Hyper-Raman scattering of light by hot phonon polaritons

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The first experimental observation of hyper-Raman scattering of light by hot polaritons excited by a tunable CO_2 laser is reported. The approach taken in these experiments has made it possible to raise the scattering intensity several orders of magnitude and to study the polariton lineshapes.

The hyper-Raman scattering of light is a nonlinear-optics process in which a photon of scattered light, $\hbar\omega_s$, is created from two (usually identical) photons of the exciting light, $\hbar\omega_l$: $\omega_s = 2\omega_l \pm \omega_p$, where ω_p is the frequency of the excitation of the medium which causes the scattering. The use of this process makes it possible to

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obtain information inaccessible to conventional spectroscopic methods; in particular, it becomes possible to study phonon polaritons in noncentrally symmetric media.[1-3] On the other hand, difficulties arise in attempts to experimentally measure the spectra of hyper-Raman scattering, because of the exceedingly low efficiency of this type of scattering. These difficulties have significantly delayed the development of experimental work, and they have essentially ruled out the acquisition of quantitative data on the shapes and widths of the lines in the polariton spectra.

It is therefore interesting to study hyper-Raman scattering by polaritons during the coherent excitation of the polaritons by the beam from an external IR laser (hot-polariton hyper-Raman scattering). In the present paper we report the first implementation of this experimental idea. The estimates in Ref. 4 show that the gain in the intensity of the hyper-Raman scattering by hot polaritons over the intensity of hyper-Raman scattering by noise polaritons can reach 10^4–10^5 under realistic conditions. Furthermore, in measurements of the linewidths the significant dispersion of the polaritons, $\omega_p = \omega_p(\mathbf{k})$ demands not only a high spectral resolution of the measurement apparatus but also a high resolution in wave-vector space (in **k** space). In other words, it is necessary to detect the light scattered by polaritons in a very small solid angle. Hot-polariton hyper-Raman scattering is extremely attractive from this point of view, since both the spectral resolution and the angular resolution are determined by the parameters of the laser sources.

Hot-polariton hyper-Raman scattering may be thought of as a nonlinear-optics four-wave mixing $\omega_s = \omega_l + \omega_l - \omega_p$. We assume that the medium is transparent at the frequencies ω_l and ω_s and that the strong absorption of the IR wave at frequencies ω_p in the region of lattice resonances can be taken into account by introducing a complex polariton wave vector $\mathbf{k}_p = \mathbf{k}'_p + i\mathbf{k}'_p$, where $\mathbf{k}''_p$ determines the spatial damping of the polariton wave. Using the standard method of nonlinear optics under these assumptions, we find the following expression for the scattering intensity:

$$I_s \sim |e_s \chi^{(3)}(\omega_s = 2\omega_l - \omega_p) e_l e_l e_p|^2 I_l^2 I_p (\Delta k^2 + k''^2)^{-1} .$$

Here the tensor $\chi^{(3)}$ represents the cubic nonlinear susceptibility of the crystal; $\Delta\mathbf{k} \equiv \mathbf{k} - \mathbf{k}'_p = (2\mathbf{k}_l - \mathbf{k}_s) - \mathbf{k}'_p$; e_i are the polarization unit vectors; $\mathbf{k}_i$ are the wave vectors of the corresponding fields; and the subscripts l, s, and p specify the test wave, the scattered wave, and the polariton wave, respectively.

It can be seen from this expression that the shape of the line of hot-polariton hyper-Raman scattering in **k** space is Lorentzian with a width at half-maximum equal to the polariton absorption coefficient $\alpha_p = 2\mathbf{k}''_p$ and with a peak at $\Delta\mathbf{k} = 0$. By varying $\Delta\mathbf{k}$ (the scattered geometry), one can obtain, at various fixed values of ω_p, spectra in **k** space. These spectra allow direct measurements of the real and imaginary parts of the polariton wave vector. It thus becomes possible to completely reconstruct the dispersion of the complex dielectric constant $\epsilon(\omega,\mathbf{k})$.

In the experiments the test wave was the beam from a neodymium-doped yttrium aluminum garnet laser (wavelength $\lambda_l = 1.06$ μm) in Q-switched operation with a repetition frequency of 10 Hz. The polaritons are excited by a pulsed TEA CO_2 laser with a discrete tuning among vibrational-rotational transitions over the frequency

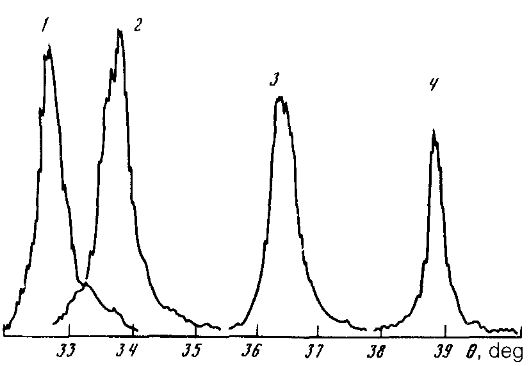

FIG. 1. Lines of hyper-Raman scattering obtained during excitation of polaritons by the beam from a CO_2 laser with output at the following frequencies: 1—940.5 cm^{-1} (P_{24}); 2—978.5 cm^{-1} (R_{24}); 3—1039.4 cm^{-1} (P_{28}); 4—1081.1 cm^{-1} (R_{24}). Here θ is the interior angle between the optic axis of the crystal and the propagation direction of the interacting waves.

interval 940–1080 cm^{-1}. The laser pulses are synchronized in time, and they are incident in a collinear fashion on the test crystal. The scattered light, propagating in the same direction, is measured with a strobable FÉU-79 photomultiplier working under corresponding conditions.

The object of the study was the centrally symmetric, uniaxial calcite, $CaCO_3$ crystal. The polariton spectra in **k** space were obtained by rotating the crystal, i.e., by varying the angle (θ) between the optic axis and the tetrad of wave vectors of the interaction waves, by virtue of the angular dependence of the refractive index for the extraordinary wave. In the experiments we achieved the interaction $\Delta\mathbf{k} = \mathbf{k}_l^o + \mathbf{k}_l^e(\theta) - \mathbf{k}_s^e(\theta) + \mathbf{k}_p^0$, where the superscript o means the ordinary wave, and e is the extraordinary wave.

Figure 1 shows spectra of the hyper-Raman scattering by hot polaritons recorded by the method described above at various fixed frequencies of the "illumination" of the polaritons. The wave vectors and the absorption of the polaritons participating in the scattering are found by approximating the **k** spectra obtained by a Lorentzian line, in accordance with the expression above. The results (Fig. 2) show that the data on the polariton dispersion, $\omega_p(\mathbf{k})$, agree well with the results calculated from IR data.[5] The data on $\alpha_p(\omega,\mathbf{k})$, however, differ significantly from the results calculated in the model

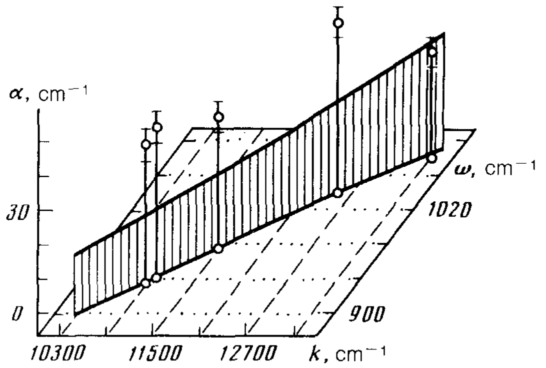

FIG. 2. Polariton dispersion $\omega_p(\mathbf{k})$ and dispersion of the absorption coefficient, $\alpha_p(\omega,\mathbf{k})$. Points—experimental results; solid lines—calculated from IR data.

of quasiharmonic oscillators with frequency-independent damping constants. This difference can be attributed to the approximate nature of the model, which ignores the frequency dependence of the density function of the two-phonon states, which actually is manifested in the IR transmission spectra of the calcite crystal.[5]

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