Nonlinear spectroscopy based on the effect of resonant optical detection

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We investigate the principles of a new type of nonlinear spectroscopy, based on the effect of resonant optical detection. It is shown that the use of one frequency-tunable light source permits measurement of the magnitude and dispersion of the nonlinear susceptibility. We discuss also a new possibility of nonlinear ultrahigh-resolution spectroscopy.

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1. The characteristics of the transitions that are allowed in Raman scattering (RS transitions) have been intensively studied of late.[1] The interest in electronic RS transition is due, in particular, to the first success in the construction, on their basis, of a source that can be tuned in a wide frequency range.[2]

The purpose of this paper is a discussion of new RS-transition spectroscopy based on recording the "zero"-frequency signal produced as a result of the effect of resonant optical detection (ROD). This effect, which is of independent physical interest, has never been discussed before. The advantages of such a spectroscopy are: a) the possibility of separately measuring the magnitude and dispersion of the imaginary and real parts of the nonlinear susceptibility of RS transitions, something that cannot be done in the known forms of nonlinear spectroscopy, including active spectroscopy (AS); b) a single method is used to record the spectral data from the IR to the UV region of the spectrum; the transition line shapes are not subject to distortion caused by accumulating parametric interaction of the waves.[1]

The ROD signal can be produced by several methods, among which greatest practical interest attaches to the following: A central-symmetry medium is: a) illuminated by a coherent source and its second harmonic, the frequency of the latter being at resonance with the RS transition frequency; b) placed in a constant electric field and exposed to the resonant radiation (the inverse Kerr effect). Registration of the ROD signal as the investigated transition is frequency-scanned yields information on the cubic susceptibility $\chi^{(3)}$; c) in the absence of an inversion center (crystals), the resonant radiation produces an ROD signal without application of a constant field, on account of the quadratic susceptibility $\chi^{(2)}$.

The general expression for the constant polarization of the medium, if the frequency condition $\omega_1+\omega_2=\omega_3=\omega_{21}+\Delta$, $\Delta\ll\omega_j$, is satisfied (ω_{21} is the frequency of the investigated transition, ω_j are the field frequencies, and Δ is the frequency detuning), is

$$P_b(0)=\chi^{(3)}_{abcd}E^*_{\bar{a}}(\omega_3)E_{\bar{c}}(\omega_1)E_{\bar{d}}(\omega_2)+\chi^{(3)}_{abcd}E^*_{\bar{a}}(\omega_3)E_{\bar{c}}(\omega_3)E_{\bar{d}}(0)$$

$$+\chi^{(2)}_{abc}E^*_{\bar{a}}(\omega_3)E_{\bar{c}}(\omega_3)+\text{c. c.}=2\eta N\hbar^{-1}(iT^{-1}-\Delta)^{-1}\kappa^*_{ab}(\omega_3)E^*_{\bar{a}}(\omega_3)$$

$$\times[\kappa_{cd}(\omega_1)E_{\bar{c}}(\omega_1)E_{\bar{d}}(\omega_2)+2\kappa_{cd}(\omega_3)E_{\bar{c}}(\omega_3)E_{\bar{d}}(0)$$

$$+(d_c)_{12}E_{\bar{c}}(\omega_3)]+\text{c. c.} \qquad (1)$$

where $\kappa_{cd}(\omega_j)$ is the scattering tensor,[3] $E(\omega_j)$ are the field amplitudes, T^{-1} is the width of the transition line, N is the particle-number density, η is the population difference between levels 1 and 2, d_{12} is the dipole moment of the transition, and $\chi^{(3)}_{abcd}$ and $\chi^{(2)}_{abc}$ are the nonlinear susceptibilities. Each of the three terms in (1) corresponds to the modifications of the ROD effect mentioned above.

3. The first term in (1) describes the onset of constant polarization when the medium is exposed to fields of frequencies ω_1, ω_2, and ω_3. In freely-oriented media, it takes the form

A_3	A_1	A_2	P(0)	$\mathcal{K}$
x	x	x	x	$G^0 + \frac{2}{15}G^s$
x	x	y	y	$\frac{1}{10}G^s + \frac{1}{6}G^a$
y	x	x	y	$-\frac{1}{15}G^s + G^0$

Polarization measurements of the irreducible components of the tensor $\chi^{(3)}$. $\mathcal{K}$ is the coefficient of A_3, A_1, or A_2 in the curly brackets of (2).

$$P(0) = -4\pi^{-1}N\eta\left[\frac{\Delta}{T^{-2}+\Delta^2}\cos(\delta z + \Delta\phi_0) + \frac{T^{-1}}{T^{-2}+\Delta^2}\sin(\delta z + \Delta\phi_0)\right] \times\left\{G^0(\omega_3, \omega_1)A_3(A_1A_2) + G^s(\omega_3, \omega_1)\left[-\frac{1}{15}A_3(A_1A_2) + \frac{1}{10}A_2(A_3A_1) + \frac{1}{10}A_1(A_3A_2)\right] + G^a(\omega_3, \omega_1)\left[\frac{1}{6}A_1(A_3A_2) - \frac{1}{6}A_2(A_3A_1)\right]\right\}, \quad (2)$$

where $A_j = E(\omega_j)\exp[-i(\phi_j + k_j z)]$, $\delta = k_1 + k_2 - k_3$ is the difference of the wave vectors, $\Delta\phi_0 = \phi_{10} + \phi_{20}$ is the difference of the boundary phases of the fields propagating along z, and $G^{0,s,a}$ are the scalar, symmetric, and asymmetric invariants of the tensor $\kappa^*_{ab}\kappa_{cd} \sim \chi_{abcd}$.[3]

In the absence of a constant field, no spatial (accumulating) parametric interaction of the fields takes place[4] and the fields are altered only as a result of absorption. The zero-frequency response of the medium at each point is connected with the local parametric interaction of the field and is determined by the ratio of their "linear" phases. Near $\delta z + \Delta\phi_0 \approx 0, \pi, \ldots$, the main contribution to the ROD signal is made by the real part of the susceptibility $\chi^{(3)}$, and at $\delta z + \Delta\phi_0 = \pi/2, 3\pi/2, \ldots$ by its imaginary part. The complete set of the components of the tensor $\chi^{(3)}$ (scalar, symmetric, and asymmetric parts) can be obtained, just as in the AS, by changing the linear polarizations of the fields (see the table).

We note one more possibility of nonlinear spectroscopy on the basis of the ROD, which is of interest primarily as a method of nonlinear spectroscopy of ultrahigh resolution. If the radiation $E(\omega_1)$ is produced in an additional cell in the opposing-wave regime, then its line shape reveals a dip of width equal to the natural width.[5] By directing the radiation $E(\omega_1)$ together with the second harmonic into a cell containing the same working medium and recording the ROD signal, we can obtain the $\chi^{(3)}$ dispersion curves without Doppler broadening.

4. The second term in (1) corresponds to the inverse Kerr effect at resonance

$$P_b(0) = -4\pi^{-1}N\eta\kappa^*_{ab}(\omega_3)\kappa_{cd}(\omega_3)\frac{\Delta}{T^{-2}+\Delta^2}E^*_a(\omega_3)E_c(0)E_d(\omega_3). \quad (3)$$

The line shape (3) coincides with the dispersion curve of the real part of the tensor χ_{abcd}. In freely-orienting media, expression (3) can be simplified just as in Sec. 3. By varying the polarization of the field $E(\omega_3)$ it is then possible to obtain a complete set of linearly-independent components of the tensor χ_{abcd}. The ratio of the dielectric-constant increment $\Delta\epsilon$ to the value of ϵ itself is

$$\Delta\epsilon/\epsilon = \frac{4\pi\chi^{(3)}}{1 + 4\pi\chi^{(1)}}|E(\omega_3)|^2, \quad (4)$$

where $\chi^{(1)}$ and $\chi^{(3)}$ are the contractions of the linear and cubic susceptibilities.

5. The third term in (13) corresponds to the known effect of nonresonant optical detection in crystals without an inversion center,[6] but at resonance with the dipole transition. For fields $E(\omega_3)$ weaker than saturating, the polarization constant coincides with (3), provided we make in the latter the substitution $\kappa_{cd}(\omega_3)E_{\bar{c}}(0) \to (d_c)_{12}$. With the aid of the ROD we can, for example, obtain information on the real part of the tensor $\chi^{(2)}$ that is responsible for the onset of the polariton wave in RS; this wave is connected in a known manner[7] with the tensor $\chi^{(3)}$ of the polariton RS. The missing information on the dipole moment $(d_c)_{12}$ can be obtained, from experiments on absorption.

6. Let us estimate the voltage u produced across the electrodes of a capacitor in which the investigated substance is placed—in methods a) and c) we have $u = 4\pi P(0)SC^{-1}$, where S and C are the area of the plates and the capacitance of the capacitor. We put $\kappa(\omega_1) \approx 10^{-22}$ to 10^{-24} cm^3, $\eta N \approx 10^{17}$ to 10^{19} cm^{-3}, $T = 10^{-9}$ to 10^{-10} sec ($\chi^{(3)} \approx 10^{-9}$ to 10^{-14} cgs esu) for gases and vapors, $\eta N \approx 10^{20}$ to 10^{21} cm^{-3}, and $T \approx 10^{-11}$ to 10^{-12} sec for liquids ($\chi^{(3)} = 10^{-8}$ to 10^{-13} cgs esu). At a laser power density $\sim 10^7$ W/cm^2 and at its second-harmonic value $\approx 10^6$ W/cm^2 we obtain $u = 10^{-3}$ to 10^{-7} V by method (a) and $u \approx 10^{-3}$ to 1 V by method (c) (at $d_{21} \approx 10^{-20}$ cgs esu and $\Delta \approx T^{-1}$) if $C = 100$ pF, and $S = 1$ cm^2. In method (b), for the same parameters of the gases, vapors, and liquids, $\Delta\epsilon/\epsilon$ amounts to 10^{-5}–10^{-10} (for $\Delta \approx T^{-1}$). Thus, the estimates demonstrate the possibility of registering the ROD effect and of producing on its basis a spectroscopy for RS transitions, including electronic transitions.

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