

# Time-Resolved Two-Dimensional Spectroscopy of Optically Driven Atomic Sublevel Coherences

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Coherences between atomic substates are driven by a resonant interaction with light and transferred between individual sublevel transitions. We present an experimental scheme, based on two-dimensional Fourier-transform spectroscopy, that allows direct observation of this coherence transfer.

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Polarized light propagating through a resonant medium induces in general not only optical polarizations in the medium, but, in the frequently encountered case of multiple substates of the electronic ground state, also population differences and coherences between these sublevels [1]. These atomic or sublevel coherences give rise to many interesting magneto-optical and nonlinear optical effects; more recently, they have been used also in optical cooling experiments [2]. The interpretation of these effects relies on a detailed understanding of the dynamics of the sublevel coherences which often cannot be observed directly but must be inferred from their effect on the optical properties. In this Letter, we present a new experiment that allows the direct observation of the processes occurring in sublevel transitions when the system interacts with a resonant optical field.

Our experimental scheme is based on the general method of time-resolved two-dimensional spectroscopy, which is used extensively in radio-frequency spectroscopy [3,4] but has not been applied to optical spectroscopy so far. The basic idea of the experiment is summarized in Fig. 1: During the so-called preparation period, a first laser pulse is applied to a transition between a near-degenerate ground state (consisting of the four sublevels  $i$ ,  $k$ ,  $r$ , and  $s$ ) and an excited state  $|e\rangle$ . It excites sublevel

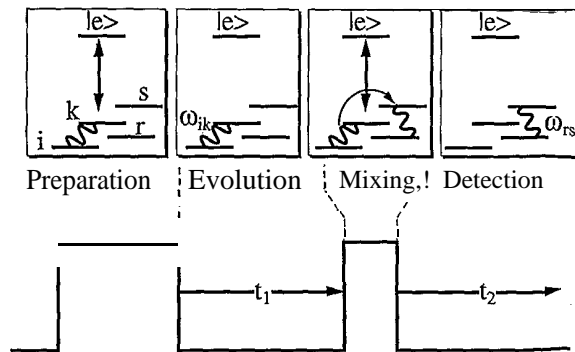


FIG. 1. Schematic representation of the two-pulse sequence used for two-dimensional spectroscopy and the effect on the atomic system. The individual periods are labeled with their conventional names.

coherence, e.g., between substates  $i$  and  $k$ . During the subsequent evolution period, the system is allowed to precess freely for a time  $t_1$  so that the sublevel coherence acquires a phase  $\omega_{ik}t_1$  proportional to the Bohr frequency  $\omega_{ik}$  of the transition in which they were created (evolution period). The second laser pulse (mixing period) then causes the coherence transfer which is to be investigated, in Fig. 1, the coherence is transferred from transition  $ik$  to transition  $rs$ . The final detection period then serves to monitor the coherences as they precess again under the free-atom Hamiltonian.

The experimental setup which was used for the measurements described here is shown schematically in Fig. 2. The atomic medium was Na vapor that was evaporated in a heated oven in the presence of 20 kPa of Ar buffer gas. A homogeneous magnetic field of 0.7 mT was applied perpendicular to the direction of the laser beams, so that the degeneracy of the sublevels within the hyperfine multiplets was lifted, as shown in Fig. 3(a).

A circularly polarized pump beam was used to create the sublevel coherence in the medium. Its intensity was controlled with an acousto-optic modulator. The pump pulses were modulated sinusoidally with a frequency of 5 MHz, near the Larmor frequency of the Na, in order to improve the efficiency of the optical pumping [5]. The modulated pulses were generated electronically and an acousto-optic modulator operating in the linear regime was used to convert the voltage signal into an intensity modulation of the pump beam. At the sample cell, the average pump beam intensity during the pulses was  $-1 \text{ W/cm}^2$ . The probe beam was derived from the same cw ring dye laser and linearly polarized with an intensity of

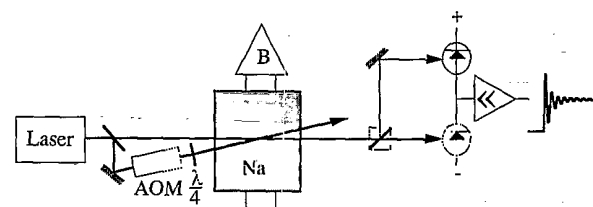


FIG. 2. Schematic representation of our experimental setup. For details see text.

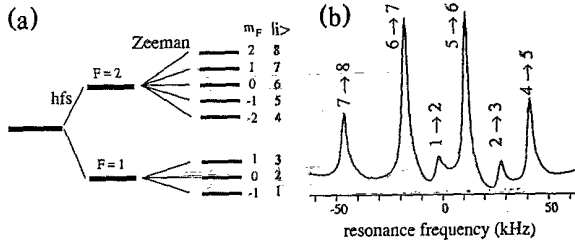


FIG. 3. (a) Level scheme of the Na ground state in a weak magnetic field with the quantization axis parallel to the direction of the magnetic field. The individual levels are labeled with the angular momentum components parallel to the direction of the magnetic field and a running index starting at the lowest energy level. (b) Spectrum of the atomic sublevel transitions obtained via Fourier transformation of the free-induction-decay signal following an intensity-modulated optical pulse. The numbers give the assignment of the individual resonances to transitions labeled by the indices of the relevant energy levels.

$-30 \text{ mW/cm}^2$ ; it overlapped the pump beam in the probe region with an angle of intersection of  $0.5^\circ$ . Behind the sample-region, the difference in dispersion between right and left circularly polarized light was measured and the resulting signal was passed through a phase-sensitive detector whose reference frequency was equal to the modulation frequency. For the experiments described here, the laser frequency was set 8.6 GHz above the center of the Na  $D_1$  resonance. Under these experimental conditions, excited-state effects can be neglected and the observed signal is determined by the ground-state orientation [11].

Let us first discuss the situation when only one laser pulse is applied. If the system is prepared in a state with nonvanishing sublevel coherences and subsequently allowed to precess under the free-atom Hamiltonian, the different coherences evolve at their individual transition frequencies:  $\rho_{ik}(t) = \rho_{ik}(0)e^{-i\omega_{ik}t}e^{-\gamma_{ik}t}$ , where the density operator element  $\rho_{ik}$  represents the coherence between states  $i$  and  $k$ . Here,  $\omega_{ik} = (E_k - E_i)/\hbar$  specifies the Bohr frequency and  $\gamma_{ik}$  the decay rate of the respective coherence. The observable free-induction-decay signal consists, in general, of a sum over such density operator components,

$$s(t) = \sum_{ik} a_{ik} \rho_{ik}(0) e^{-(i\omega_{ik} + \gamma_{ik})t}, \quad (1)$$

where the expansion coefficients  $a_{ik}$  are determined by the observation process; with our experimental setup, the measurement of the dispersion difference yields a signal that includes contributions from all six transitions with  $|\Delta m_F| = 1, \Delta F = 0$  [see Fig. 3(a)]. The different coherences, contributing to different terms in this sum (1), can be separated via Fourier transformation of the observed free induction decay. An example is shown in Fig. 3(b) where the Fourier transform of a free induction decay following an optical preparation pulse is shown. Phase-

sensitive detection was used [5], so that the origin of the frequency axis is determined by the modulation frequency. The various resonance lines correspond to individual sublevel transitions whose assignment is shown by the numbers. This time-resolved measurement of atomic sublevel coherences therefore allows the direct observation of the free evolution under the atomic Hamiltonian.

If we are interested primarily in the *effect of the optical radiation on the dynamics* of the system, it would seem tempting to perform the same experiment while irradiating the system during observation. However, such irradiation leads to a broadening of the resonance lines which often makes it impossible to follow the evolution of the individual coherences. A possible solution lies in time-resolved two-dimensional (2D) spectroscopy [4], where the state of the system immediately before and after the pulse is known, so that the overall effect of the laser pulse can be studied.

For a demonstration of how this procedure can yield information about the effect of the pulse, we write the density operator elements  $\rho_{ik}$  after the evolution period as

$$\rho_{ik}(t_1) = \rho_{ik}(0) e^{-(i\omega_{ik} + \gamma_{ik})t_1}. \quad (2)$$

where the indices  $i, k$  refer to the eigenstates of the Hamiltonian (see Fig. 3). The effect of the optical radiation on the system can be summarized by a mixing matrix  $\eta$  whose dimension in the case of the Na ground state is  $64 \times 64$ . The elements  $\eta_{ik,rs}$  of this matrix describe the transfer of coherence from transition  $nik$  to transition  $rs$  (in this context, populations are treated as transitions  $ii, rr$  with equal indices). The density operator elements during the detection period can therefore be written as

$$\rho_{rs}(t_1, t_2) = \sum_{ik} \rho_{ik}(0) e^{-(i\omega_{ik} + \gamma_{ik})t_1} \times \eta_{ik,rs} e^{-(i\omega_{rs} + \gamma_{rs})t_2} \quad (3)$$

and the observed signal is

$$s(t_1, t_2) = \sum_{rs} a_{rs} \sum_{ik} \rho_{ik}(0) e^{-(i\omega_{ik} + \gamma_{ik})t_1} \times \eta_{ik,rs} e^{-(i\omega_{rs} + \gamma_{rs})t_2} \quad (4)$$

This signal now depends obviously on both parameters  $t_1$  and  $t_2$ . By recording the free induction decay after the second pulse for a set of  $t_1$  values, one therefore obtains a two-dimensional data set. Via a two-dimensional Fourier transformation, it is possible to obtain a 2D spectrum [4]:

$$f(\omega_1, \omega_2) = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 s(t_1, t_2) e^{i\omega_1 t_1} e^{i\omega_2 t_2}. \quad (5)$$

An example of a resulting 2D spectrum is shown in Fig. 4. For this experiment, the system was prepared with an initial pulse of 100- $\mu\text{sec}$  duration; the evolution time  $t_1$  was incremented from 0 to 283.5  $\mu\text{sec}$  in steps of 4.5  $\mu\text{sec}$ . The resulting data set was Fourier transformed and the absolute value displayed in a pseudo-3D representation [Fig. 4(a)] and as a contour plot [Fig. 4(b)]. In

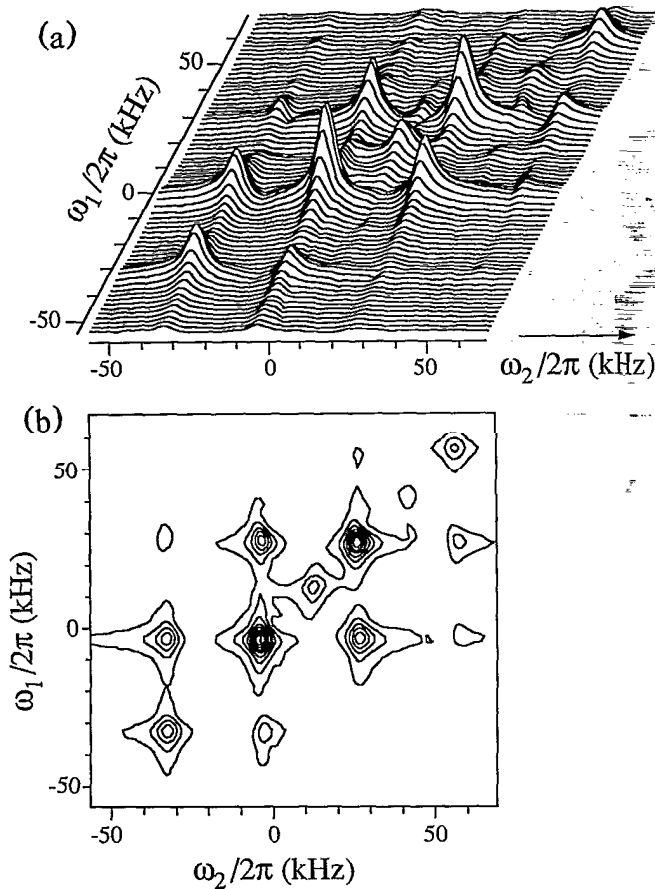


FIG. 4. Example of a 2D spectrum. (a) A pseudo-3D representation and (b) a contour plot of the sample data set. The data were recorded with the laser wavelength tuned 8.6 GHz above the center of the  $D_1$  resonance line.

principle, every element  $\eta_{ik,rs}$  of the mixing matrix can give rise to a resonance line in this spectrum. However, as can be seen from the spectrum, the total number of resonance lines is much smaller. This reduction is due to several selection rules, the most important of which is given by the nature of our observable which allows only detection of density-matrix elements with  $|\Delta m_F|=1$ .

The resonance lines along the main diagonal  $\omega_1 = \omega_2$ , the so-called diagonal peaks, are due to coherences that were not affected by the second pulse; for vanishing length of the second pulse, only these peaks exist [see Fig. 3(b)]. All the remaining peaks indicate that the pulse has transferred coherence from one transition to another. They are usually referred to as cross peaks. The width of the resonance lines in both dimensions is identical to those of Fig. 3, since line broadening by optical pumping is absent during the evolution and detection periods.

The redistribution of the sublevel coherences by the optical field can be monitored by recording a sequence of such spectra with increasing length of the mixing pulse. The transfer of coherence between the different transitions leads then to changes in the intensities of the corre-

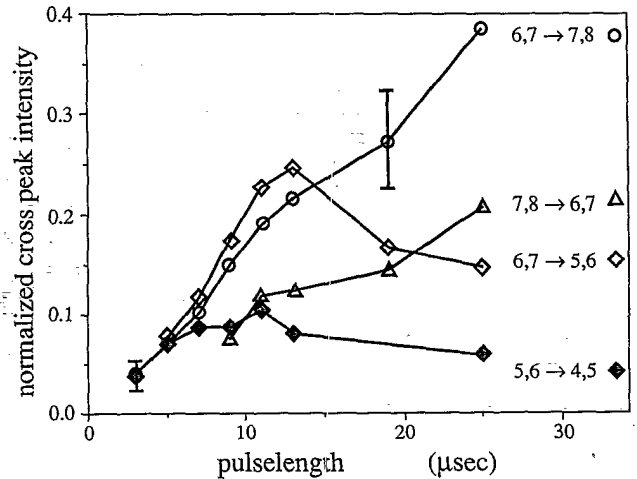


FIG. 5. Normalized intensities of the various cross peaks as a function of the length of the mixing pulse. The experimental parameters were the same as in Fig. 4. As shown by the representative error bars, the signal-to-noise ratio decreases for longer pulse lengths.

sponding resonance lines. Figure 5 shows a partial analysis of these data for the Na system. The different curves show the transfer of coherence between a representative set of adjacent  $|\Delta m_F|=1$  transitions of the  $F=2$  multiplet. Since the stability of our experimental setup was not sufficient to allow quantitative measurements of the resonance line intensities over an extended period of time, we were forced to normalize these values. For this analysis, we measured the intensity of the cross peaks and normalized each value to the sum of the intensities of the diagonal peaks. The data obtained in this way clearly show an exchange of coherence among the different transitions as the pulse length is increased.

For a comparison of these results with theoretical calculations, the equation of motion has to be solved. In the present experiment, a total of sixteen energy levels are involved (eight in the  $^2S_{1/2}$  ground state of Na and eight in the  $^2P_{1/2}$  excited state), so that the equation of motion involves a total of 255 independent variables. The shortest time constant involved in the equation of motion is the dephasing time of the optical coherences, which in our case is of the order of  $10^{-10}$  sec, while the duration of the experiment is of the order of  $10^{-4}$  sec. Accordingly, the equation of motion has to be integrated over 6 orders of magnitude, representing a rather high computational effort. We are currently investigating possibilities for suitable approximations that allow an approximate integration of the equations of motion and thereby a direct comparison between theory and experiment. Qualitatively, the experimental data indicate that a description of the process in terms of rate equations may be possible.

In the spectrum shown in Fig. 4, there appear only the six transitions that are also seen in the one-dimensional spectrum. However, in principle, all possible transitions

can be excited by the laser pulse and the corresponding coherences can be transferred into the six transitions that are directly visible [6]. Under typical experimental conditions, the cross peaks indicating these transfer processes have a smaller amplitude so that the transitions with higher amplitudes must be suppressed to make the less intense lines visible.

In conclusion, we have reported a new experimental method which allows for the first time a direct observation of the creation, redistribution, and decay of sublevel coherences in a medium irradiated by optical radiation. While the principal effects of the light on these coherences, such as light shift and damping [7], have been known for some time, it was not possible to observe these effects in the time domain, as the coherences evolve. Such an observational tool appears especially useful whenever the system under study is too complex for a theoretical analysis, i.e., when it is too complex for an analytical solution of the equation of motion and driven too far from equilibrium to allow a perturbation treatment.

The method presented here has of course a much wider range of applications than could be demonstrated. An important extension is the application to the observation of transitions that cannot be observed directly but whose coherences can be transferred to directly observable transitions. Information gained via this procedure should be of great importance for the analysis of all optically resonant processes in multilevel systems. The transfer that is observed does not have to be initiated by the light-shift effect, as in the example shown. The method presented here could therefore be useful for other time-resolved laser experiments [8], where, e.g., the dynamics of molecular reactions [9] or fast dynamics in solids [10] are stud-

ied with ultrashort pulses. Such an experiment could consist of two excitation pulses, separated by a period  $t_1$ , and a probe pulse, separated by a period  $t_2$  from the second excitation pulse. Another possible experiment that is especially suited to study exchange processes that are not caused by the laser pulse consists of three excitation pulses, with the separation between the second and the third pulse held fixed.

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