Theory of degenerate four-wave mixing in resonant Doppler-broadened media. - II. Doppler-free heterodyne spectroscopy via collinear four-wave mixing in two- and three-level systems

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J. Physique **43** (1982) 57-65 JANVIER **1982**, PAGE 57

Classification
Physics Abstracts
32.80K — 42.50 — 42.65B

Theory of degenerate four-wave mixing in resonant Doppler-broadened media. II. Doppler-free heterodyne spectroscopy *via* collinear four-wave mixing in two- and three-level systems (*)

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(*Reçu le 23 juillet 1981, accepté le 25 septembre 1981*)

Résumé. — Dans cet article, nous analysons une nouvelle technique spectroscopique consistant à irradier un échantillon par un faisceau laser comportant deux fréquences ($\omega + \Delta \pm \delta/2$) et un faisceau sonde ($\omega$) se propageant en sens opposé. Deux ondes conjuguées de fréquences $\omega \pm \delta$, réémises par l'intermédiaire de processus non linéaires à quatre ondes, interfèrent avec l'onde sonde pour créer un signal de battement hétérodyne à la fréquence δ. Les propriétés de ce battement sont étudiées ici grâce à un calcul de la réponse non linéaire du milieu irradié, effectué au troisième ordre de perturbation en fonction des champs incidents. En milieux gazeux résonnants, la forme de raie est caractérisée par un doublet sans élargissement Doppler (séparation 3 $\delta/2$ pour des résonances à un photon, $\delta/2$ pour des transitions à deux photons). A l'aide d'une détection synchrone du battement hétérodyne, on peut analyser séparément parties réelle (dispersion) et imaginaire (absorption) de la susceptibilité non linéaire. Dans le cas de transitions à un photon, le retard de phase du signal est lié à la durée de vie des niveaux de la transition et permet une étude de la dynamique de la relaxation en phase gazeuse (collisions inélastiques, diffusion de la vitesse, etc...). Ceci est d'un intérêt particulier pour les résonances de croisement par effet Doppler, pour lesquelles seul le niveau commun fournit une contribution. Dans les systèmes à trois niveaux, on prédit aussi une augmentation sélective de l'émission conjuguée grâce à des processus résonnants à deux photons de type Raman. La plupart des prédictions théoriques ont été observées expérimentalement.

Abstract. — In this article, we analyse a new sensitive spectroscopic technique in which a sample cell is irradiated by a two-frequency pump beam ($\omega + \Delta \pm \delta/2$) and a counter-propagating probe beam (ω). The phase-conjugate fields re-emitted at frequencies $\omega \pm \delta$, *via* four-wave mixing processes, are detected through their heterodyne beating with the probe field. The properties of the heterodyne beat signal are studied by means of a perturbation calculation of the nonlinear response of the medium, carried out to the third order in the incident fields. In resonant gas media, the emission lineshape exhibits a Doppler-free doublet structure [frequency splitting 3 $\delta/2$ for single-photon resonances, and $\delta/2$ for two-photon transitions]. By using a phase-sensitive detection of the beat signal, one can separately analyse real (dispersion) or imaginary parts (absorption) of the nonlinear susceptibility. For single-photon transitions, the signal phase shift is related to the atomic levels lifetime and allows one to study the relaxation dynamics in gas phase (like quenching collisions, velocity diffusion, etc...). This is particularly interesting for cross-over resonances, in which only the common level contributes. In three-level systems, one also predicts a selective resonant enhancement of the phase-conjugate emission through Raman-type two-photon processes. Most of these predictions have been experimentally verified.

1. **Introduction.** — In a previous article [1], we have presented an analysis of the angular dependence of degenerate and nearly-degenerate four-wave mixing (NDFWM) in resonant Doppler-broadened systems ([1]). We have shown that, when the incident frequency is resonant for a single-photon transition, both strength and lineshape of the phase-conjugate emission strongly depend on the pump-probe incidence angle, θ. Doppler-free lineshapes are observed at grazing incidence, $\theta = 0$. On the other hand, a lineshape Doppler-broadening appears when θ increases.

Recent experiments [2-4] have shown that NDFWM *via* multifrequency incident irradiation provides a sensitive way of analysing the features of phase-conjugate emission, when the re-emitted electro-

(*) Work supported in part by D.R.E.T. (Paris).

(**) Associé au C.N.R.S., L.A. n° 282.

([1]) This article [*J. Physique* **42** (1981) 711] will be referred to as I in the following. In particular, references to its equations and formulae will be preceded by I.

magnetic (e.m.) field is detected through its heterodyne beating with one of the input e.m. fields. This detection technique combines the advantages of heterodyne amplification with the sensitivity of high-frequency detection. For sufficiently high detection frequencies, the amplitude noise of the laser beams becomes smaller than the photon shot-noise, and it is then possible to reach the signal shot-noise limit [4]. However, in *non-collinear* optically-heterodyned NDFWM [2], in addition to the residual Doppler-broadening there is also an angle-dependent frequency-shift of the emission peak [see Eq. (I, 64)]. For these reasons, *collinear* NDFWM appears more appropriate for high-resolution Doppler-free studies [3, 4].

In this article, our purpose is to describe the properties of reasonantly-enhanced collinear NDFWM in two- or three-level gas systems. It is shown that this yields an elegant method to analyse the various Doppler-free contributions to the nonlinear susceptibility of the medium. Phase-sensitive detection of the heterodyne beat signal allows one to observe either nonlinear absorption or dispersion [3]. We also emphasize the main difference between single-photon resonances, where the Doppler-free character originates in velocity selection processes, and two-photon transitions in which the compensation of the Doppler effect is realized for every atomic velocity group *via* a cancellation of the global linear momentum of the absorbed photons [5]. In a following article, the effect of level degeneracy and laser beam polarization will be considered.

2. **Induced polarization and heretodyne beat signal in collinear NDFWM.** — One considers the configuration of figure 1 in which a nonlinear gas medium

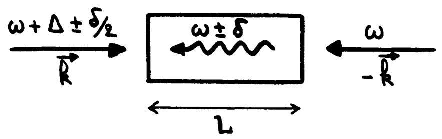

Fig. 1. — Configuration of the incident and re-emitted e.m. fields in collinear nearly-degenerate four-wave mixing.

(length L) is irradiated by three collinear plane waves (frequencies $\omega + \Delta \pm \delta/2$, wavevector $\mathbf{k}$ and frequency ω, wavefactor $-\mathbf{k}$). One assumes $\delta \ll c/L$ to preserve phase-matching. The incident e.m. field is thus written as ($Oz /\!/ \mathbf{k}$)

$$E(z, t) = \sum_{\nu = 0, +, -} E^{\nu}(z, t) \tag{1}$$

with

$$E^{\pm}(z, t) = \tfrac{1}{2}\, \mathcal{E}^{\pm}\, e^{i[(\omega + \Delta \pm \delta/2)t - kz + \varphi_{\pm}]} + \text{c.c.} \tag{2}$$

and

$$E^{0}(z, t) = \tfrac{1}{2}\, \mathcal{E}^{0}\, e^{i(\omega t + kz + \varphi_0)} + \text{c.c.}\,. \tag{3}$$

As shown below, through resonant FWM processes, two phase-conjugate fields are re-emitted in direction $-\mathbf{k}$, with frequencies $\omega \pm \delta$ and phases $\varphi_0 \pm (\varphi_+ - \varphi_-)$:

$$E^{\mathrm{r}} = \tfrac{1}{2}\, \mathcal{E}^{\mathrm{r}}(\pm)\, e^{i[(\omega \pm \delta)t + kz + \varphi_0 \pm \varphi]} + \text{c.c.}\,. \tag{4}$$

with

$$\varphi = \varphi_+ - \varphi_- \,. \tag{5}$$

Since the total transmitted power per unit surface in direction $-\mathbf{k}$ is given by

$$I = c\varepsilon_0 \overline{(E^0 + E^{\mathrm{r}})^2_{\mathrm{av.}}} \tag{6}$$

the re-radiated fields interfere with the incident E^0 field serving as a local oscillator to yield an heterodyne beat signal at frequency δ :

$$I_{\mathrm{r}}(\delta) = \tfrac{1}{2}\, \varepsilon_0\, c\, \mathcal{E}^0 [\mathcal{E}^{\mathrm{r}}(+) + \mathcal{E}^{\mathrm{r}*}(-)]\, e^{i(\delta t + \varphi)} + \text{c.c.}\,. \tag{7}$$

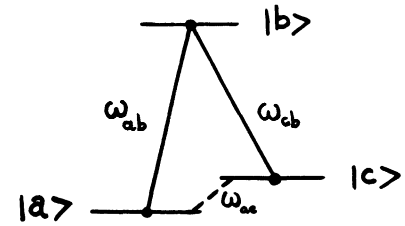

Fig. 2. — Resonance three-level system.

The beat signal lineshape, $\mathcal{E}^{\mathrm{r}}(\pm)$, depends on the details of the atomic system. For instance, for the three-level (a-b-c) system considered in figure 2, the equations of motion for the density matrix are :

$$\dot{\rho}_{\mathrm{aa}} = \gamma_{\mathrm{a}}(n_{\mathrm{a}} - \rho_{\mathrm{aa}}) - \left(i\, \frac{\mu_{\mathrm{ba}} E}{\hbar}\, \rho_{\mathrm{ab}} + \text{c.c.} \right)$$

$$\dot{\rho}_{\mathrm{bb}} = \gamma_{\mathrm{b}}(n_{\mathrm{b}} - \rho_{\mathrm{bb}}) + \left(i\, \frac{\mu_{\mathrm{ba}} E}{\hbar}\, \rho_{\mathrm{ab}} - i\, \frac{\mu_{\mathrm{cb}} E}{\hbar}\, \rho_{\mathrm{bc}} + \text{c.c.} \right)$$

$$\dot{\rho}_{\mathrm{cc}} = \gamma_{\mathrm{c}}(n_{\mathrm{c}} - \rho_{\mathrm{cc}}) + \left(i\, \frac{\mu_{\mathrm{cb}} E}{\hbar}\, \rho_{\mathrm{bc}} + \text{c.c.} \right)$$

$$\begin{aligned}
\dot{\rho}_{ab} &= (-\gamma_{ab} + i\omega_{ab})\,\rho_{ab} + i\frac{\mu_{ab}E}{\hbar}(\rho_{bb} - \rho_{aa}) - i\frac{\mu_{cb}E}{\hbar}\rho_{ac} \\
\dot{\rho}_{ac} &= (-\gamma_{ac} + i\omega_{ac})\,\rho_{ac} + i\frac{E}{\hbar}(\mu_{ab}\,\rho_{bc} - \rho_{ab}\,\mu_{bc}) \\
\dot{\rho}_{bc} &= (-\gamma_{bc} - i\omega_{cb})\,\rho_{bc} + i\frac{\mu_{bc}E}{\hbar}(\rho_{cc} - \rho_{bb}) + i\frac{\mu_{ba}E}{\hbar}\rho_{ac}\,.
\end{aligned} \tag{8}$$

The notations are the same as the ones used in reference [1] [Eqs. (I, 6-14) and (I, 74-75)]. Let us remind that $\hat{\mu}$ is the electric dipole operator. The matrix elements $\mu_{ij} = \langle i \mid \hat{\mu} \mid j \rangle$ are assumed real and $\mu_{ac} = 0$; n_j is the equilibrium population of level j, γ_{ij} are the relaxation rates and

$$\dot{\rho} = \left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial z}\right)\rho\,, \tag{9}$$

where v is the velocity component along the Oz axis. The induced electric dipole polarization is given by

$$P = \mu_{ba}\langle \rho_{ab} \rangle + \mu_{bc}\langle \rho_{cb} \rangle + \text{c.c.} \tag{10}$$

in which $\langle\ \ \rangle$ means velocity-averaged. This polarization re-radiates an e.m. field, which, in the slowly-varying field-envelope approximation, is given by [see Eqs. (I, 2-5); the gas sample is assumed to be optically thin] :

$$E^{r} = -\,i\frac{kL}{2\,\varepsilon_0}[\mu_{ba}\langle \rho_{ab} \rangle + \mu_{bc}\langle \rho_{cb} \rangle] + \text{c.c.} \tag{11}$$

ρ_{ab} and ρ_{cb} are obtained through a perturbation expansion in the incident e.m. fields. Making the rotating-wave approximation, one gets, at the third order [6] :

$$\begin{aligned}
\rho_{ab}^{(3)} = \left(\frac{i}{2}\right)^3 \sum_{\mu,\nu,\lambda} \frac{e^{i[\Phi_\mu - \Phi_\nu + \Phi_\lambda]}}{L_{ab}(\omega_\mu - \omega_\nu + \omega_\lambda)} \Bigg\{ & n_{ab}\,\alpha_\mu\,\alpha_\nu\,\alpha_\lambda \left[\frac{1}{L_a(\omega_\mu - \omega_\nu)} + \frac{1}{L_b(\omega_\mu - \omega_\nu)}\right] \times \\
& \times \left[\frac{1}{L_{ab}(\omega_\mu)} + \frac{1}{L_{ab}^*(\omega_\nu)}\right] + n_{cb}\frac{\beta_\mu\,\beta_\nu\,\alpha_\lambda}{L_b(\omega_\mu - \omega_\nu)}\left[\frac{1}{L_{cb}(\omega_\mu)} + \frac{1}{L_{cb}^*(\omega_\nu)}\right] \\
& + \frac{\alpha_\mu\,\beta_\nu\,\beta_\lambda}{L_{ac}(\omega_\mu - \omega_\nu)}\left[\frac{n_{ab}}{L_{ab}(\omega_\mu)} + \frac{n_{cb}}{L_{cb}^*(\omega_\nu)}\right]\Bigg\}
\end{aligned} \tag{12}$$

$\rho_{cb}^{(3)}$ is obtained by exchanging a and c, β and α.

In (12), the following notations are used :

$$n_{ij} = n_j - n_i \tag{13}$$

$$L_{ij}(\omega_\mu - \omega_\nu + \omega_\lambda) = \gamma_{ij} + i[\omega_\mu - \omega_\nu + \omega_\lambda - \omega_{ij} - (k_\mu - k_\nu + k_\lambda)\,v] \tag{14}$$

$$L_j(\omega_\mu - \omega_\nu) = \gamma_j + i[\omega_\mu - \omega_\nu - (k_\mu - k_\nu)\,v] \tag{15}$$

$$\Phi_\nu = \omega_\nu\,t - k_\nu\,z + \varphi_\nu \tag{16}$$

$$\alpha_\nu = \mu_{ab}\,\mathcal{E}^\nu/\hbar\,; \quad \beta_\nu = \mu_{bc}\,\mathcal{E}^\nu/\hbar\,. \tag{17}$$

The frequency, wavevector and phase of the re-emitted field are given by [cf. Eqs. (11-12)] :

$$\begin{aligned}
\omega_r &= \omega_\mu - \omega_\nu + \omega_\lambda \\
k_r &= k_\mu - k_\nu + k_\lambda \\
\varphi_r &= \varphi_\mu - \varphi_\nu + \varphi_\lambda\,.
\end{aligned} \tag{18}$$

The signal of interest is related to the fields re-radiated in direction $-k$, at frequencies $\omega \pm \delta$ [Eq. (4)]. For instance, the re-emitted field at frequency $\omega + \delta$ corresponds to the conditions

$$\omega_\mu = \omega + \Delta + \delta/2\,,\ \omega_\nu = \omega + \Delta - \delta/2\,,\ \omega_\lambda = \omega \tag{19}$$

or

$$\omega_\mu = \omega\,, \quad \omega_\nu = \omega + \Delta - \delta/2\,, \quad \omega_\lambda = \omega + \Delta + \delta/2\,. \tag{20}$$

To get the beat signal lineshape, one finally has to average the corresponding contributions of $\rho_{ab}^{(3)}$ and $\rho_{cb}^{(3)}$ over the Maxwellian distribution (r.m.s. thermal velocity, u) :

$$\langle \rho \rangle = \int_{-\infty}^{+\infty} \frac{\mathrm{d}v}{u\sqrt{\pi}} \mathrm{e}^{-v^2/u^2} \rho(v) . \tag{21}$$

All the integrations will be performed in the Doppler limit,

$$ku \gg \gamma_{ij}, \gamma_j . \tag{22}$$

In the following, without loss of generality, one assumes $\mathcal{E}^+ = \mathcal{E}^-$, i.e., $\alpha_+ = \alpha_- = \alpha$ and $\beta_+ = \beta_- = \beta$.

3. **Two-level system.** — 3.1 AMPLITUDE OF THE RE-EMITTED FIELD. — In this section, one considers in detail the case of a two-level system, a-b. The polarization induced at frequency $\omega + \delta$ is given by [Eq. (12) with $\beta_\mu = 0$ and (19-20)] :

$$\rho_{ab}^{(3)}(\omega + \delta) = -\frac{i}{8} n_{ab} \alpha^2 \alpha_0 \frac{\mathrm{e}^{i[(\omega+\delta)t + kz + \varphi + \varphi_0]}}{\gamma_{ab} + i(\omega + \delta - \omega_{ab} + kv)} \times$$
$$\times \sum_{j=a,b} \left\{ \frac{1}{\gamma_j + i\delta} \left[\frac{1}{\gamma_{ab} + i(\omega + \Delta + \delta/2 - \omega_{ab} - kv)} + \frac{1}{\gamma_{ab} - i(\omega + \Delta - \delta/2 - \omega_{ab} - kv)} \right] \right.$$
$$\left. + \frac{1}{\gamma_j + i(2\,kv - \Delta + \delta/2)} \left[\frac{1}{\gamma_{ab} + i(\omega - \omega_{ab} + kv)} + \frac{1}{\gamma_{ab} - i(\omega + \Delta - \delta/2 - \omega_{ab} - kv} \right] \right\} . \tag{23}$$

Velocity-integration of ρ_{ab} is performed in reference [6], when it is assumed that Δ and δ stay inside the Doppler linewidth (Δ, $\delta \lesssim ku$). In that case, by using the properties of the plasma dispersion function [7], one easily shows that the first term of (23) provides a contribution proportional to $\gamma^{-2}(ku)^{-1}$, the second term a contribution of order $\gamma^{-1}(ku)^{-2}$ and the two last terms contributions of order $(ku)^{-3}$. In addition, the first term alone exhibits sharp frequency-variations (linewidth $\sim \gamma$), in contrast with the three other contributions which vary on a frequency interval $\sim ku$. At the lowest order in γ/ku one gets

$$\langle \rho_{ab}^{(3)}(\omega + \delta) \rangle = -\frac{i}{8} n_{ab} \alpha^2 \alpha_0 \frac{\sqrt{\pi}}{ku} \frac{\mathrm{e}^{i[(\omega+\delta)t + kz + \varphi + \varphi_0]}}{\gamma_{ab} + i(\Omega - \omega_{ab} + 3\,\delta/4)} \sum_{j=a,b} \frac{F(\Delta - \delta/2)}{\gamma_j + i\delta} \tag{24}$$

where

$$\Omega = \omega + \frac{\Delta}{2} \tag{25}$$

and

$$F(x) = \exp[-(x/2\,ku)^2] . \tag{26}$$

The amplitude of the re-emitted field [Eqs. (4-11)] is given by

$$\mathcal{E}^{r}(+) = \frac{-kL}{8\,\varepsilon_0} n_{ab} \alpha^2 \alpha_0 \mu_{ba} \frac{\sqrt{\pi}}{ku} \frac{F(\Delta - \delta/2)}{\gamma_{ab} + i(\Omega - \omega_{ab} + 3\,\delta/4)} \sum_j \frac{1}{\gamma_j + i\delta} \tag{27}$$

$\mathcal{E}^{r}(-)$ is obtained by changing δ in $-\delta$ [8].

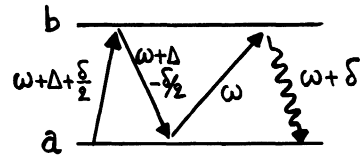

Fig. 3. — Process inducing phase-conjugate emission at frequency $\omega + \delta$ in collinear resonant four-wave mixing.

The origin of $\mathcal{E}^{r}(+)$ lies in the nonlinear process shown in figure 3, in which three quanta ($\omega + \Delta + \delta/2$, $\omega + \Delta - \delta/2$, ω) are exchanged with the incident fields, and a fourth quantum is re-emitted at frequency $\omega + \delta$ [3]. The resonance condition for one-quantum-absorption is

$$\omega + \Delta + \delta/2 - kv = \omega_{ab} \tag{28a}$$

and, for three-quanta transition :

$$(\omega + \Delta + \delta/2 - kv) - (\omega + \Delta - \delta/2 - kv) + (\omega + kv) = \omega_{ab} . \tag{28b}$$

Therefore, one gets, for the resonance frequency,

$$\omega = \omega_{ab} - \frac{\Delta}{2} - \frac{3\,\delta}{4} \tag{29a}$$

and, for the selected velocity group,

$$2\,kv = \Delta - \delta/2\,. \tag{29b}$$

This allows us to interpret the resonant frequency-denominator, and the weighting coefficient F in equation (27). In the same way, $\mathcal{E}^r(-)$ is resonantly enhanced for $\omega = \omega_{ab} - \frac{\Delta}{2} + \frac{3\,\delta}{4}$.

In (27), the $(\gamma_j + i\delta)^{-1}$ contribution characterizes the response of the populations of levels a and b to the amplitude-modulation of the incident field [9] along the **k** direction, whose intensity is given by [Eqs. (2-6)] :

$$I_{\mathbf{k}}(\delta) = \varepsilon_0\, c\mathcal{E}^+\, \mathcal{E}^-\, \cos(\delta t + \varphi)\,. \tag{30}$$

3.2 LINESHAPE OF THE HETERODYNE BEAT SIGNAL. — As discussed in the beginning of section 2, $\mathcal{E}^r(+)$ and $\mathcal{E}^r(-)$ interfere with E^0 to yield an heterodyne beat signal at frequency δ [Eq. (7)].

$$I_r(\delta) = -\,\frac{\hbar\omega L}{16}\,\frac{\sqrt{\pi}}{ku}\,S\,e^{i(\delta t+\varphi)} + \text{c.c.} \tag{31}$$

the lineshape of which is given by

$$S = n_{ab}\,\alpha^2\,\alpha_0^2 \sum_{j=a,b} \frac{1}{\gamma_j + i\delta}\left[\frac{F(\Delta - \delta/2)}{\gamma_{ab} + i(\Omega - \omega_{ab} + 3\,\delta/4)} + \frac{F(\Delta + \delta/2)}{\gamma_{ab} - i(\Omega - \omega_{ab} - 3\,\delta/4)}\right]. \tag{32}$$

As a function of the incident frequency, the predicted structure is a doublet (splitting $3\,\delta/2$) which may be observed either in absorption (« heterodyne saturated absorption ») or in dispersion (« saturated dispersion »), depending on the phase of the detected signal. This has been observed in I_2 at 514.5 nm [3]. For $\delta \ll ku$, the lineshape is of the form :

$$\sum_{j=a,b} \frac{1}{\gamma_j + i\delta}\left[\frac{1}{\gamma + i(\nu + 3\,\delta/4)} + \frac{1}{\gamma - i(\nu - 3\,\delta/4)}\right] \tag{33}$$

with ν the frequency detuning. When the splitting $3\,\delta/2$ is smaller than the homogeneous linewidth, the doublet is not resolved and the signal has the usual Lorentz absorption shape, $\gamma/(\gamma^2 + \nu^2)$. In addition to lineshape studies, there is another important feature, which is the phase delay between the incident driving modulation [Eq. (30)] and the induced beat signal [Eq. (31)]. As shown by equation (32), the signal phase shift is the sum of two contributions, one coming from the modulation induced in the atomic populations, φ_P, and the other one reflecting the frequency response of the induced optical dipole [« lineshape correction », φ_D]

$$\varphi_S = -\,\text{Arg}\,(S) = \varphi_P + \varphi_D \tag{34}$$

with

$$\varphi_P = -\,\text{Arg}\left(\sum_j \frac{1}{\gamma_j + i\delta}\right). \tag{35}$$

On line-centre ($\Omega = \omega_{ab}$), the lineshape correction factor is given by :

$$\tan\varphi_D = \frac{3\,\delta}{4\,\gamma_{ab}}\,. \tag{36}$$

R. K. Raj [12] has analysed the signal lineshape (33) in detail, for various values of δ/γ_{ab}, and has shown how to extract from it the phase correction, φ_D. Thus the signal phase delay allows one to measure φ_P [Eq. (35)], and to perform population relaxation studies [3-4].

An interesting case occurs when the a level is long-living (ground or metastable state). If δ, $\gamma_a \ll \gamma_b$, the contribution of level b is negligible and equation (35) yields

$$\tan\varphi_P \simeq \delta/\gamma_a\,. \tag{37}$$

The signal phase-shift can thus be assigned to the a level.

3.3 DISCUSSION. — The measurement of the phase delay of the heterodyne beat signal can be used to study the relaxation of the population of the energy levels, *via* equations (35-37). In this sense, it is comparable to the well-known phase-shift method in modulated fluorescence [measurement of the phase-shift between a driving amplitude-modulated light source and the modulation induced in the fluorescence from the excited levels] [13]. However, the technique described here is much more powerful since the optical frequency resolution [cf. Eqs. (29) and (32)] allows one to select a *single transition* and a *single velocity group*. For this reason, it provides a way of studying relaxation-induced velocity changes. After diffusion in the velocity-space, atoms contribute to the beat signal for a different resonance frequency (appearance of a « pedestal ») with a *larger phase delay* (since the atoms get an apparently longer lifetime). This phenomenon can be induced by elastic velocity-changing collisions and has been observed in I_2 [3]. M. Pinard also observed it in metastable neon, by modulating the laser beam polarization in velocity-selective optical pumping [14]. Similar effects — induced by radiative trapping of the resonance line — have been observed in the resonance state of neon, 1 s_2 [15-16].

4. **Heterodyne spectroscopy in resonant three-level systems.** — In this section, we analyse the new features appearing in resonant three-level systems of the type shown in figure 2. In that case, one has to consider the general expressions given in section 2 [Eqs. (10-17)] and to integrate them over the velocity distribution (21). This is carried out in the same way as in section 3. Like for two-level systems, in the Doppler limit, only the process described by (19) yields non-zero contribution [the process (20) is $(\gamma/ku)^2$ smaller]. After velocity integration of $\rho_{ab}^{(3)}$ and $\rho_{cb}^{(3)}$, and using equations (4-7-11), we get $I_r(\delta)$ in the form of equation (31), with now the beat signal lineshape given by [6]

$$S = S(\omega_{ab}) + S(\omega_{cb}) + S\left(\frac{\omega_{ab} + \omega_{cb}}{2}\right) \tag{38}$$

with

$$\frac{S(\omega_{ab})}{n_{ab}} = \frac{F(\Delta - \delta/2)}{\gamma_{ab} + i(\Omega - \omega_{ab} + 3\,\delta/4)}\left[\sum_{j=a,b}\frac{\alpha^2\,\alpha_0^2}{\gamma_j + i\delta} + \frac{\alpha\beta\alpha_0\,\beta_0}{\gamma_{ac} + i(\delta - \omega_{ac})}\right] + \\ + \frac{F(\Delta + \delta/2)}{\gamma_{ab} - i(\Omega - \omega_{ab} - 3\,\delta/4)}\left[\sum_{j=a,b}\frac{\alpha^2\,\alpha_0^2}{\gamma_j + i\delta} + \frac{\alpha\beta\alpha_0\,\beta_0}{\gamma_{ac} + i(\delta + \omega_{ac})}\right] \tag{39}$$

and

$$S\left(\frac{\omega_{ab} + \omega_{cb}}{2}\right) = \frac{n_{ab}\,\alpha^2\,\beta_0^2\,F(\Delta - \delta/2 - \omega_{ac}) + n_{cb}\,\alpha_0^2\,\beta^2\,F(\Delta - \delta/2 + \omega_{ac})}{(\gamma_b + i\delta)\,[\bar{\gamma} + i(\Omega - \bar{\omega} + 3\,\delta/4)]} + \\ + \frac{n_{ab}\,\alpha^2\,\beta_0^2\,F(\Delta + \delta/2 - \omega_{ac}) + n_{cb}\,\alpha_0^2\,\beta^2\,F(\Delta + \delta/2 + \omega_{ac})}{(\gamma_b + i\delta)\,[\bar{\gamma} - i(\Omega - \bar{\omega} - 3\,\delta/4)]} \tag{40}$$

$S(\omega_{cb})$ is obtained from (39) by exchanging a and c, α and β. In these equations, F and Ω are given by (25-26) and

$$\bar{\gamma} = \frac{\gamma_{ab} + \gamma_{bc}}{2}; \quad \bar{\omega} = \frac{\omega_{ab} + \omega_{cb}}{2}. \tag{41}$$

The origin of the three distinct contributions to S is easily understood when $\delta \ll \gamma_i, \gamma_{ij}$. Indeed, for $\delta \to 0$, one tends to a saturated-absorption-type configuration in a three-level system [5]. In that case, $S(\omega_{ab})$ and $S(\omega_{cb})$ describe the ordinary two-level a-b and c-b resonances. On the other hand, $S[(\omega_{ab} + \omega_{cb})/2]$ corresponds to the well-known cross-over resonances [17] in which one wave saturates one transition, and the counter-propagating wave probes the coupled transition. For large δ's, all three resonances split in 3 $\delta/2$ doublets.

4.1 LINESHAPE OF THE CROSS-OVER BEAT SIGNAL. — We consider the case $\delta \ll ku$, only. Then (40) becomes :

$$S(\bar{\omega}) = \frac{n_{ab}\,\alpha^2\,\beta_0^2\,F(\Delta - \omega_{ac}) + n_{cb}\,\alpha_0^2\,\beta^2\,F(\Delta + \omega_{ac})}{\gamma_b + i\delta} \times \\ \times \left[\frac{1}{\bar{\gamma} + i(\Omega - \bar{\omega} + 3\,\delta/4)} + \frac{1}{\bar{\gamma} - i(\Omega - \bar{\omega} - 3\,\delta/4)}\right]. \tag{42}$$

The cross-over exhibits a doublet structure similar to the one predicted for two-level systems [Eq. (33)]. However, the beat signal phase shift is now related to the common level b only

$$\tan \varphi_P = \delta/\gamma_b\,. \tag{43}$$

This comes from the fact that only the population of level b is modulated through the involved nonlinear process. The $(\omega + \Delta \pm \delta/2)$ wave interacts with either transition, a-b for instance, and the counter-propagating wave (ω) thus interacts with the coupled transition b-c to create a macroscopic dipole polarization oscillating at frequency $\omega \pm \delta$ and resonant around $\bar{\omega} - \Delta \mp 3\,\delta/4$.

This noteworthy property of the cross-over phase shift can be used to disentangle intricate spectra. R. K. Raj [12] employs it to assign the numerous cross-over resonances of the $X^1\,\Sigma_g^+(v'' = 0) \to B^3\,\pi_{0_u^+}$, P(13) and R(15) transitions of I_2 ($\lambda = 514.5$ nm), by utilizing the fact that the phase shift of the ground-state cross-overs is larger than the one associated with excited-state cross-overs. Also the pressure-variations of cross-over phase-shifts have allowed R. K. Raj *et al.* [3, 12] and D. Bloch *et al.* [4, 6] to study the effect of quenching collisions in both excited and ground states of I_2, and in the metastable $2s_{1/2}$ state of H and D.

4.2 Raman-induced resonant enhancement of three-level heterodyne beat. — Equation (39) shows that the emission resonant around $\Omega = \omega_{ab}$ presents a doublet structure which is not always symmetrical, contrary to two-level resonances. Additional Raman resonances around $\delta = \pm\,\omega_{ac}$ can make the lineshape asymmetrical. Let us consider two cases, for an a-c splitting resolved ($\omega_{ac} \gg \gamma_{ac}$).

4.2.1 *Off-Raman-resonance.* — If $|\,\omega_{ac} \pm \delta\,| \gg \gamma_{ac}$, the signal lineshape given by (39) is symmetrical (for $\delta \ll ku$) and reduces to the ordinary two-level contributions, (32).

4.2.2 *Resonant Raman modulation.* — If

$$\delta \sim \omega_{ac} \gg \gamma_{ac}\,,\ \gamma_a,\ \gamma_b\,,$$

the predominant contribution in equation (39) is

$$S(\omega_{ab}) \simeq n_{ab}\,\frac{F(\Delta - \delta/2)}{\gamma_{ab} + i(\Omega - \omega_{ab} + 3\,\delta/4)} \times \times\,\frac{\alpha\beta\alpha_0\,\beta_0}{\gamma_{ac} + i(\delta - \omega_{ac})}\,. \tag{44}$$

The doublet is now entirely asymmetrical since the $\Omega = \omega_{ab} - 3\,\delta/4$ resonance stays alone. The origin of this effect lies in the resonant Raman process which singles out the P.C. emission at frequency $\omega + \delta$. This process, in which the atom goes from a to c by absorbing one quantum at frequency $\omega + \Delta + \delta/2$ and emitting one quantum at frequency $\omega + \Delta - \delta/2$ is represented in figure 4, along with the third interaction with a quantum ω which induces an e.m. polarization oscillating at frequency $\omega + \delta$.

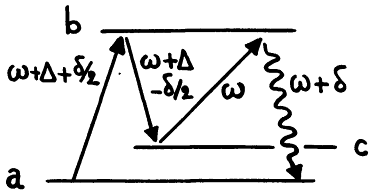

Fig. 4. — Resonant Raman enhancement of phase-conjugate emission in three-level four-wave mixing.

The resonance conditions in the atomic rest frame are :

(i) One-photon absorption,

$$\omega + \Delta + \delta/2 - kv = \omega_{ab}\,. \tag{45a}$$

(ii) Two-photon Raman process,

$$(\omega + \Delta + \delta/2 - kv) - (\omega + \Delta - \delta/2 - kv) = \omega_{ac}\,. \tag{45b}$$

(iii) Three-photon transition,

$$(\omega + \Delta + \delta/2 - kv) - (\omega + \Delta - \delta/2 - kv) + + (\omega + kv) = \omega_{ab}\,. \tag{45c}$$

Conditions (45*a-c*) are similar to the ones for two-level systems, (28), and yield both the resonance frequency, $\omega = \omega_{ab} - \Delta/2 - 3\,\delta/4$, and the correspondingly selected velocity group, $kv = \Delta/2 - \delta/4$. On the other hand, condition (45*b*), $\delta = \omega_{ac}$, is particular to the three-level system and describes a *velocity-independent* forward Raman scattering process (due to co-propagating waves). Thus the beat enhancement described by (44) appears as an interference between two Doppler-free processes, the first one coming from velocity-independent Raman scattering, and the second one coming from velocity-selection by counter-propagating waves in a saturated-absorption-type configuration.

This signal enhancement, which is a remarkable feature of high-frequency heterodyne spectroscopy, should allow one to single out a particular resonance in complex spectra, and therefore to clarify their assignment. One should get information on both optical spectrum and radio-frequency spectrum, by studying the heterodyne beat amplitude *versus* RF modulation frequency. Both amplitude and phase information are useful, and the possibility of observing a single dispersion lineshape (by an appropriate choice of the phase) is of fundamental interest for metrological purpose.

5. Heterodyne two-photon absorption.

— In this last section, we study the beat signal lineshape when the frequency of the incident e.m. fields is resonant for a two-photon transition. For this, we consider the cascade three-level system of figure 5, and suppose that the incident laser frequencies are nearly resonant for the two-photon transition a-c ($2\,\omega \simeq \omega_{ac}$) but far off-resonance from single-photon transition :

$$|\,\omega_{ab} - \omega\,| \simeq \left|\,\omega_{ab} - \frac{\omega_{ac}}{2}\,\right| = \delta\omega \gg ku,\ \Delta,\ \delta,\ \gamma_{ij}\,. \tag{46}$$

The equations of motion for the density matrix have been given in reference [1] [Eq. (I, 75), or equivalently Eqs. (8) with ω_{cb} replaced by $-\,\omega_{bc}$]. One

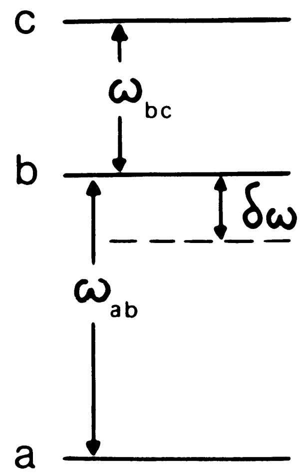

Fig. 5. — Cascade three-level system.

assumes that only the ground state is populated ($n_a = N$, $n_b = n_c = 0$). Because of (46), the second-order population changes are negligible compared with the two-photon coherence, $\rho_{ac}^{(2)}$, driven at the sum frequency, $\omega_\mu + \omega_\nu$, close to ω_{ac} [cf. Eq. (I, 76)]. And the third-order optical polarization reduces to [instead of Eq. (12)] :

$$\rho_{ab}^{(3)} \simeq - i \frac{N}{8(\delta\omega)^2} \sum_{\mu,\nu,\lambda} \alpha_\mu \beta_\nu \beta_\lambda \frac{e^{i[\Phi_\mu + \Phi_\nu - \Phi_\lambda]}}{L_{ac}(\omega_\mu + \omega_\nu)} . \quad (47)$$

[The notations are defined in (14-17).] The frequency and wavevector of the re-emitted field are now given by

$$\begin{aligned} \omega_r &= \omega_\mu + \omega_\nu - \omega_\lambda \\ k_r &= k_\mu + k_\nu - k_\lambda . \end{aligned} \quad (48)$$

For instance, the field emitted at frequency $\omega + \delta$ in direction $-k$ is related to the following conditions :

$$\omega_\mu = \omega + \Delta + \delta/2 , \quad \omega_\nu = \omega , \quad \omega_\lambda = \omega + \Delta - \delta/2 ,$$

or

$$\omega_\mu = \omega , \quad \omega_\nu = \omega + \Delta + \delta/2 , \quad \omega_\lambda = \omega + \Delta - \delta/2 ,$$

in which case, if one neglects the Doppler effect at frequency $\Delta + \delta/2$, one gets

$$L_{ac}(\omega_\mu + \omega_\nu) = \gamma_{ac} + i(2\,\omega + \Delta + \delta/2 - \omega_{ac}) . \quad (49)$$

The e.m. field emitted at frequency $\omega + \delta$ is driven through a velocity-independent, stationary, two-photon coherence, and its amplitude is given by [cf. Eqs. (4-11)]

$$\mathcal{E}^r(+) = - \frac{kL}{2\,\varepsilon_0} \frac{N}{(\delta\omega)^2} \frac{\mu_{ba}\, \alpha\beta\beta_0}{\gamma_{ac} + i(2\,\omega + \Delta + \delta/2 - \omega_{ac})} . \quad (50)$$

The nonlinear process triggering this emission is schematized in figure 6. The resonance is now simply

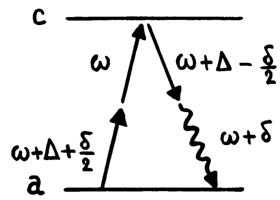

Fig. 6. — Process inducing phase-conjugate emission at frequency $\omega + \delta$ in two-photon resonant four-wave mixing.

related to Doppler-free two-photon absorption in a standing-wave [18, 19],

$$(\omega + \Delta + \delta/2 - kv) + (\omega + kv) = \omega_{ac}$$

i.e.

$$\omega = \frac{\omega_{ac}}{2} - \frac{\Delta}{2} - \frac{\delta}{4} . \quad (51)$$

All atoms contribute, independently of their velocity. $\mathcal{E}^r(+)$ and $\mathcal{E}^r(-)$ interfere with E^0 serving as a local oscillator to yield an heterodyne beat signal at frequency δ [Eq. (7)]

$$I_r(\delta) = - \frac{\hbar\omega L}{4} N \frac{\alpha\alpha_0\, \beta\beta_0}{(\delta\omega)^2} T\, e^{i(\delta t + \varphi)} + \text{c.c.} \quad (52)$$

the lineshape of which is given by :

$$T = \frac{1}{\gamma_{ac} + i(2\,\Omega + \delta/2 - \omega_{ac})} + \frac{1}{\gamma_{ac} - i(2\,\Omega - \delta/2 - \omega_{ac})} \quad (53)$$

[with φ and Ω defined by (5) and (25)].

The two-photon heterodyne beat signal exhibits the following properties :

(i) The signal shows a resonant doublet structure with a frequency splitting, $\delta/2$. When this doublet is resolved, one gets either two-photon absorption or two-photon dispersion, depending on the detection phase.

(ii) The signal amplitude no longer depends on δ. This allows one to utilize large detection frequencies without signal reduction [20].

(iii) Due to the large frequency detuning, $\delta\omega$, the overall phase shift of the beat signal does not depend on the population relaxation rates, and vanishes independently of δ.

Table I. — *Properties of Doppler-free heterodyne spectroscopy* [*δ is the detection frequency*].

	Two-photon resonance	One-photon resonance
Lineshape	$\delta/2$ doublet	3 $\delta/2$ doublet
Amplitude	δ-independent	δ-dependent
Phase shift	zero	relaxation-dependent
Velocity	velocity-independent	velocity-selective

The comparative features of two-photon and single-photon heterodyne spectroscopy are summarized in table I. Two-photon heterodyne spectroscopy has been observed in excited neon [15, 16] and in rubidium [16, 21], in which all the above properties have been demonstrated.

6. **Conclusion.** — In this article, we have analysed a spectroscopic technique in which phase-conjugate fields re-emitted *via* collinear nearly-degenerate four-wave mixing are detected through their heterodyne beating with one of the incident e.m. fields. In gas media, it provides a sensitive Doppler-free spectroscopic technique allowing one to explore either one-photon or two-photon transitions in an unified way, and to analyse the various contributions to the nonlinear susceptibility of the irradiated medium, $\chi^{(3)}$. From a phase-sensitive detection of the heterodyne beat signal, one can separately analyse real (dispersion) and imaginary part (absorption) of the nonlinear susceptibility. In the case of single-photon transitions, phase analyses provide both atomic levels relaxation measurements and spectrum assignments. Also noteworthy is the predicted resonant Raman enhancement of heterodyne saturated absorption in three-level systems. This technique should lead to sensitive Raman scattering studies. In the case of two-photon resonances, this method is of particular interest for studying transitions between ground state and long-living non-radiative levels (like metastable states).

The present theoretical analysis has been limited to the third-order nonlinear response of the irradiated medium. A natural extension would be to consider the effect of higher order interaction processes, like power-induced line broadening and phase shift. Also we did not consider the effect of level degeneracy and polarization of the incident fields. The latter subject will be dealt with in a forthcoming paper.

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[9] Worth noticing are the similarities between non-collinear DFWM and collinear NDFWM. In DFWM, the joint effect of either pump wave and object wave is to create a *spatial modulation* of population (« population grating », e.g. [10, 11]), which scatters the return pump wave counter-directionally to the object wave. In collinear NDFWM, the e.m. field incident along direction **k** induces a *time-modulation* of population, which in turn modulates the transmission of the counter-propagating wave, thus creating two side-bands at $\omega \pm \delta$.

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