Pump-Probe Experiments with a Single Molecule: ac-Stark Effect and Nonlinear Optical Response

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We have measured the ac-Stark effect on single terrylene molecules in p-terphenyl crystals at superfluid helium temperatures. With the pump beam far enough from resonance, the molecular transition shifts as expected, i.e., proportional to the pump intensity and to the inverse pump detuning. Experiments closer to resonance with stronger beams show Autler-Townes-like structures that can be well reproduced by means of Bloch equations with two intense laser fields. These experiments are a demonstration of nonlinear optical effects with the localized electronic states of a single molecule trapped in a solid.

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Quantum optics, the study of the interaction of simple quantum systems with coherent light, has long been a testing ground for basic quantum mechanics. The many concepts it has bred may become crucial to the working of future nanoelectronic devices at the molecular scale. This remote aim requires experimental tests of the validity of quantum concepts in complex systems such as are found in condensed matter. Many of the quantum optical experiments done to date were performed on atoms or ions in vapors, beams, or traps. Atoms have the advantage of being simple, isolated from outside perturbations, and fairly well understood theoretically. Nonlinear spectroscopy [1] and, more recently, laser cooling [2] developed largely thanks to atoms. Here, we consider a particular class of experiments, those where two laser beams (a pump and a probe) act simultaneously on a quantum system. Several experiments in atomic physics fall into this category. For instance, in sub-Doppler spectroscopy, a strong pump beam "tags" atoms by saturating one of their transitions, while the probe beam reads the absorption change. More generally, a strong pump beam, by coupling two resonant levels, "dresses" atoms with laser photons, leading to changes in the response of the dressed atom to a probe beam [3] that appear as shifts of the levels and changes of their relaxation rates. For a slightly detuned pump, the transition of the dressed atom is shifted in proportion with pump intensity, and multiphoton resonances appear, which may exhibit gain for the probe beam [4]. For a resonant pump, transitions between dressed atom levels lead to three components in the emission spectrum [5] (the Mollow triplet), while the probe absorption spectrum shows a complex shape with amplification at strong pump saturation. The absorption spectrum from the excited

state to a third level shows a splitting known as the Autler-Townes effect. The shift of atomic levels under pump light, often called light shift, can be interpreted as an ac-Stark effect, where the quadratic effect of the relatively weak pump laser field is amplified by near resonance with the transition. While being perhaps the simplest manifestation of the dressing of atoms by laser photons, the light shift is the cornerstone of powerful laser-cooling methods [2] and of proposed nondestructive quantum measurements of photons [6].

For all their importance as models, atoms present some difficulties of their own (such as hyperfine sublevels), which make simpler two-level systems desirable in certain cases. In the present work, we wish to show that quantum optical experiments of the pump-probe type are also feasible with systems different from atoms [4] or small molecules in the gas phase [7], namely, localized electronic states in solids. Since these states are subject to very strong interaction with their surroundings, subtle and weak quantum effects are easily hidden by inhomogeneous broadening, a multiplicity of vibrational levels, or complex dynamics over a broad range of times. Although such techniques as hole burning do help eliminate inhomogeneous broadening [8], attempts to perturb spectral holes by an intense pump beam would give rise—besides other complications—to a strong background and make detection of the probe signal very difficult. A different approach is to use a single quantum system at a well-defined resonance. In this way, inhomogeneous broadening is absent and background can be largely reduced. Organic molecules dispersed in transparent solids provide good examples of such localized electronic states, displaying sharp zero-phonon lines. These lines may be isolated in the fluorescence excitation spectra of small dilute samples

at helium temperatures [9]. Ground and excited electronic states of these molecules are nondegenerate and are hardly perturbed by acoustic phonons. Relaxation from higher vibrationally excited states is so fast that electronic states of the molecules behave as if they were simple nonde-generate levels, at least for many of the properties probed by cw lasers. During the past few years, several experi-ments were performed on single molecules, including the study of saturation, bunching and antibunching of fluores-cence photons, and magnetic resonance within the triplet state [10]. So far, the results of the experiments have been well described by Bloch equations with a few lev-els. Still, since some quantum optical effects might be affected by the multiplicity of vibrational levels or by ma-trix states, it is important to check whether other kinds of quantum optical experiments apply to molecules in solids. The present Letter reports experiments done in parallel by two groups, demonstrating the first optical pump-probe experiments on single molecules. These results open a new field of nonlinear quantum optical experiments on systems in condensed matter, quite different from isolated atoms, ions, or molecules.

The Bordeaux setup for the study of single molecules is based on a confocal microscope, where the same parabolic mirror focuses the exciting light and collects the molecular fluorescence [11]. The light from a single-mode dye laser was frequency shifted by two acousto-optical modulators, providing pump and probe beams at different frequencies. The setup in Munich used a lens for focusing and a paraboloid for fluorescence collection [12]. Pump and probe beams were given by two single-mode dye lasers. In both experiments, the beams were superposed in a short length of optical fiber to ensure good overlap on the sample. The molecules studied were terrylene in sublimation-grown p-terphenyl crystals [13]. There are four main insertion sites of the terrylene molecule in the crystal, of which the most photostable, X_2 at 578.5 nm, was chosen for the measurements. Since the intersystem crossing yield to the triplet state is very weak in terrylene [13,14], the saturation intensity is high, which is favorable for observing the effects of an intense pump. The intense fluorescence excitation signals are proportional to the population of the molecule's excited state.

In addition to the two singlet states addressed by the lasers, terrylene has three triplet sublevels. Since the population rates a_i of these states are small, the excited singlet state population p_5 in the five-level system is related to that, p_2, in the two-level system by

$$p_5 = p_2 \bigg/ \left(1 + p_2 \sum_i a_i \tau_i \right), \tag{1}$$

τ_i being the lifetime of triplet sublevel i. For small variations of p_2 around its average value, the variations of p_5 are those of p_2, reduced according to Eq. (1). Therefore we did our calculations on a two-level molecule subjected to the sum of two near-resonant laser fields.

Spontaneous emission and pure dephasing are taken into account by the usual relaxation times T_1, T_2 in optical Bloch equations. The experimental data could be reproduced without adding dephasing ($1/T_2 = 1/2T_1$). The laser field strengths E_i were characterized by the Rabi frequencies Ω_i, with $\Omega_i = |\vec{\mu}_{12} \cdot \vec{E}_i|/\hbar$, where $\vec{\mu}_{12}$ is the dipole moment of the molecular transition. When the pump is far from resonance ($\Delta > \Omega_1$), the molecular transition is shifted by

$$\delta = -\Omega_1^2/2\Delta \tag{2}$$

to the first order in pump intensity, $\Delta = \omega_L - \omega_0$ being the detuning between pump and molecule. When the pump is closer to resonance, the shift may be calculated using an effective Hamiltonian [3], but a more general approach is to calculate the experimental signal using Bloch equations with pump and probe fields. This enables one to include a possible dephasing. The first order in probe intensity can be calculated analytically [5]. The pump-molecule system presents three eigenvalues which, for large detuning, can be interpreted [4,15] as the light-shifted transition at $\omega_0 + \delta$, a three-photon resonance at $2\omega_L - \omega_0 - \delta$, and a third resonance at ω_L corresponding to stimulated Rayleigh scattering. The effect of a resonant pump was difficult to observe experimentally on a single molecule with a weak probe because of the strong fluorescence background, and we had to increase the scanning intensity. In order to describe on-resonance data recorded with arbitrary pump and probe fields (hereafter called fixed and scanning fields, respectively), we numerically computed the full solution of the Bloch equations in steady state, by expanding the density matrix in Fourier series of the difference between fixed and scanning frequencies. We recursively solved for the population of the excited state and the coherence responsible for absorption or amplification of the scanning beam. These simulations are equivalent to the continued fraction method of [16] and were used to interpret experimental data for strong fixed and scanning fields. Oscillations appeared in the simulated excited population as a function of the frequency difference of the lasers at high fields ($\Omega > 3\Gamma$, Γ being the width of the transition), as reported in [16,17]. They arise from a kicked-oscillator behavior in the beating of two strong laser fields. This effect would be too small to detect as a population change in a single molecule, but might appear as a transfer of photons between the laser beams, as has been observed for atoms in vapors [17].

We first consider measurements of the light shift of the molecular line by a near-resonant pump. The fixed laser's intensity, given as the ratio I/I_s, where I_s is the saturation intensity, was adjusted to values between 1 and 40, while the scanning laser had a weaker intensity of about $0.5I_s$. The saturation intensity was of the order of 10 W cm^{-2}. This value looks much higher than the usual saturation intensities of allowed transitions in two-level systems.

It is probably due to the unfavorable orientation of the transition dipole moment of terrylene in a p-terphenyl crystal which is oriented along the long molecular axis and therefore lies almost perpendicular to the crystal surface, i.e., almost perpendicular to the polarization of the laser. In order to measure the shift, the line position as measured by the scanning laser was determined with and without the fixed laser. The laser(s) and the molecular transition could drift during the measurement, since, for all results presented here, the lasers were used without additional frequency stabilization. The effects of these drifts were minimized by recording unshifted and shifted lines alternately, and by averaging the data. Some of our results are shown in Fig. 1 for the dependence of the shift on pump intensity and in Fig. 2 for its dependence on the inverse of the pump detuning, yielding the expected linear behaviors. The error bars on the points were estimated from the standard deviation of several measurements (4–6). The error becomes larger when the pump is near resonance, because the background and its noise increase. The plots of Figs. 1 and 2 are consistent with the simple perturbation formula (2), at least within the range of intensities and of detunings investigated. A deviation from Eq. (2) is expected for weak detuning, but is probably less than the experimental error. The slope of the plot of shift versus detuning directly gives the Rabi frequency Ω_1 of the pump beam ($\Omega_1/2\pi = 93$ and 153 MHz for the data sets presented). Ω_1 is related to the transition dipole moment and to its orientation. The

knowledge of Ω_1 from the light-shift data complements earlier saturation studies [13,18]. These results confirm for the first time to our knowledge that the ac-Stark effect may be observed on localized electronic states in condensed matter with an accuracy similar to that for atoms or small molecules in the gas phase. The many vibrational levels of a molecule and a matrix do not significantly affect the shift despite their large density of states, because they are largely uncoupled from the driving laser fields.

Next, the pump laser beam was brought into resonance with the molecule, while the second beam was scanned across the resonance. The total fluorescence signal was recorded as a function of the scanning frequency. In order to obtain measurable signals, the scanning power had to be of the same order as the fixed one. Two examples of the observed structures are presented in Fig. 3. They generally have a W shape, attributable to the Autler-Townes splitting effect for weak probe power. The splitting between the two side wings tends to twice the pump Rabi frequency for $\Omega \gg \Gamma$ (for the molecule presented, $\Gamma/2\pi \approx 40$ MHz). Asymmetric profiles, not shown here, arose when the pump was slightly detuned from resonance. The intensity of the central peak relative to the wings increases with the Rabi frequency of the scanning beam. The experimental spectra are compared in Fig. 3 with theoretical simulations of the excited state population. The values of the Rabi frequencies were derived from light-shift measurements, i.e., the only adjustable parameters used in the calculation of the theoretical curves are the background and the overall intensity of the structure. The quantitative agreement is quite satisfactory. It might seem surprising that the total signal decreases when a weak resonant probe wave is

FIG. 1. Light shift of the zero-phonon line of a single terrylene molecule in a p-terphenyl crystal at 1.8 K. The shift varies linearly with the intensity of the near-resonant pump beam, detuned by 400 MHz to the blue from the molecular line. The error bars are estimated from the dispersion of several measurements. The inset, pertaining to a different molecule in different experimental conditions (1.4 K), shows the unshifted molecular line (a) recorded with the probe beam alone, and the light-shifted line (b) with the pump detuned by 190 MHz to the blue side of the line.

FIG. 2. Variations of the light shift with pump detuning, at constant pump intensity. The two plots relate to two different molecules measured with different setups, under different illumination conditions.
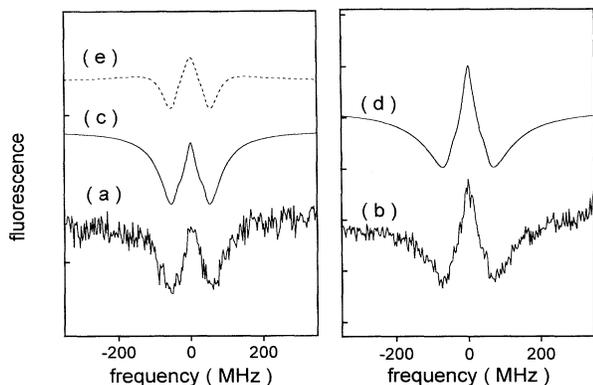
FIG. 3. Experimental (a,b) and calculated $(c-e)$ profiles of the total fluorescence signal when two strong beams excite a single molecule simultaneously, one of them at resonance, the other being scanned. The half-maximum linewidth is $\Gamma/2\pi = 40$ MHz. The Rabi frequencies (determined from light-shift measurements) are $\Omega_1/2\pi = \Omega_2/2\pi = 44$ MHz for curves a,c,e, $\Omega_1/2\pi = 44$ MHz, $\Omega_2/2\pi = 62$ MHz for b,d. Theoretical curves c,d are calculated without dephasing, while curve e with a pure dephasing of 12 MHz clearly differs from the experimental data. This is consistent with a pure dephasing less than a few MHz in this system at 1.4 K.

added to the pump. However, the relative phase of pump and probe being random, the probe subtracts as often as it adds to the pump. The subtraction effect dominates in the regime of pump saturation. The good agreement with theory indicates that no pure dephasing component need be included for terrylene in p-terphenyl at 1.4 K, as was also found in linewidth measurements on this system [19]. The broken curve in Fig. 3 (curve e) shows a calculated profile with a dephasing of 0.3Γ, clearly different from the experimental data. The very strong effect of dephasing on the expected excitation profile suggests using such pump-probe experiments to study dephasing and spectral diffusion on a molecule-by-molecule basis.

These first results show the possibility of nonlinear and quantum optical experiments on single large molecules in condensed matter, even though the small shifts measured are much weaker than matrix-induced inhomogeneous broadening and site splitting. The matrix does not blur the spectra, apart from noise introduced by the background, which limits their overall sensitivity to probe beams. We think that such nonlinear measurements might be used to probe dephasing and spectral diffusion on single molecules. The variations of the excited state population are indirect evidence for the transfer of photons between probe and pump beams by a single molecule, which could

be used in schemes like a single-molecule laser. The light shift could also be used for nondestructive measurements of the number of pump photons using a single molecule.

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