PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

High-Resolution Spectroscopy with Multiple-Beam Laser Techniques [and Discussion]

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High-resolution spectroscopy with multiple-beam laser techniques

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The spectroscopy of dilute vapours is ordinarily limited by Doppler broadening. By using two counterpropagating light beams from the same laser, it is possible to get over this limit, and to attain true natural widths.

Some methods use the saturation of ordinary one-photon transitions, and permit the selection of the signal given by the particular class of atoms whose velocity is perpendicular to the light beams: Lamb-dip spectroscopy, self-saturated absorption or dispersion, polarization spectroscopy.

The second possibility is to produce double-photon transitions ($E_2 - E_1 = 2h\nu$) in such a manner that the Doppler shifts of the two photons exactly cancel each other, and all the atoms undergo the transition together for the true value of the laser frequency: Doppler-free multiphoton spectroscopy.

Introduction

It has been possible, with the use of lasers, to develop special techniques that get over the Doppler limit in the spectroscopy of vapours. These techniques use generally two counterpropagating light beams from the same laser: parallel to the z axis, we have a forward wave with the wavevector $\boldsymbol{k}$ and a backward wave with the opposite wavevector $-\boldsymbol{k}$. The various Doppler-free techniques share the characteristic that the sign of the Doppler shift, $\boldsymbol{k}.\boldsymbol{v} = \pm kv_z$, changes either with the sign of the velocity component, v_z, or with the sign of the wavevector $\boldsymbol{k}$.

I shall first discuss the technique that employs the saturation of an ordinary one-photon transition. After that I shall consider the technique based on multiphoton transitions.

2. Saturation of a one-photon transition

This technique uses two fundamental concepts: the concept of saturation, and the concept of velocity class. I shall describe these two concepts.

(*a*) *Saturation*

The phenomenon of saturation appears in the interaction of atoms with a resonant light wave of high intensity. Let n_0 and n_1 be the populations of the two atomic levels E_0 and E_1 interacting with that light wave of frequency $\omega_1 = (E_1 - E_0)/\hbar$. The evolution of these populations are given by the following differential equations:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\frac{n_1}{\tau} + \sigma\frac{P}{S}(n_0 - n_1) \quad \text{and} \quad \frac{\mathrm{d}n_0}{\mathrm{d}t} = +\frac{n_1}{\tau} - \sigma\frac{P}{S}(n_0 - n_1),$$

where τ is the mean lifetime of the excited level E_1, and P/S represents the intensity of the light wave (the power P divided by the cross-sectional area S of the laser beam). Note that

$dn_1/dt = -dn_0/dt$ because n_1+n_0 is constant, equal to the total number N of the atoms ($n_1+n_0 = N$).

In the right-hand side of these equations, the first term n_1/τ represents the loss or gain by spontaneous emission from the excited level E_1 to the ground level E_0; the second term, proportional to the light intensity P/S, represents the joint action of absorption and of stimulated emission (the coefficient σ is proportional to the cross section of the interaction between photons and atoms).

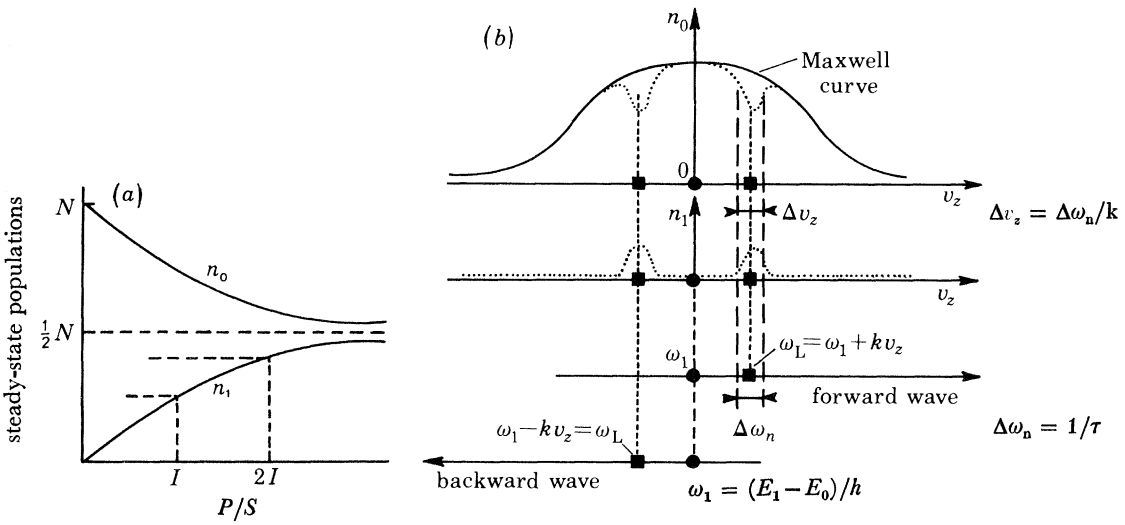

FIGURE 1. Principle of saturation spectroscopy. (*a*) Saturation: population n_0 of the ground level, and population n_1 of the excited level as a function of the laser intensity P/S: ($n_0+n_1 = N$). (*b*) Velocity classes: the Maxwell curve above represents the distribution of the atoms as a function of their velocity component v_z in the direction of the light beam.

In most experiments, one observes only the stationary régime where the populations are constant. Setting $dn_1/dt = dn_0/dt = 0$, we obtain easily the steady-state populations:

$$n_0 = N\frac{1/\tau + P/S}{1/\tau + 2P/S} \quad \text{and} \quad n_1 = N\frac{P/S}{1/\tau + 2P/S}.$$

They depend on the intensity P/S of the light wave; that dependence is not linear as is shown in figure 1*a*. When the light intensity P/S increases indefinitely, the two populations n_0 and n_1 tend toward the same limit $\frac{1}{2}N$: the saturation of the interaction. The important point used in the Doppler-free technique is not the saturation itself but the *nonlinearity*: the population n_1 of the excited state is less than doubled when the light intensity P/S is doubled from I to $2I$; this nonlinearity is stronger when one is approaching saturation.

(*b*) *Velocity class*

I shall now take into account the Doppler shift, which depends on the component v_z of the atomic velocity in the direction z of the wave propagation. Figure 1*b* represents the Maxwell distribution of the atoms (number of atoms plotted against their velocity component v_z). If the laser emits a light wave of frequency ω_L propagating in the z direction, an atom of velocity component v_z sees in its own frame the frequency $(\omega_L - kv_z)$. As a consequence the laser beam interacts only with those atoms having a velocity v_z such that $\omega_L = \omega_1 + kv_z$. This correspondence between ω_L and v_z is illustrated in figure 1*b* by a frequency axis parallel to the v_z axis; the

frequency scale is chosen in such a manner that the velocity zero corresponds to the exact frequency ω_1 of the atomic transition, and the velocity v_z corresponds to the laser frequency $\omega_L = \omega_1 + kv_z$. The Maxwell curve can be interpreted, with this new horizontal ω axis, as the number of atoms interacting with the laser beam of frequency ω.

In fact the interaction frequency is not defined with an infinite precision; the interaction has some width on the frequency scale, which is the natural width $\Delta\omega_n = 1/\tau$ (inverse of the life-time). To this natural width $\Delta\omega_n$ corresponds, on the velocity scale, some interval $\Delta v_z = \Delta\omega_n/k$. All the atoms belonging to this interval Δv_z constitute the velocity class interacting with the laser beam.

If the laser beam is reflected backwards with a mirror, the Doppler shift is inverted for the backward wave, which interacts with the atoms having a velocity v_z such that $\omega_L = \omega_1 - kv_z$. This new correspondence between ω_L and v_z is illustrated in figure 1*b* by another frequency axis in the opposite direction: the same laser frequency ω_L corresponds now to the opposite value of v_z. That is to say: the same Doppler shift $\omega_L - \omega_1$ is obtained by inverting simultaneously the sign of v_z and the sign of k. As a consequence the backward wave interacts with other atoms, constituting another velocity class. The dotted curves on figure 1*b* represent the changes in the populations n_0 and n_1 resulting from the interaction with the two waves.

(*c*) *Principle of saturation spectroscopy: saturated absorption*

The principle of saturation spectroscopy derives immediately from the foregoing: when the laser frequency ω_L is different from the transition frequency ω_1, the two waves, forward and backward, interact with different atoms, belonging to two different velocity classes. On the other hand, if the laser frequency becomes equal to the transition frequency, the two velocity classes merge into each other, i.e. the two waves now interact with the same atoms.

We obtain now: half the number of atoms (only one velocity class) interacting with twice the light intensity (the two waves together). Because of the nonlinearity of the interaction, the response of the system is less than for two independent velocity classes: fewer atoms leave the ground level and are excited to the upper level; fewer photons are absorbed. We deduce that the transmitted light intensity through the absorbing cell is greater (Lee & Skolnik 1967; Letokhov 1967); or the fluorescence light re-emitted by the absorbing cell is less (Freed & Javan 1970) (see figure 2*a*). This modified response of the absorbing medium is obtained over a frequency interval corresponding to the width of the velocity classes, i.e. of the order of the natural line width $\Delta\omega_n$: one observes a narrow curve superimposed on the broad Doppler curve (see figure 2*a*).

I have explained the principle of saturation spectroscopy for an absorbing medium (where $n_0 \gg n_1$). But in fact the phenomenon has been explained and observed for the first time for the amplifying medium that exists inside a laser cavity (and where $n_0 \ll n_1$). In that case the nonlinearity of the interaction also gives a smaller response of the system when the two velocity classes merge each into the other, i.e. when the laser frequency ω_L (determined by the cavity length) is exactly equal to the atomic frequency ω_1 of the amplifying transition. Then one observes less amplification, that is to say a smaller intensity of the laser beam; it is the so-called Lamb dip illustrated in figure 2*b* (Lamb 1964; Szöke & Javan 1966). Many experiments have been done following the schemes of figure 2 for the purpose of frequency stabilization or spectroscopic measurements; it is what is called Lamb-dip spectroscopy.

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Both the sensitivity and the feasibility of the saturation technique have been strongly improved by the two modifications illustrated in figure 3*a* (Bordé 1970; Hänsch *et al.* 1971*a–c*; Ouhayoun *et al.* 1972).

(i) The intensities of the two counterpropagating light beams are no longer equal: one beam

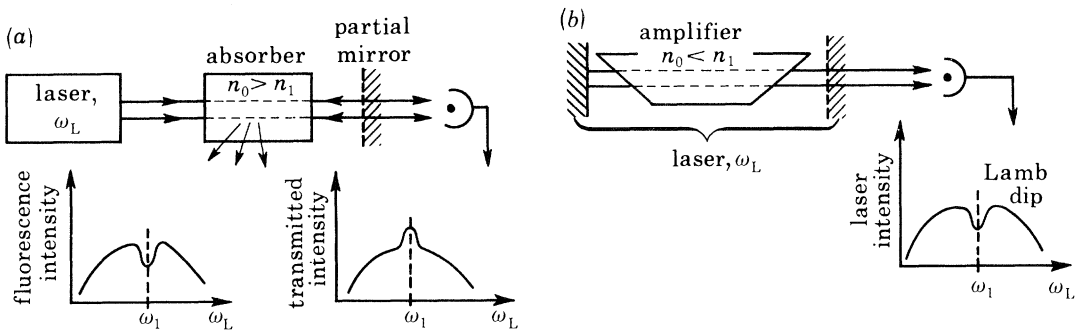

FIGURE 2. Principle of Lamb-dip spectroscopy: (*a*) with an absorbing medium (when $\omega_L = \omega_1$ there is less absorption); (*b*) with an amplifying medium (when $\omega_L = \omega_1$ there is less amplification).

of strong intensity is called the saturating beam (or sometimes the pumping beam); the other beam of weak intensity is called the probe beam. As a consequence, the merging of the two velocity classes when $\omega_L = \omega_1$ is equivalent, for the probe beam, to a stronger change in intensity, and that magnifies the nonlinear effect.

(ii) The directions of the two beams can be slightly tilted in such a manner that one can measure separately the intensity of the weak probe beam after its passage through the absorbing cell. Thus one measures the absorption of the probe beam, which is greatly reduced by the interaction of the saturating beam, when $\omega_L = \omega_1$.

The small tilt angle changes slightly the definition of the velocity classes for the two light beams; this produces a small broadening of the observed narrow curves. But the separation of the two beams permits the use of a chopping wheel on the saturating beam and the big improvement of lock-in detection, which produces narrow curves on a flat background.

As an example, figure 4 shows the hyperfine spectrum of the D_1 line of sodium obtained by Hänsch *et al.* (1971*c*), using this technique: four components are visible, which are predicted between the two hyperfine sublevels ($F = 0$ and 1) of the ground level $3S_{\frac{1}{2}}$ and the two hyperfine sublevels ($F = 0$ and 1) of the excited level $3P_{\frac{1}{2}}$. The Doppler width is almost 2000 MHz, i.e. the whole distance between the farthest peaks. The inverted peaks in the middle are parasitic signals, called crossovers. Such crossover peaks appear in all saturation spectra at mid-distance from the true peaks, when one velocity class corresponding to the first transition $(E_1 - E_0)$ coincides with one velocity class corresponding to the second transition $(E_2 - E_0)$ (Schlossberg & Javan 1966).

(*d*) *Saturated dispersion*

The general relation between absorption and dispersion is well known. The saturation of absorption also corresponds to a change in the index of refraction of the vapour, which is called saturated dispersion and was already predicted by Lamb in his theory of gas lasers (Lamb 1964). This saturated dispersion plays a role in the frequency stabilization of lasers on the Lamb dip (Barger & Hall 1969). Clear evidence of saturated dispersion was given by using a ring

interferometer (Bordé *et al.* 1973). But in practice, the observation of saturated dispersion is much easier by interferences of polarized light. That introduces us to polarization spectroscopy.

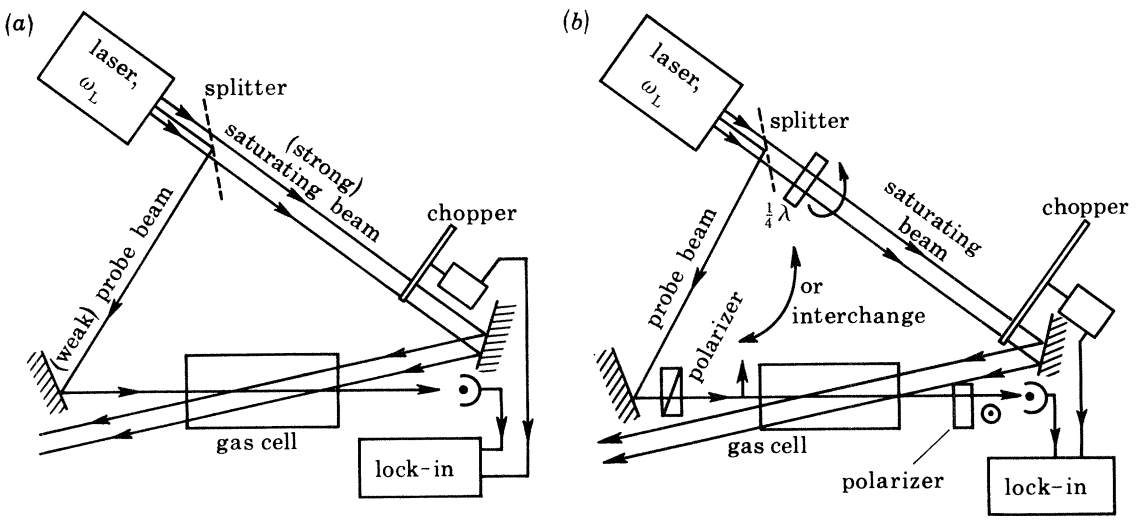

FIGURE 3. Experimental set-ups for saturation spectroscopy: (*a*) saturated absorption; (*b*) polarization spectroscopy.

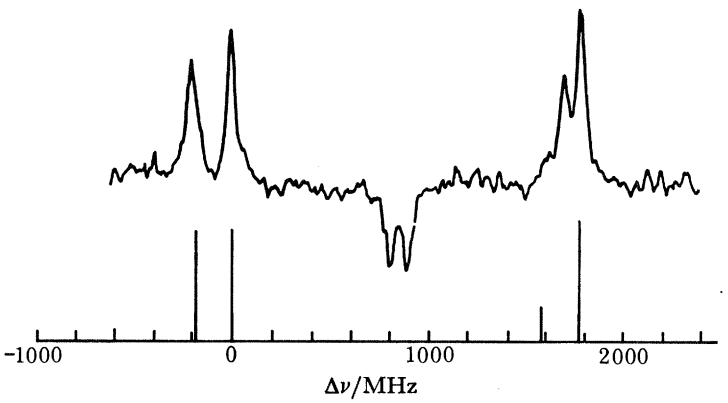

FIGURE 4. Saturated spectrum of the sodium D_1 line. The four theoretical peaks are shown on the bottom of the figure. The inverted peaks in the middle of the experimental curves are the parasitic crossover (Hänsch *et al.* 1971*c*).

(*e*) *Polarization spectroscopy*

The experimental scheme for polarization spectroscopy is very similar to the classical scheme for saturated absorption, as can be seen on figure 3*b*; but the two beams have different polarizations and one detects a change in the polarization of the probe beam induced by the saturating beam.

In the original scheme proposed by Wieman & Hänsch (1976), the saturating beam is circularly polarized by the use of a $\frac{1}{4}\lambda$ plate; it induces a circular anisotropy of the atomic vapour. The probe beam is linearly polarized, i.e. it is equivalent to the superposition of two circularly polarized counter-rotating waves. If these two counter-rotating polarizations have different absorptions or dispersions inside the saturated vapour, their superposition, at the exit of the

vapour cell, no longer gives the initial linear polarization. The crossed polarizer introduced before the photoreceiver gives very sensitive detection of these changes in polarization.

In another scheme (Keller & Delsart 1977), one interchanges the $\frac{1}{4}\lambda$ plate and the polarizer; the saturating beam is linearly polarized and induces in the vapour linear dichroism and birefringence; on the other hand the probe beam is circularly polarized. The probe beam is still analysed at the exit of the vapour cell by a polarizer; it may be shown that the signal on

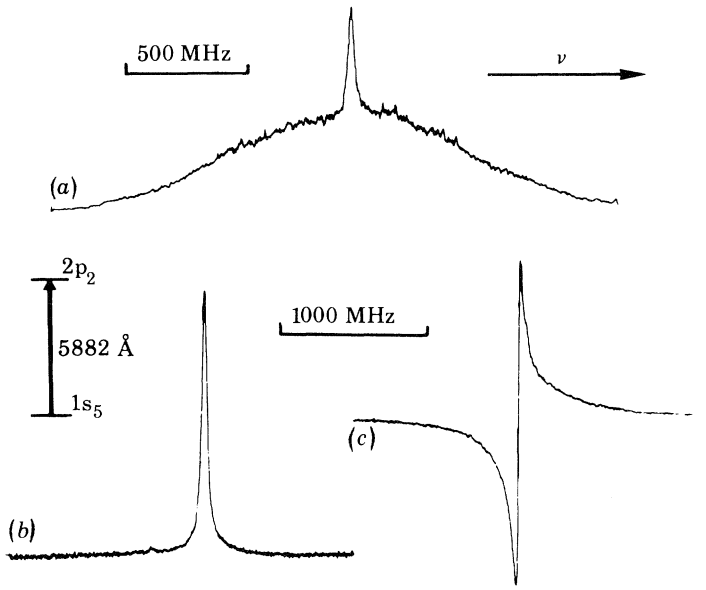

FIGURE 5. Doppler-free spectrum of the $\lambda = 5882$ Å (588.2 nm) neon transition: (*a*) saturated absorption; (*b*) polarization spectroscopy showing the laser-induced dichroism; (*c*) polarization spectroscopy showing the laser-induced birefringence (Delsart & Keller 1977).

the photoreceiver is a combination of dichroism and birefringence, depending on the orientation of that polarizer. A proper choice of its orientation and a subtracting technique permit one to obtain signals that represent either pure dichroism (figure 5*b*) or pure birefringence spectra (figure 5*c*); one recognizes in this latter case the classical shape of the dispersion curve plotted against frequency. It is also possible to interpret these polarization signals as forward scattering of light by the atoms of the gas (Gawlik & Series 1979).

Another advantage of polarization spectroscopy is the suppression of the broad signal background observed in saturated absorption (figure 5*a*), when collisions redistribute the velocities of the pumped atoms over the Doppler profile, because these velocity-changing collisions drastically reduce the laser-induced anisotropy (the curves in figure 5 are obtained in the same experimental cell of neon).

Many spectroscopic measurements have been made with the saturation technique, which can also use optogalvanic detection and which have permitted numerous metrological applications. Other papers in this symposium are devoted to these techniques.

3. Multiphoton transitions

The suppression of Doppler broadening can also be realized in multiphotonic transitions, where the atom absorbs simultaneously the energies of several photons to jump from the ground level to an excited level E_e. I shall consider two-photon transitions, such as $E_e - F_0 = 2\hbar\omega_L$ (figure 6*a*).

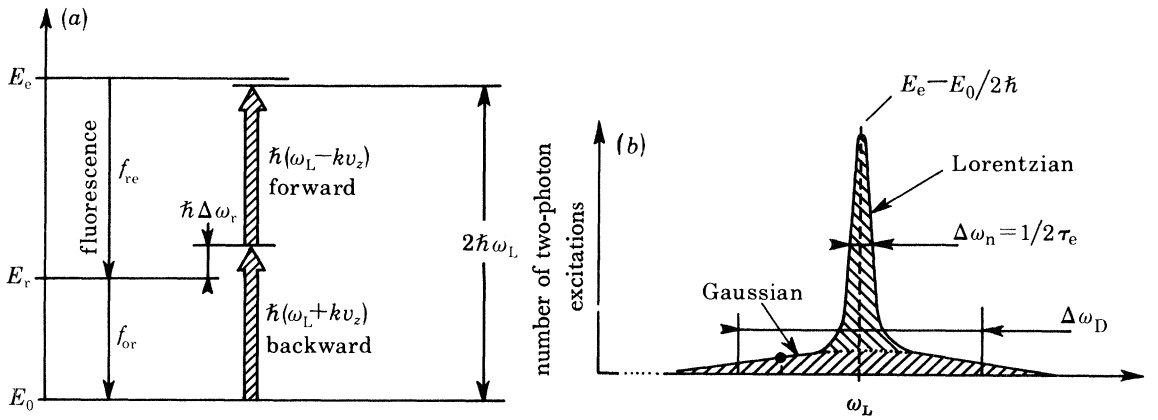

FIGURE 6. Principle of Doppler-free two-photon transitions: (*a*) energy diagram; (*b*) theoretical line shape.

(*a*) *Principle of Doppler-free two-photon transitions*

The possibility of producing such transitions was calculated by Gröppert-Mayer (1931) at the beginning of quantum mechanics. It was one of the first applications of the perturbation theory to second order. This calculation requires a summation on all the other levels. But we assume that only one term of this summation, corresponding to the intermediate level E_r, has a predominant role; we can then interpret the calculation in the following manner: after absorption of the first photon, the atom is in the virtual state E_r with the energy defect $\hbar\Delta\omega_r = E_0 + \hbar\omega_L - E_r$. Because of the uncertainty principle, the atom remains in this virtual state during the short time $\Delta t_r \approx 1/\Delta\omega_r$; the atom has a very small probability of absorbing a second photon during this very short time Δt_r unless the electromagnetic wave has a very high intensity. This indicates why the energy defect $\Delta\omega_r$ appears in the denominator of the two-photon probability, $\mathscr{P}^{(2)}$, which is also proportional to the square of the light intensity, P/S:

$$\mathscr{P}^{(2)} \approx C_t\, \tau_e\, (\omega_L/\Delta\omega_r)^2 f_{0r} f_{re} (P/S)^2,$$

where τ_e is the lifetime of the E_e level and f_{0r} and f_{re} are the oscillator strengths of the one-photon transitions. Owing to the necessity of high intensity, the multiphotonic transitions were observed first in the radiofrequency range, more than 20 years ago (Hughes *et al.* 1950; Brossel *et al.* 1953; Kusch 1954). In the optical range it was necessary to wait for the high power of laser sources (Abella 1962).

Suppose now that the two-photon transition is produced with a laser beam reflected on itself with a mirror, as in Lamb-dip spectroscopy. In the rest frame of one particular atom the two waves have slightly different frequencies, $(\omega_L - kv_z)$ and $(\omega_L + kv_z)$. If the atom absorbs one photon from each wave, the two opposite Doppler shifts cancel out and the total energy of the two photons is equal to $2\hbar\omega_L$, independent of the atomic velocity v_z. The resonance condition of the two-photon transition is fulfilled at the same value of the laser frequency ω_L for all the atoms, irrespective of their velocities.

(*b*) *Theoretical line-shape*

In practice the atoms can also absorb two photons from the same travelling wave, but that absorption is still subject to Doppler broadening. As a consequence, when we sweep the laser frequency ω_L, the number of two-photon excitations must vary, as indicated in figure 6*b*; it is the superposition of two curves:

(i) one Lorentzian curve of high intensity and narrow width, corresponding to the absorption of one photon of each counterpropagating light wave by all the atoms together (the width of this narrow curve is equal to the natural width $1/\tau_e$ for the energy gap $2\omega_L$, i.e. one half of this for the laser frequency ω_L);

(ii) one curve of weak intensity, a broad Gaussian curve (with Doppler width $\Delta\omega_D$), which corresponds to the absorption of two photons propagating in the same direction backward or forward by two symmetrical velocity classes ($+v_z$ or $-v_z$).

If the two counterpropagating waves have the same polarization, a simple discussion shows that the area of the narrow curve is twice the area of the broad curve. Normally the Doppler width of the Gaussian curve is 100 or 1000 times the natural width of the Lorentzian curve, and the Gaussian will appear as a very small background.

The principle of this effect was noticed first by Vasilenko *et al.* (1970). In our laboratory we later came independently to the same idea; our calculations showed the possibility of actually carrying out high-resolution experiments (Cagnac *et al.* 1973):

(i) the possibility of obtaining sufficient signal with the small power of c.w. dye lasers in monomode operation;

(ii) the possibility of reducing the light shifts (or dynamical Stark shifts) far below the natural width;

(iii) selection rules in some respect analogous to quadrupolar transitions;

(iv) generalization to multiphotonic transitions with three or more photons (by momentum conservation, one shows the nullity of the Doppler shift when the aggregate momentum of the photons is zero, i.e. the vectorial sum of their wavevectors is zero: $\Sigma\, \boldsymbol{k}_i = 0$).

(*c*) *Experiments*

The first experimental demonstrations, in Paris and in Harvard (Biraben *et al.* 1974; Levenson *et al.* 1974) were performed with pulsed dye lasers; however, the precision of the measurements is increased by the use of c.w. dye lasers in monomode operation.

The light coming from the laser is focused in the experimental cell with a lens, to increase the energy density P/S (the number of irradiated atoms decreases as S, but the two-photon probability increases as $(P/S)^2$ in such a manner that the signal increases as $1/S$). The transmitted light is refocused from the other side into the cell by a concave mirror, whose centre coincides with the focus of the lens (figure 7).

The first concave mirror in figure 7 is not essential, but in many experiments the energy density is increased by placing the experimental cell in a spherical concentric Fabry–Perot cavity. The windows of the experimental cell must be tilted at the Brewster angle to reduce the losses in the cavity. The length of this cavity is piezoelectrically locked on the laser frequency, to maximize the signal transmitted through it.

In all cases, an optical isolator must be interposed between the laser and the experiment, to

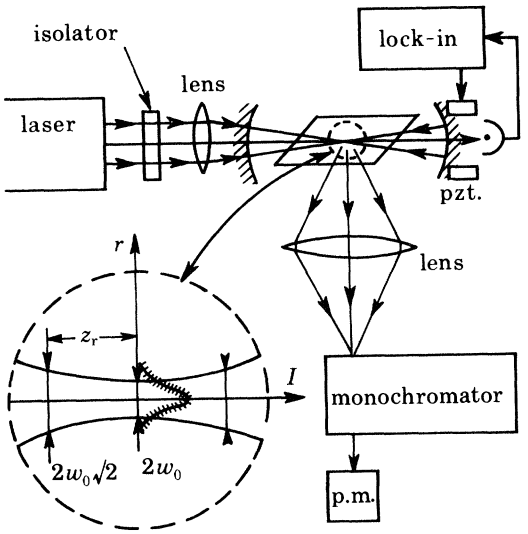

FIGURE 7. Experimental set-up for Doppler-free two-photon spectroscopy. Inside the dotted circle is represented the waist of the laser Gaussian beam which replaces the focus of geometrical optics: the superimposed curve with small bars represents the light intensity I as a function the radial distance r.

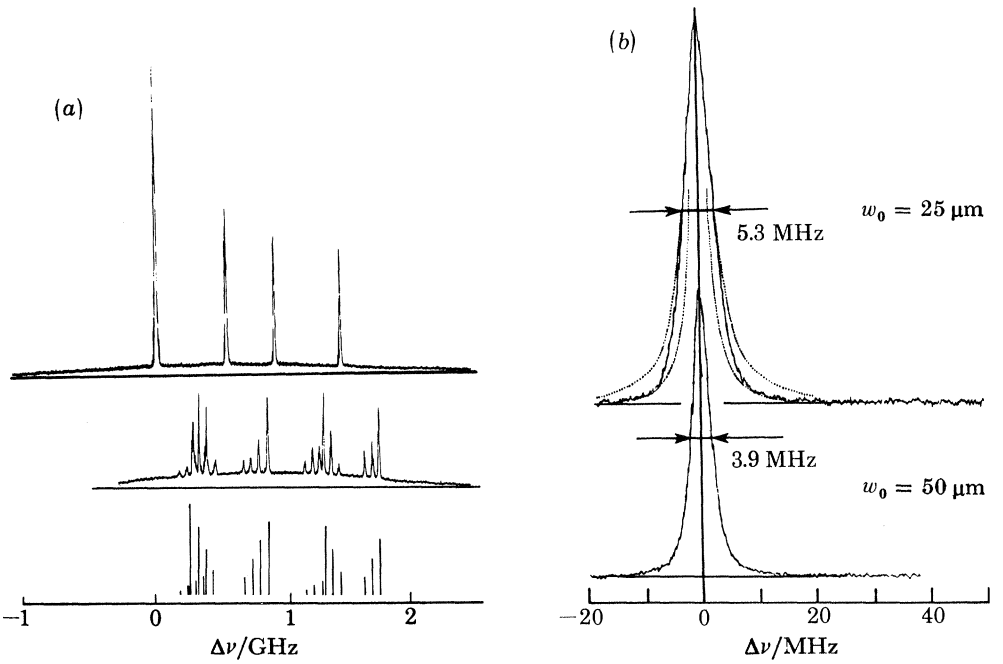

FIGURE 8. Two-photon transition 3S—4D in sodium: (*a*) recordings against the laser frequency in zero magnetic field (top curve) and in a small magnetic field of 170 G (17 mT) (middle curve) (below is the theoretical Zeeman pattern); (*b*) recordings of the first peak of (*a*) on an enlarged scale. The comparison between the two curves recorded with different waist radii w_0 shows the effect of the transit time through the laser beam. The dotted curves superimposed on the upper recording are pure Lorentzian curves coinciding with the experimental curve either on the wings or at mid-height (Biraben *et al.* 1979).

prevent the return beam from perturbing the laser (a $\frac{1}{4}\lambda$ plate or a Faraday glass in an axial magnetic field achieves this).

The two-photon resonance is detected by collecting fluorescence photons emitted from the excited level at a frequency ω_{er}, which is different from the exciting frequency ω_L (figure 6*a*) and can be selected with an interference filter or a monochromator. This allows the complete elimination of stray light from the laser, despite its high intensity, and the observation of very small signals on a black background. For very highly excited states (near the ionization limit), one can use other, more sensitive techniques: thermoionic detection (Harvey & Stoicheff 1977) or optogalvanic detection.

As an example, I show in figure 8*a* one recording of the 3S—4D two-photon transition in sodium, where the photomultiplier current is plotted against the laser frequency. Here also the two levels 3S and 4D are split in two sublevels (by fine interaction for the 4D level $\rightarrow J = \frac{3}{2}$ and $J = \frac{5}{2}$; by hyperfine interaction for the 3S level $\rightarrow F = 0$ and $F = 1$), and we obtain four neighbouring transitions. It is possible to observe on this recording the small Doppler background, which gives an idea of the Doppler broadening of 2000 MHz. The width of the narrow peaks is of the order of 10 MHz and is due principally to the frequency jitter of the laser; but that can be improved.

Figure 8*b* shows one of these four peaks recorded with a better stability of the laser (frequency jitter smaller than 1 MHz). That permits the evaluation of the broadening due to the short transit time of the atoms through the laser beam. The broader curve has been recorded with a waist radius of the Gaussian light beam $w_0 = 25$ μm, which gives a transit time shorter than the lifetime. The corresponding line shape can be calculated exactly (Biraben *et al.* 1979) and is quite different from a Lorentzian profile, as can be seen in figure 8*b* (the dotted lines represent two Lorentzian curves, the first coinciding with the wings, the second with the half-height of the experimental curve). The narrower experimental curve has been recorded with a double waist radius ($w_0 = 50$ μm). The transit time is double, and its shape is much closer to the Lorentzian shape.

4. Conclusion

I have described the general properties of these two methods for high-resolution spectroscopy, but shortage of time precludes the description of all the applications that have been already realized in atoms or in molecules. These applications are similar for the two methods: measurements of fine or hyperfine splittings, isotopic shifts, Zeeman or Stark effects in small external fields, the study of collisions, and many applications for metrology, which have so far been developed with the saturation technique and are discussed elsewhere in this symposium. There is also insufficient time to describe the use of transient methods in these two techniques.

In conclusion I shall try to compare these two Doppler-free techniques.

(*a*) In their principles both techniques use the sign inversion of the Doppler shift with the sign of the wavevector $\boldsymbol{k}$, but in the two-photon technique the two opposite Doppler shifts cancel out by summation for all the atoms, whereas in the saturation technique one selects the signal given by the small fraction of the atoms whose velocity component $v_z = 0$.

(*b*) The required light power is less for the saturation technique than for the two-photon technique, but the power difference is not great because of the small fraction of atoms that contribute to the saturation signal, and because of the high sensitivity of two-photon detection with a wavelength distinct from that of the laser. Some milliwatts are enough for current

saturation experiments, but many two-photon experiments have been done with about 100 mW. Moreover it is possible to increase the two-photon signal with powerful pulses, which are not useful in the saturation technique.

(*c*) Light shifts, caused by non-resonant irradiation of one-photon transitions, do not exist in the saturation technique because the irradiation is resonant; but they can perturb slightly the two-photon transitions. Nevertheless in most cases it is easy to reduce these light shifts to be much smaller than the natural line width.

(*d*) The parasitic signals called 'crossover', on the other hand, perturb saturation spectra (and can be dangerous in the interpretation of complex molecular spectra), whereas they do not exist in two-photon spectra.

(*e*) The line shapes of two-photon transitions are very simple, as they are simple Lorentzian curves, whereas the line shape in the saturation technique is quite complicated (its calculation involves the averaging of a nonlinear effect that depends on the velocity component v_z). If collisions are taking place, the two-photon line shape remains Lorentzian and it is easy to measure the broadening and the shift, whereas the velocity-changing collisions complicate still more the saturation line shape.

(*f*) The finite transit time of the atoms through the laser beam produces analogous broadenings in the two techniques. The large light beams (10 cm or more) used in the saturation technique to reduce this broadening in very narrow molecular transitions seems not to be possible with two-photon transitions because the energy density would be too small. But it is possible to use the Ramsey fringes technique (Baklanov *et al.* 1976; Salour *et al.* 1977).

The two techniques have different advantages or disadvantages; in fact they have both their own field of applications: the saturation technique for the lower excited levels, and the two-photon technique for the higher excited levels.

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Discussion

G. W. Series, F.R.S. (*University of Reading, U.K.*). Those of us who have followed Professor Cagnac's work know that he has carried out experiments with *three-photon* interactions. Have any spectroscopic applications been found for three-photon processes?

B. Cagnac. The cancellation of Doppler broadening can be generalized to n-photon transitions with $n \geqslant 3$, if the light beams form a star in such a manner that the vectorial sum of the photons' momenta is zero (the Doppler shift can be explained by the momentum conservation of the whole system photons + atom). We have experimentally demonstrated the reality of this effect for a three-photon transition. From the point of view of the selection rules, the three-photon and two-photon processes are strictly complementary. But in fact, it seems to me that the Doppler-free three-photon processes will be useful only in exceptional cases, because of the practical difficulties and particularly because of the problem of the light shifts.

The light shift and the two-photon probability are calculated to the same order of the perturbation calculation (the second order); this is why it is easy to reduce the light shifts far below the natural width in conditions where the two-photon probability is not too small. But the three-photon probability is calculated to a superior order, and when this probability is not too small, it is practically impossible to cancel exactly the light shifts. The Doppler-free three-photon processes gave us an exciting experiment, but they cannot really give a general method.

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