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Indirect Observation of «Forbidden» Raman Transitions by Laser-Induced Coherence Transfer.

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Abstract. – We demonstrate a new spectroscopic technique that makes it possible to obtain information from «forbidden» Raman transitions. The technique, which is based on time-resolved two-dimensional spectroscopy, uses laser-induced transfer of sublevel coherence from the Raman-inactive transition to an allowed Raman transition.

The spectroscopy of transitions between atomic sublevels is a well-established technique [1-3] which has found additional interest recently, since spectroscopy of atomic vapours which are cooled and trapped by laser light has become feasible [4]. Apart from the purely spectroscopic interest, the information which the technique provides about the internal degrees of freedom of the atoms is also important, *e.g.*, for understanding the mechanical forces due to the interaction with resonant radiation: the interaction of the atoms with the radiation field and therefore the character of the mechanical forces depend on the internal state of the atoms as well as on the polarization of the light. The long lifetime of coherences between ground-state sublevels makes it possible to achieve significant polarization of these sublevel multiplets, even at very low laser intensities. For the same reason, the natural width of these resonance lines is in general quite small and the observed linewidths are determined by the experimental technique.

In this article, we are not concerned with the *direct* observation of sublevel coherences by classical magnetic-resonance spectroscopy, but we consider only methods that rely on laser-induced Raman transitions [1], thereby providing much higher sensitivity. Like every other spectroscopic technique, these Raman spectra are subject to certain selection rules, which limit the range of transitions that can be probed in such experiments. It is the main purpose of this letter to introduce a technique which can circumvent these selection rules and yield spectra of transitions that are not accessible to direct observation. In the case of the Na ground state, which we use for our demonstration, it can provide spectroscopic information about all possible transitions between Zeeman substates. The sensitivity of this method is linear in the probe beam intensity so that the perturbation of the system by the probe beam can be kept small without sacrificing too much sensitivity.

Raman experiments of the type considered here can, at least conceptually, be divided into

an excitation and a detection step. In the excitation step, the laser radiation excites coherences between the various substates of the electronic ground state. These coherences evolve under the Hamiltonian of the atom, thereby acquiring phase information that is characteristic of the transition in which they are excited. This phase information can be observed by another Raman process which may be excited either by the same laser beam as the one used for the excitation process, or by a separate probe beam. During detection, some of the incident photons are converted into Raman-shifted photons that are usually detected by a heterodyne technique, using the unshifted part of the probe laser beam as the local oscillator.

During a Raman process, a single photon interacting with an atomic system can exchange up to two quanta of angular momentum; a transfer of two quanta corresponds then to the conversion of a right circularly polarized photon into a left circularly polarized one. Depending on the system under investigation, monitoring with a low-intensity laser beam can therefore detect coherences between angular-momentum substates of the electronic ground state whose magnetic quantum numbers differ by $\Delta m_F = 0, \pm 1$ and ± 2, independent of the direction of the quantization axis. Signal contributions from transitions with $\Delta m_F = \pm \pm 2$ have, in fact, been observed in metastable helium [5], as we as in alkali atomic vapours [6, 7]. In the latter case, where the electronic angular momentum of the ground state is $J = 1/2$, the two quanta cannot be absorbed by the electronic angular momentum alone and the process can therefore occur only if the surplus angular momentum can be transferred to the nuclear spin. The process is therefore forbidden in the case of vanishing nuclear spin and becomes inefficient if the hyperfine interaction is small compared to the optical linewidth, as in the case of pressure-broadened Na vapour. The detection process is then sensitive primarily to coherences between adjacent sublevels, $|\Delta m_F| = 1$.

This is demonstrated in fig. 1, which shows a Raman spectrum of the Na ground state. It was obtained by exciting sodium vapour in a transverse magnetic field with a strong, circularly polarized laser pulse, monitoring the response of the system with a weak, linearly polarized laser beam [8] and subsequently Fourier-transforming the free induction decay signal measured after the end of the pump pulse. At the field strength of 0.7 mT used for this experiment, the linear and the quadratic terms of the electron-Zeeman interaction must be taken into account for the calculation of the energy of the ground-state sublevels. If the quantization axis is chosen along the direction of the magnetic field, the first-order Zeeman interaction leads to an energy level splitting of $\Delta m_F \cdot 5\,\mathrm{MHz}$ (in frequency units). The second-order Zeeman interaction leads to an additional shift of the order of $\Delta m_F^2 \cdot 15\,\mathrm{kHz}$, so that all transitions within a hyperfine multiplet are nondegenerate. In addition, the nuclear Zeeman interaction shifts the Zeeman transitions of the $F = 1$ multiplet with respect to those

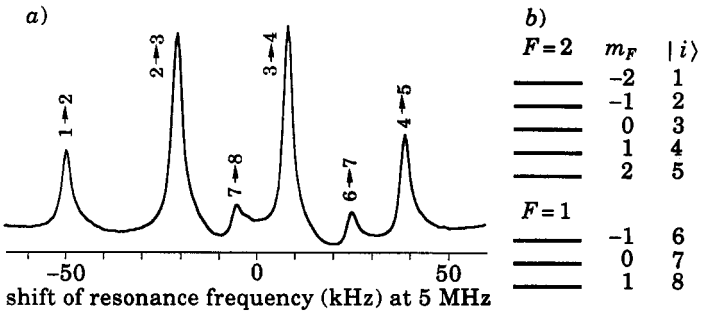

Fig. 1. – *a*) Raman spectrum of the Na ground state showing the assignment of the six frequency components to the transitions between Zeeman sublevels of the electronic ground state. *b*) Corresponding energy level scheme showing the number $|i\rangle$ used in the assignment.

of the $F = 2$ multiplet. The four major resonances of this spectrum can therefore be assigned to the four $|\Delta m_F| = 1$ transitions of the $F = 2$ ground-state multiplet. The corresponding transitions of the $F = 1$ multiplet are also visible, but no $|\Delta m_F| = 2$ transitions can be seen. This direct observation of Raman beats therefore provides information on only a fraction of the transitions that can be excited in the system. While it is possible to circumvent this selection rule by using higher probe beam intensities, such a procedure leads to reduced spectral resolution.

These selection rules are important primarily for the detection process, where low-intensity light is used in order to minimize the perturbation of the system. The excitation process, on the other hand, can be performed with higher intensity radiation. Via multiple Raman processes, it is therefore possible to excite a coherent superposition of all substates of the electronic ground state. The density operator of the system then includes nonzero elements for all possible transitions. This has been demonstrated earlier in the context of laser-induced spin-echo experiments [9]. In those experiments, the sublevel coherence created by the first pulse is allowed to precess in an inhomogeneous transverse magnetic field, thereby acquiring a phase equal to the product of the Larmor frequency times the delay between the two pulses. The effect of the second pulse is a mixing of these coherences between different transitions, induced by light-shift and optical-pumping effects. The acquired phase information is conserved during this mixing process, so that the coherences retain a «memory» of their history during the transfer process. After the second pulse, the evolution continues in the same inhomogeneous magnetic field with the Bohr frequency of the current transition. Coherence that is transferred from a $\Delta m_F = 2$ into $\Delta m_F = -1$ transition, for example, appears therefore to evolve backward in time at half the original speed, compared to the evolution between the two pulses. In this case, the sum of the two phases adds up to zero at a time $t_2 = 2t_1$ after the refocussing pulse, independent of the local field strength, causing an echo to appear in the Raman-active $|\Delta m_F| = 1$ transition.

While this experiment allows an indirect observation of the coherence excited in the «forbidden» Raman transitions with $\Delta m_F = 2$, it does not provide any spectroscopic information. The reason is basically that the phase information which is acquired in the $\Delta m_F = 2$ transition is exactly cancelled by the refocussing process when the coherence is actually observed. In order to conserve the phase information, the experiment must therefore be performed in a homogeneous magnetic field. The spectroscopic information, *i.e.* the frequencies and amplitudes of the sublevel spectrum, can then be obtained by repeating the experiment for different delays t_1 between the two pulses. More precisely, if the first pulse excites sublevel coherences ρ_{ij}, we can write the density operator after the first pulse as

$$\rho(t_1 = 0) = \sum_{ij} \rho_{ij}(0). \tag{1}$$

These coherences evolve between the two pulses under the Hamiltonian of the free atom in the magnetic field as

$$\rho(t_1) = \sum_{ij} \rho_{ij}(0) \exp[i\Omega_{ij} t_1], \tag{2}$$

where Ω_{ij} represents the Bohr frequency of transition ij. At this point, the second laser pulse is applied to the system. We summarize its effect by a propagator U with dimension N^2 where N is the dimension of the density operator: the density operator element associated with a particular transition rs is given as

$$\rho_{rs}(t_1, t_2 = 0) = \sum_{ij} U_{rsij} \rho_{ij}(0) \exp[i\Omega_{ij} t_1]. \tag{3}$$

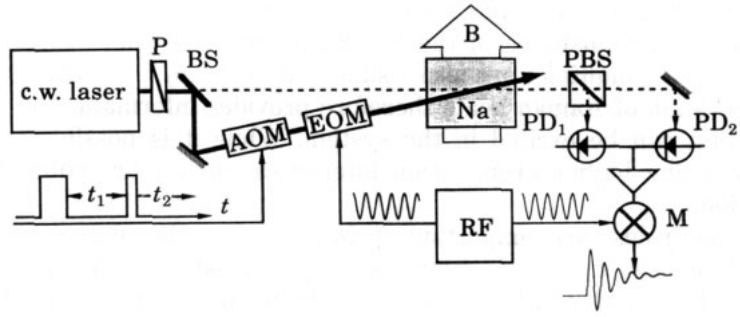

Fig. 2. – Experimental set-up used for the indirect detection of Raman transitions. P = polarizer, BS = beam splitter, AOM = acousto-optic modulator, EOM = electro-optic modulator, RF = radio-frequency synthesizer, B = magnetic field, PBS = polarizing beam splitter, $PD_{1,2}$ = photodiodes, M = mixer.

The matrix U describes the redistribution of coherence between the various sublevel transitions; for the purpose of demonstrating this method, the details of this operator are not important, except that at least one element U_{rsij} must be nonzero for $rs \neq ij$. At a time t_2 after the second pulse, the coherences have acquired phase information from their new transitions:

$$\rho_{rs}(t_1, t_2) = \exp[i\Omega_{rs} t_2] \sum_{ij} U_{rsij} \rho_{ij}(0) \exp[i\Omega_{ij} t_1]. \tag{4}$$

The signal which is observed after the second pulse is proportional to these density operator elements. Spectroscopic information can be obtained if the resulting signal is Fourier-analysed with respect to both (independent) variables t_1 and t_2. The resulting two-dimensional spectrum contains resonance lines at the frequencies $(\Omega_{ij}, \Omega_{rs})$ with amplitude proportional to $U_{rsij}\rho_{ij}(0)$.

The experimental set-up used for the implementation of this procedure is shown in fig. 2. The measurements reported here were performed on the Zeeman sublevels of the $3s\ ^2S_{1/2}$ sodium ground state. The atomic vapour was contained in a glass cell at a temperature of 145 °C. 200 mbar of Ar was added as a buffer gas to make the optical resonance line homogeneous and extend the time that the atoms spend inside the laser beam. A transverse magnetic field of $B = 0.7$ mT was applied. The laser beams used in the experiment were derived from a single-mode c.w. ring dye laser (short-term linewidth $\leqslant 500$ kHz). The laser frequency was set near the Na-D_1 line ($\lambda = 589.6$ nm) with a detuning Δ optimized for an efficient coherence transfer; in this particular experiment, it was set to $\Delta/2\pi = 7$ GHz above the centre of the (pressure-shifted) Na-D_1 line where the light-shift effect of the pump laser beam dominates over the damping effect. The laser beam was split into a pump beam (solid line in fig. 2, intensity $\sim 100\ \mathrm{mW/mm^2}$) and a probe beam (dashed line in fig. 2, intensity $\sim 100\ \mu\mathrm{W/mm^2}$) which overlapped in the sample region at an angle of less than 1°. The laser pulses were generated by an acousto-optic modulator (AOM) driven by a computer-controlled digital delay generator. For the experiment presented here, the duration of the first pulse was set to 200 μs, the duration of the second pulse to 5 μs. The pump pulses were then passed through an electro-optic modulator (EOM) which modulated the polarization between the opposite circular polarizations at a frequency $\omega_m/2\pi = 5$ MHz, close to the Larmor frequency of the system. This procedure leads to an efficient excitation of sublevel coherences in the transverse magnetic field [10].

After propagating through the vapour cell, the probe beam was passed into a polarization-selective detector [8] which measures the circular birefringence of the sample

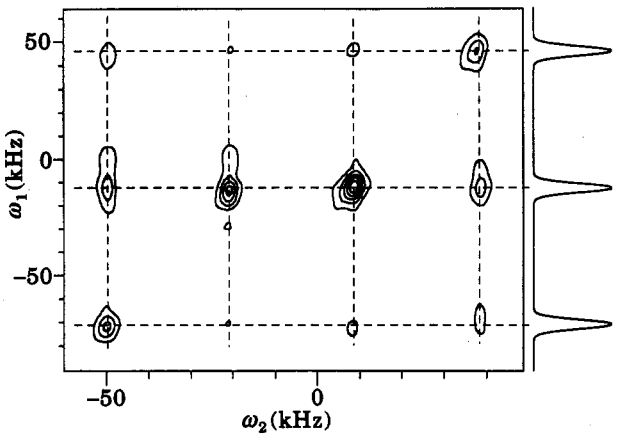

Fig. 3. – Experimental spectrum of the $|\Delta m_F| = 2$ transitions in the $F = 2$ hyperfine multiplet of the Na ground state observed via transfer into $|\Delta m_F| = 1$ transitions. The two-quantum spectrum appears along the vertical (ω_1) axis. The theoretical spectrum is shown in one-dimensional form vertically on the right-hand side. The horizontal (ω_2) axis corresponds to the precession frequency during detection. The dashed lines indicate the resonance frequencies of the $\Delta m_F = 2$ transitions (horizontal lines) and $\Delta m_F = 1$ transitions (vertical lines).

and produces a signal proportional to the ground-state magnetization component parallel to the direction of the laser beam. The signal was then passed through a phase-sensitive detector whose reference frequency was derived from the RF synthesizer used to drive the EOM; the signal frequency range was thereby shifted to an experimentally more convenient region close to zero. After digitization, the signal was transferred to the computer which controlled the experiment. This procedure was repeated for a sequence of equidistant t_1 values, so that the signal was obtained as a function of the two independent time variables t_1 and t_2. This two-dimensional data set was Fourier-transformed with respect to both time variables.

The number of resonance lines appearing in the resulting two-dimensional spectrum under these conditions can be quite large: the first pulse excites in general all possible transitions which are then converted into observable single-quantum coherence by the second pulse. In the case of the Na ground state, a total of 84 resonance lines are then possible. The overlap between the various resonance lines can make the analysis of the spectrum rather difficult. It is therefore often advantageous to reintroduce selection rules into the experimental procedure that reduce the number of resonance lines in the spectrum. One possible selection scheme utilizes the different sensitivity of the different transitions to shifts in the phase of the modulation [9].

For our demonstration of the method, we have used this selection mechanism to eliminate all resonances except those which are due to $\Delta m_F = 2$ transitions after the first pulse. The absolute value of a resulting two-dimensional spectrum is displayed in fig. 3 as a contour map. The vertical (ω_1) axis corresponds to the Fourier transform of the time-domain variable t_1 and the corresponding resonances indicate the precession frequency of the respective coherences between the two pulses. The theoretical two-quantum spectrum of the $F = 2$ multiplet is shown in one-dimensional form on the right and the horizontal dashed lines indicate the positions of the three possible transitions. The horizontal axis gives the precession frequency after the second pulse and the vertical dashed lines indicate the positions of the allowed $\Delta m_F = 1$ Raman transitions. Each of the 12 resonance lines in the two-dimensional spectrum is therefore due to coherence which has been transferred from a two-quantum ($\Delta m_F = 2$) transition into a single-quantum ($\Delta m_F = 1$) transition. As an example, consider the resonance

line at the lower left ($\omega_1 = -70\,\text{kHz}$, $\omega_2 = -50\,\text{kHz}$). The first frequency indicates that the coherence was created in the transition $1 \rightarrow 3$ ($m_F = -2 \rightarrow m_F = 0$) by the first pulse. After evolving in this transition for the duration t_1, the second pulse transferred the coherence to the transition $1 \rightarrow 2$ ($m_F = -2 \rightarrow m_F = -1$), where it was observed during the continuing evolution. The asymmetry of this spectrum (only two-quantum transitions along ω_1, only one-quantum transitions in the direction of ω_2) is partly due to the selection rules which allow only $\Delta m_F = 1$ during detection, partly to our elimination of all but the $\Delta m_F = 2$ transitions during t_1.

As in the case of direct observation of sublevel transitions, the width of the resonance lines observed here is independent of the width of the optical resonance line and of the frequency spectrum of the pump or probe laser. Since the *natural* width of the transitions is negligibly small, the *observed* width is due primarily to magnetic-field inhomogeneity and to lifetime broadening by the diffusion of the atoms out of the laser beam which leads to a lifetime broadening of the resonance lines. Furthermore, the resolution that can be achieved in a spectrum obtained via Fourier transformation of time domain data is always limited by the length of the observation period used. In the experiment reported here, the resolution that can be achieved along the ω_1-axis is therefore limited by the maximum duration of the delay between the two pulses.

The applicability of this experimental scheme is of course not limited to the situation described here. In similar form, it is applied very successfully in the field of magnetic-resonance spectroscopy [11] for the observation of resonances that are not or only weakly coupled to the radiation field. In the field of laser spectroscopy, it could be applied to other forms of Raman spectra, but also quite generally whenever it is possible to transfer spectroscopic information from one transition to another. As an example, it has been demonstrated that the phase information acquired in one transition can be converted into a population difference which is then transferred to other transitions by relaxation processes [12].

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