PHYSICAL REVIEW B VOLUME 50, NUMBER 18 1 NOVEMBER 1994-II

Autler-Townes modulation of coherent transients in photoexcited color centers

C. J. M. Tavares, M. A. Costa Neto, and R. Sitters
Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands

N. B. Manson
Laser Physics Centre, Research School of Physical Sciences, Australian National University, Canberra ACT2601, Australia

M. Glasbeek
Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands

(Received 2 May 1994)

It is shown that for inhomogeneously broadened transitions Autler-Townes interactions can be resolved in the time domain by performing a modified echo experiment. Constructive and destructive interferences of the Autler-Townes components in electron spin triplet states are observed in the optically detected spin-echo amplitude decay signals for two different triplet-state color center model systems in calcium oxide and diamond crystals, respectively.

The study of quantum interference effects in three- and four-level atomic systems is currently of considerable interest. In part the interest stems from developments in quantum optics such as lasing without population inversion.[1] As is well known, when in a three-level system one of the possible transitions is coherently driven while probing a second transition, the latter will be split (Autler-Townes splitting[2]). The splitting is characteristic of the perturbation exerted by the driving radiation field on the quantum system. Obviously, in order to resolve Autler-Townes (AT) splitting spectrally, inhomogeneous (Doppler) broadening effects should be less than the AT splitting itself. Since Autler-Townes splittings are usually small (on the order of a few MHz), up to now by far most of the experimental results have been obtained for atomic systems in the gas phase.[3] Time-resolved behavior of atomic Autler-Townes spectra has also been reported.[4] Recently, AT splittings have also been observed at radio frequencies for a color center in a crystalline environment.[5]

In this paper we show for two different three-level electron spin systems that information concerning Autler-Townes interactions is also accessible in cases where inhomogeneous broadening of the electron spin transitions is much larger than the induced AT splitting. The experiment comprises a modified Hahn-echo experiment using techniques for the optical detection of the spin resonances in the microwave region. As is well known,[6] in a two-pulse echo experiment the elimination of the influence of inhomogeneous broadening is accomplished by two resonant pulses (of frequency ω_{12}) with a time interval of τ. The pulses give rise to a coherent response at 2τ (the echo), irrespective of the amount of inhomogeneous broadening. In the echo experiments discussed here, during the rephasing interval (between τ and 2τ), a second microwave field is applied in order to coherently drive another transition of the three-level system (of frequency ω_{13}). As a result of the driving field at ω_{13}, levels 1 and 3 each will exhibit an Autler-Townes doublet splitting. It will be shown below that this splitting will give rise to amplitude-modulation effects of the echo (detected at ω_{12}), the periodicity of the echo modulation being characteristic of the Autler-Townes doublet splitting. The observations are reminiscent of the nuclear-modulation effects in electron spin-echo signals well known in magnetic resonance.[7]

We consider a three-level system with a Hamiltonian of the form

$$H=H_0+V(t)=H_0-\mu H_1\cos\omega t \ , \tag{1}$$

where H_0 is the time-independent part and $V(t)$ is representative of the dipolar coupling of the system to the magnetic-field component of the monochromatic radiation field. Coherent excitation of the $1\leftrightarrow3$ transition assuming negligible relaxation gives rise to

$$\psi(t)=a_1e^{-iE_1t/\hbar}\psi_1(t)+a_3(t)e^{-iE_3t/\hbar}\psi_3(t) \ . \tag{2}$$

The coefficients $a_j(t)$ with $j=1,3$ are sought in the standard rotating-wave approximation[3,8] from the coupled differential equations which follow when Eq. (2) is substituted into $H\Psi(t)=i\hbar\dot{\Psi}(t)$. In the echo experiment, coherent excitation is at ω_{12}, but since $\Psi_1(t)$ is mixed with $\Psi_3(t)$ by the driving field near ω_{13} [cf. Eq. (2)], the oscillating dipole moment giving rise to the echo at 2τ is given as

$$\langle D(t)\rangle=\frac{d}{2}\left[\left[1-\frac{\Delta\omega}{2\varpi}\right]\cos\left[\omega_{12}+\frac{\Delta\omega}{2}+\varpi\right]t\right.$$
$$\left.+\left[1+\frac{\Delta\omega}{2\varpi}\right]\cos\left[\omega_{12}+\frac{\Delta\omega}{2}-\varpi\right]t\right] \ . \tag{3}$$

In Eq. (3), d is equal to the transition dipole moment for the $1\leftrightarrow2$ transition, $\Delta\omega=\omega-\omega_{13}$, and $\varpi=\frac{1}{2}\{(\Delta\omega)^2+\omega_1^2\}^{1/2}$, where ω_1 characterizes the Rabi

0163-1829/94/50(18)/13795(4)/$06.00

frequency for the coherently driven $1 \leftrightarrow 3$ transition. It thus follows that at exact resonance (i.e., when $\omega = \omega_{13}$), the echo is phase shifted by $\pm\omega_1 t/2$, *this phase shift being typical of the Autler-Townes effect.* Since in our optical probe method we are able to detect echo phase shifts (*vide infra*), we can measure the Autler-Townes effect in the time domain.

Experimentally, time-resolved Autler-Townes effects in electronic spin triplet resonances were observed for the photoexcited triplet state of the F_2^{2+} defect in additively colored calcium oxide in zero magnetic field,[9] and for the triplet ground state of the N-V center in diamond[10,11] in a small magnetic field. The technique of optical detection of spin echoes has been extensively treated in the literature[12] and is briefly visualized as follows. In the optically detected Hahn-echo decay experiment, typically a $\pi/2$-τ-π-τ-$\pi/2$ pulse sequence at a microwave frequency of ω_{12} is applied (cf. inset of Fig. 2 below). In this sequence the first two pulses serve to generate the coherent echo at 2τ after the first pulse. The final $\pi/2$ pulse then converts the spin polarization representative of the spin coherence into a population difference of the states Ψ_1 and Ψ_2. As reported elsewhere,[9,12] the latter population difference is a determining factor for the emission intensity as probed for our laser-pumped color center systems. The change in the emission intensity monitored as the time interval τ progresses is thus characteristic of the decay with time of the spin-echo amplitude. The spectrometer for optical detection of the spin-coherent transients is similar to that described previously.[9] A block diagram of the experimental setup is given in Fig. 1. Optical excitation was by means of the 514-nm line of a cw Ar^+ ion laser. The emissive light from the crystalline sample (which is immersed in a bath of pumped liquid helium at a temperature of about 1.3 K) was detected in a direction perpendicular to the excitation pathway using a Monospek 1000 monochromator and a GaAs photomultiplier tube. Two microwave channels were used so that microwave excitation of the sample at two differing microwave frequencies and the desired pulse ordering could be realized. Microwaves were generated using low-power HP sweep oscillators and amplified by traveling-wave tube amplifiers. Pulsing of the microwave power (at a repetition rate of ~30 Hz) was by means of p-i-n diodes which were triggered by a pulse generator. The microwave power was transmitted to a semirigid cable which was immersed in the liquid helium and to which a helix (one for each channel) was attached. The microwave-induced changes in the emission from the color center were monitored using phase-sensitive lock-in detection.

Yellow-colored calcium oxide crystals contain F_2^{2+} defects which consist of a nearest-neighbor oxygen divacancy containing two electrons.[9] Upon photoexcitation, the F_2^{2+} defect is excited into its phosphorescent $^3B_1$ state for which the no-phonon emission peaks at 683 nm. Extensive studies of spin coherence at the zero-field resonance frequencies ($|D|-|E|=1870$ MHz and $|D|+|E|=2230$ MHz) in the excited $^3B_1$ state of the F_2^{2+} defect have been carried out previously.[9,13] Figure 2 shows typical optically detected spin-echo amplitude decays generated (at 1.3 K) in the absence and in the presence of the driving second microwave frequency, ω_{13}. As noted above, during the rephasing interval, at $\tau < t < 2\tau$, the driving field ω_{13} gives rise to phase shifts of the spin-coherent components which result in echo signals phase shifted by $(\Delta\omega/2 \pm \bar{\omega})\tau$ with respect to the phase of the echo in the absence of ω_{13}. As is readily visualized in the vector model,[12] the final probe pulse samples the phase-coherent polarization at 2τ directed perpendicular to the microwave field in the rotating frame at ω_{12}. In other words, the applied probe-pulse method enables

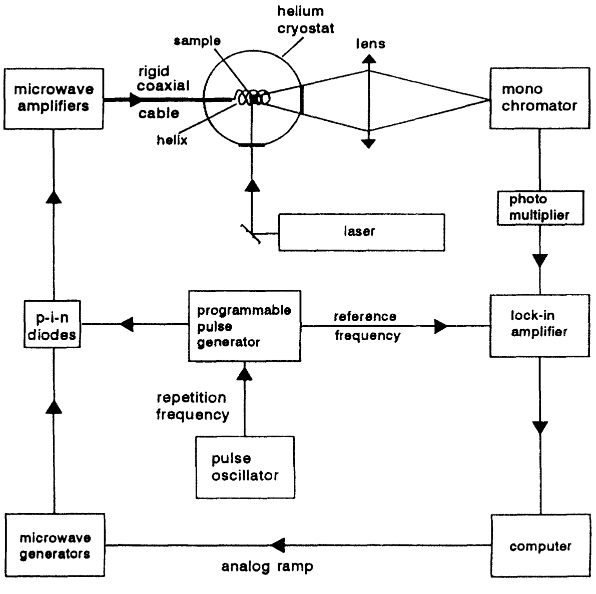

FIG. 1. Block diagram of experimental setup for two-frequency optically detected spin-echo experiment.

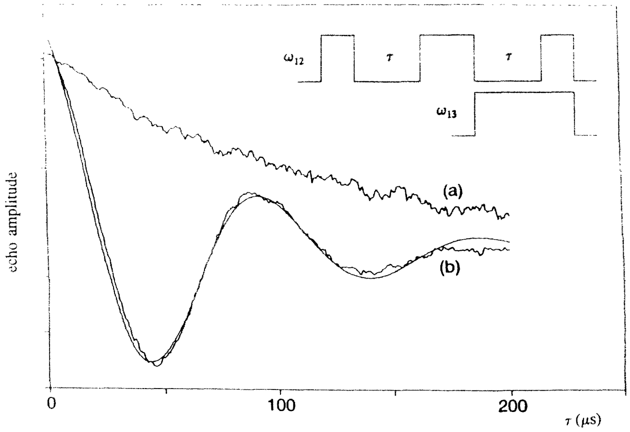

FIG. 2. Optically detected Hahn-echo decay (in arbitrary units) of the $|D|-|E|$ zero-field transition (at 1870 MHz) of the F_2^{2+} center in CaO in the photoexcited $^3B_1$ state at 1.3 K (a) without pumping the $|D|+|E|$ transition; (b) with the simultaneous pumping at $\tau < t < 2\tau$ of the $|D|+|E|$ transition (at 2230 MHz); see also insert. Drawn line is simulated Autler-Townes modulation.

us to measure induced phase shifts of the echo polarization when the second microwave frequency is on (in the time interval $\tau<t<2\tau$). The probed polarization, representative of the coherence at 2τ, will be given by $R(2\tau)$. The probed polarization, representative of the coherence at 2τ, will be given by $R(2\tau)=R_0\cos(\Delta\omega/2\pm\bar{\omega})\tau$. As illustrated by Fig. 2, indeed the effect of the second microwave field when driving the $1\leftrightarrow3$ transition near resonance is to modulate the echo amplitude decay of the $|D|-|E|$ transition of the $F_2{}^{2+}$ center in its photoexcited triplet state. The latter experimental data were fitted to a monoexponentially damped cosine functional form. The fit to the data of Fig. 2, as depicted by the drawn line, illustrates that good agreement is obtained with the functional dependence predicted on the basis of Eq. (3) using $\Delta\omega=0$, $\omega_1=21$ kHz, and a decay time of 67 μs for the exponentially decaying damping function. It is also found that when the frequency of the driving field is tuned away from resonance then the frequency and the depth of the modulations become less until the off-resonance frequency differs by more than 10 MHz, after which the modulation effects are no longer observable. Since $\omega_1\propto P^{1/2}$, where P denotes the power of the radiation field at ω_{13}, and since at exact resonance the periodicity of the induced Autler-Townes modulation varies proportionally to $\omega_1\tau$, it is also expected that this periodicity is proportional to $P^{1/2}$. In Fig. 3 we present the optically detected Hahn-echo decays of the $F_2{}^{2+}$ center $|D|-|E|$ transition recorded for a series of different power levels of the pumping frequency ω_{13}. Experimentally, the power level of the microwaves reflected by the helix in the microwave circuit will be affected proportionally to the applied microwave power, and hence the measurement of the reflected power level can serve as a measure of the applied microwave power level. This measure expressed as a percentage of the maximum possible power is included in Fig. 3. We find that the modulation frequency as deduced from the simulations of the experimental results as a function of $P^{1/2}$ clearly shows a linear dependence, this result being further support for the idea that the observed modulation effects originate in the Autler-Townes effect.

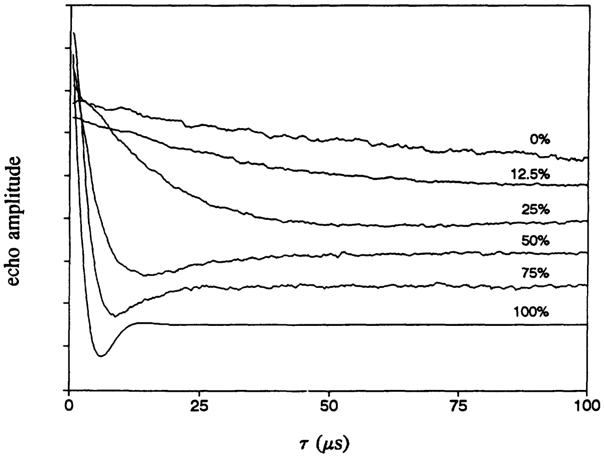

FIG. 3. Autler-Townes modulation of the $|D|-|E|$ zero-field transition (at 1870 MHz) of the $F_2{}^{2+}$ center in CaO in the photoexcited ${}^3B_1$ state for a series of power levels of the pumped $|D|+|E|$ transition (at 2230 MHz).

Similar results were obtained for another luminescent color center, the N-V center in diamond. The N-V center in diamond consists of a substitutional nitrogen atom adjacent to a carbon-atom vacancy having trapped an additional electron.[10,11] In optically detected spin-locking,[14] two-laser hole-burning,[15] and nearly degenerate wave-mixing[16] studies of the N-V center, it was shown that the defect possesses an electronic triplet spin ground state. Microwave resonance in the triplet ground state, performed at 1.3 K and giving rise to a change in the spin alignment of the ground-state triplet spin levels, affects the optical absorption at 514 nm and, as a result of this, a change in the intensity of the zero-phonon emission at 637 nm is observed [optically detected magnetic resonance (ODMR)]. In the presence of a small magnetic field of ≈ 10 G along the [100] crystallographic direction, the degeneracy of the upper two zero-field spin levels in the ground state is lifted and, since all N-V centers are magnetically equivalent for the chosen direction of the magnetic field, two ODMR transitions at frequencies of 2862 and 2895 MHz are observed. Autler-Townes resonances in the resulting triplet level system have been observed in the optically detected Hahn-echo decay of the N-V center. The decays shown in Fig. 4 were observed when driving the 2862-MHz transition while detecting its effect on the echo observed for the 2895-MHz transition. Again the influence of the applied microwave power on the magnitude of the modulation frequency and modulation depth is clear. Also, the experimental echo decay curves could be fitted using Eq. (3). Analogous to the results mentioned above for the photoexcited $F_2{}^{2+}$ center,

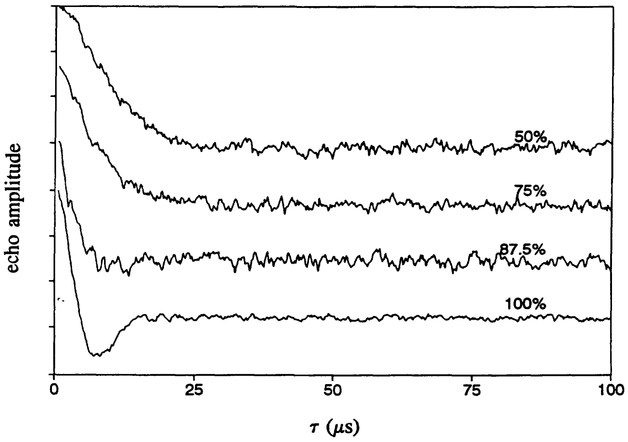

FIG. 4. Autler-Townes modulation as observed in the optically detected spin-echo signal (in arbitrary units) of the N-V center in diamond, in the presence of a magnetic field of 10 G along the [100] crystallographic axis. $\omega_{12}=2895$ MHz, $\omega_{13}=2862$ MHz. Power level (in percentage of maximum power) for ω_{13} is as indicated.

a linear increase of the Autler-Townes splitting with $P^{1/2}$ is obtained.

In summary, it has been shown for two model triplet spin quantum systems that, in case the spectral resolution of Autler-Townes splitting is hampered by inhomogeneous broadening effects, the frequency characteristic of the splitting can still be observed in the time domain by making use of coherent averaging techniques. Results of an optical probe-pulse detection method have been presented which show constructive and destructive interference effects originating in Autler-Townes splittings.

This work was supported in part by the ECTS program of the European Community Action Scheme and by the Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Scientific Research (NWO).

---

[1] M. O. Scully and M. Fleischhauer, Science **263**, 337 (1994); O. Kocharovskaya, Phys. Rep **219**, 175 (1992); S. E. Harris, Phys. Rev. Lett. **62**, 1033 (1989); A. Nottelmann, C. Peters, and W. Lange, *ibid.* **70**, 1783 (1993).

[2] S. H. Autler and C. H. Townes, Phys. Rev. **100**, 703 (1955); R. M. Whitley and C. R. Stroud, Phys. Rev. A **14**, 1498 (1976); Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984), p. 418.

[3] See, e.g., P. L. Knight and P. W. Milonni, Phys. Rep. **66**, 21 (1980); J. L. Picqué and J. Pinard, J. Phys. B **9**, L77 (1976); H. R. Gray and C. R. Stroud, Opt. Commun. **25**, 359 (1978); P. T. H. Fisk, H.-A. Bachor, and R. J. Sandeman, Phys. Rev. A **33**, 2418 (1986).

[4] Y. S. Bai, T. W. Mossberg, N. Lu, and P. R. Berman, Phys. Rev. Lett. **57**, 1692 (1986).

[5] X.-F. He, P. T. H. Fisk, and N. B. Manson, J. Appl. Phys. **72**, 211 (1992).

[6] C. P. Slichter, *Principles of Magnetic Resonance* (Springer, Berlin, 1990).

[7] J. Schmidt and D. J. Singel, Annu. Rev. Phys. Chem. **38**, 141 (1987).

[8] C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics* (Wiley, New York, 1977).

[9] D. J. Gravesteijn and M. Glasbeek, Phys. Rev. B **19**, 5549 (1979); M. Glasbeek and R. Hond, *ibid.* **23**, 4220 (1981).

[10] G. Davies and M. F. Hamer, Proc. R. Soc. London Ser. A **348**, 285 (1976).

[11] J. H. N. Loubser and J. H. van Wyk, Diamond Res. **11**, 4 (1977); Rep. Prog. Phys. **41**, 1202 (1978); J. Walker *ibid.* **42**, 1605 (979).

[12] W. G. Breiland, H. C. Brenner, and C. B. Harris, J. Chem. Phys. **62**, 3458 (1975); H. C. Brenner, in *Triplet State ODMR Spectroscopy,* edited by R. H. Clarke (Wiley, New York, 1982), p. 185; M. Glasbeek, Trends Chem. Phys. **1**, 191 (1991).

[13] R. Vreeker and M. Glasbeek, J. Chem. Phys. **86**, 2606 (1987).

[14] E. van Oort, N. B. Manson, and M. Glasbeek, J. Phys. C **21**, 4385 (1988).

[15] N. R. S. Reddy, N. B. Manson, and E. R. Krausz, J. Lumin. **38**, 46 (1987).

[16] D. A. Redman, S. Brown, R. H. Sands, and S. C. Rand, Phys. Rev. Lett. **67**, 3420 (1991).