# Active spectroscopy of hyper-Raman scattering of light

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A method is proposed of increasing the intensity of hyper-Raman scattering (HRS) of light, based on phasing the vibrations (or rotations) of the molecules of the scattering medium by external radiation. This method makes it possible, under no-threshold conditions, to measure the HRS tensor with an effectiveness higher by several orders than in ordinary spontaneous scattering. It is also shown that the use, within the framework of this method, of linearly and circularly polarized input fields makes it possible to determine the dispersion of the HRS tensor. The proposed method can be called the method of active HRS spectroscopy, in analogy with the case of active spectroscopy of ordinary Raman scattering.

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The nonlinear light-scattering tensor $\chi_{ijk}$ is usually measured in the process of hyper-Raman scattering (HRS) by the investigated molecules[1,2]. We recall that HRS differs from ordinary Raman scattering (RS) in that two pump quanta and not one participate in the scattering, and the corresponding term in the expansion of the induced dipole moment d in powers of the pump fields $E^{l1,l2}$ takes the form

$$d_i=\chi_{ijk}E_j^{l1}E_k^{l2}. \qquad (1)$$

The use of HRS for the measurement of $\chi$, however, has certain shortcomings. In the case of spontaneous HRS the scattering efficiency is low (estimates by Akhmanov and Klushko[3] give for the scattered power a value $\sim 10^{-5}$ W at a pump intensity 1 GW/cm$^2$). In the case of stimulated HRS, on the other hand, the presence of a scattering threshold makes it possible to investigate only the strongest lines of the nonlinear-scattering spectrum. In addition, the threshold itself is sufficiently high here (stimulated HRS can be relatively easily observed only under resonance conditions[4], but it is possible in this case to obtain information on the tensor $\chi$).

In the spectroscopy of ordinary RS, these shortcomings do not occur when the method of active spectroscopy of Raman scattering (ASRS) is used[5]. In this method one investigates a four-photon parametric (and consequently without a threshold) process of frequency conversion in two-photon resonance with the investigated Raman-active transition. In the present paper we propose a new modification of active spectroscopy, namely active spectroscopy of hyper-Raman scattering (ASHRS), with the aid of which it is possible, under low-threshold conditions, to measure the tensor $\chi$ with an efficiency much higher than in spontaneous HRS. The gist of the ASHRS is to apply to the gas of the investigated molecules, together with the pump radiation, also radiation with frequency $\omega_r$ approximately equal to the frequency of the scattering transition $\omega_{21}$. The nonlinear polarization at the Stokes frequency $\omega_s$ is then[6]

$$P_\alpha=\frac{1}{2}NE_\beta^{l1}E_\gamma^{l2}\sum_{m_1m_2}\langle 2|\overset{*}{\chi_{\alpha\beta\gamma}}|1\rangle\rho_{21}^*,$$

where the summation is over the magnetic sublevels of the working levels 1 and 2; N is the molecule density; $\rho_{21}$ is the off-diagonal matrix element of the density matrix induced by the additional illumination field $\mathbf{E}^r$

$$\rho_{21}=-\frac{(n_1-n_2)\langle 2|d_\delta^*|1\rangle}{2\hbar(\omega_r-\omega_{21}+i/\tau)}E_\delta^r;$$

$n_{1,2}$ are the population of the m-states of the levels 1 and 2; $\tau$ is the relaxation time; $\alpha$, $\beta$, $\gamma$, $\delta$ are the indices of the circular polarizations ($\alpha, \beta, \gamma, \delta = 0, \pm 1$).

We use the relation

$$\sum_{m_1m_2}\langle 2|\chi_{\alpha\beta\gamma}|1\rangle\langle 1|d_\delta|2\rangle=\chi^{(1)}d^{(1)}/\sqrt{3},$$

$$\chi^{(1)}=\sum_j(-1)^j(2j+1)^{1/2}\begin{pmatrix}1 & 1 & j\\ -\beta & -\gamma & \beta+\gamma\end{pmatrix}\begin{pmatrix}j & 1 & 1\\ -\beta-\gamma & \alpha & \delta\end{pmatrix}\chi_j^{(1)}, \qquad (2)$$

where $d^{(1)}$ and $\chi_j^{(1)}$ are the reduced matrix elements of the dipole moment and of the vector points of the tensor $\chi$, and we solve the abbreviated equation for the field at the frequency $\omega_s$. We then obtain for the maximum value of intensity $I_s$ of the scattered radiation (the synchronism condition is assumed satisfied)

$$I_{s\,max}=12\left(\frac{\pi}{c}\right)^2\left(\frac{\omega_s}{\omega_r}\right)^2\left|\frac{\chi^{(1)}}{d^{(1)}}\right|^2 I_{l1}I_{l2}I_r, \qquad (3)$$

where $I_{l1,\,l2,\,r}$ are the intensities of the corresponding input waves (the value of $I_{s\,max}$ is attained over the absorption length of the field $\mathbf{E}^r$).

It is seen from (2) and (3) that contributions to $I_s$ are made only by those parts of the tensor $\chi$ which are transformed in accordance with the vector representation of the rotation group (the reason is that the dipole interaction with the field $\mathbf{E}^r$, which induces the HRS, is of the vector type)1). As follows from (2), the tensor $\chi$ contains in a general case three different vector parts $\chi_j^{(1)}$ (j = 0, 1, 2). In the degenerate case $(\omega_{l1}=\omega_{l2})\,\chi_1^{(1)}=0$ and $\chi^{(1)}=\chi_2^{(1)}/\sqrt{5}$ if $\beta=\gamma=\delta=1$, and $\chi^{(1)}={}^1\!/_3\chi_0^{(1)}+(2\sqrt{5}/15)\chi_2^{(1)}$, if $\beta=\gamma=\delta=0$. Thus, by measuring $I_{s\,max}$ we can find the value of $|\chi^{(1)}|^2$, and by using circularly and linearly polarized input fields we can separately measure $\chi_2^{(1)}$ and $\chi_0^{(1)}$. We note that if the dispersion of the tensor $\chi$ can be neglected, then a simple connection exists between $\chi_0^{(1)}$ and $\chi_2^{(1)}$, namely $\chi_0^{(1)}=(\sqrt{5/2})\chi_2^{(1)}$. The dispersion of the tensor $\chi$ can be assessed from the degree to which this equation is not satisfied.

Expression (3) describes in essence, just as in ASRS, resonant four-photon parametric process (in contrast to ASRS we use here, however, a single-photon resonance). Consequently, the ASHRS method can be used to measure the nonlinear scattering tensor with the same efficiency as in the measurement of the RS tensor by the ASRS method, since the process is the result of cubic nonlinearity in both cases.

Finally, we note the gain in the scattering power $\eta$, obtained in ASHRS in comparison with the case of HRS. In the latter, the power scattered by unit volume into a solid angle $\Omega$ can be easily estimated from the expression (1)[3]

$$M_{sp}=2^4\pi\Omega\omega_s^4N\chi^2I_{l1}I_{l2}/3c^5.$$

Here $\eta \sim I_{s\,max}\Delta/M_{sp}$, where $\Delta$ is the area of the cross-sections of the pump and illumination beams. At $N \sim 10^{19}$ cm$^{-3}$, $d^{(1)} \sim 10^{-19}$ cgs esu, $\omega_s \sim 2\times10^4$ cm$^{-1}$, $\omega_r \sim 10^3$ cm$^{-1}$, $\Omega \sim 0.1$ sr, $\Delta \sim 0.1$ cm$^2$ and $I_r \sim 25$ kW/cm$^2$, we obtain $\eta \sim 10^3$.

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[1)] In ordinary HRS, a contribution to the scattering can be made also by the octupole part of the tensor $\chi$. [6] It can be investigated if the interaction inducing the HRS also contains this part. This can be done, for example, by placing the investigated molecules also in a constant electric field.

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