe individual single molecules in solids by both absorption and fluorescence excitation spectroscopy when the molecules are trapped (doped) in solids² and the samples are cooled to liquid helium temperatures to reduce phonon vibrations. Most of the recent research efforts using single-molecule spectroscopy (SMS) have concentrated on the ultrasensitive measurement of host-guest interactions in solids, for example, single molecule spectral diffusion (or spontaneous motion in frequency space caused by changes in the nearby environment) and single molecule spectral hole-burning (optical modification of the absorption of the single molecule).³ Here, we show that the solid host acts as a useful trap for the single molecule, allowing observation of a uniquely quantum-mechanical effect, photon antibunching, which was first observed for Na atoms in a low-density beam.⁴

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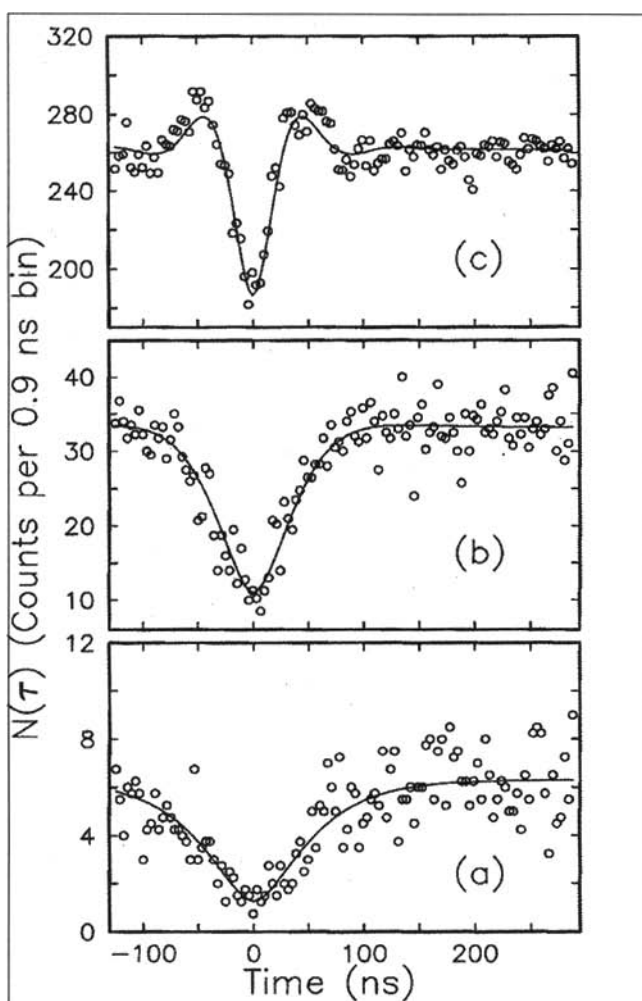
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Physically, an optical field that exhibits photon antibunching is one in which the photons "space themselves out in time," that is, the probability for two photons to arrive at the detector at the same time is small. This special correlation property only occurs for certain purely quantum-mechanical optical fields; in fact, simple classical light such as that from an incandescent lamp exhibits photon bunching rather than antibunching. One light source that is naturally antibunched is the fluorescence emission from a single atom (or molecule). This can be understood as follows: In the correlation measurement, the joint probability for the arrival of a photon at time $t = 0$ and the arrival of a photon at time $t > 0$ is recorded. The detection of a fluorescent photon at $t = 0$ prepares the atom in its ground state since it just emitted this photon. The probability of emitting a second photon at $t = 0$ is zero since the atom cannot reradiate from the ground state. On the average, a finite time (approximately half a Rabi period) has to elapse to have a finite probability for the atom to be in the excited state and hence emit a second photon. Of course, if more than one atom is emitting, the antibunching effect quickly disappears, since the atoms emit independently.

In the SMS experiments,⁵ the correlation between photons emitted by an optically pumped single pentacene molecule (in a p-terphenyl host at 1.5 K) was investigated on time scales comparable to the excited state lifetime of 24 ns. To measure the correlation function, a so-called Hanbury Brown-Twiss setup was used in which the fluorescence emission was divided by a beamsplitter and detected by two phototubes. Using electronics similar to that used for the single atom case,⁴ the distribution of delay times τ between

the detection of successive fluorescence photons called $N(\tau)$ was measured.

The figure shows the measured distribution of time delays $N(\tau)$ for different levels of pumping intensity, as measured by the Rabi frequency Ω_R . Starting with trace (a), as $\tau \rightarrow 0$, $N(\tau)$ goes to zero when the background due to accidental pair correlations has been removed. For long times ($100 \text{ ns} \leq \tau \leq 300 \text{ ns}$) $N(\tau)$ reaches a constant value. The correlation tending to zero at short times is just the antibunching phenomenon. The solid lines are fits to the data as derived from the corresponding optical Bloch equations for the three-level pentacene molecule (including the lowest triplet state). The theory reproduces the experimental data very well and the Rabi frequencies obtained from the fits are in good agreement with those calculated from direct



The intensity correlation for fluorescence emission from a single pentacene molecule in a p-terphenyl crystal as given by the distribution of measured time delays $N(\tau)$. Antibunching is clearly seen for $\tau \rightarrow 0$. The different traces correspond to different Rabi frequencies Ω_R : (a) 11.2 MHz; (b) 26.2 MHz; (c) 68.9 MHz. The deviation from zero at $\tau = 0$ is due to accidental pair correlations caused by Rayleigh and Raman background radiation. The laser excitation wavelength is $\approx 593.4 \text{ nm}$.

intensity measurements.⁵ At the highest power level, [trace (c)] the correlation function shows—besides the antibunching—Rabi oscillations that are damped out during the excited state lifetime.

Single molecule antibunching in solids differs from the earlier single ion experiments^{1,4} in three ways. First, the system under study here is a three-level, rather than a two-level system. Secondly, and more importantly, the ion experiments detected the resonance fluorescence from the two-level system, while this experiment detects the Stokes-shifted fluorescence from the excited singlet state that terminates on various excited vibrational levels of the ground state, and the antibunching is not significantly affected. Finally, here the solid acts as a useful trap for the study of quantum optical effects of a single molecule for which the effects of the phonon excitations of the host can be made unimportant by cooling the entire sample to low temperatures. In particular, no corrections due to transit time effects and/or secular motion are required. It is to be expected that applications of SMS to other molecule-host combinations can be used to observe additional quantum optical effects.

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New Questions in the Multiphoton Ionization of Atoms

By G.N. Gibson* and R.R. Freeman, AT&T Bell Laboratories, Holmdel, N.J., and T.J. McIlrath, University of Maryland, College Park, Md.

Multiphoton ionization (MPI) of atoms by intense laser fields has now received over a decade of research. Despite great progress in understanding this seemingly simple process, new observations continue to be made that challenge the accepted picture. The most recent set of experiments highlight the important role of excited states in the MPI process.

Early on, MPI was generally considered to be a non-resonant process in which the detailed atomic structure was not thought to play an important role. However, using electron spectroscopy with ultrashort (100 fsec) laser pulses, it was found that resonances play a dominant role.¹ The resonances result from the shifting of the excited states by the AC Stark shift in and out of resonance with the laser during the course of the laser pulse. Typically, the electron spectra