

Hyper-Raman scattering of polaritons in liquid carbon tetrachloride

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This letter reports the first observation of light scattering by vibrational polaritons in a liquid. At small scattering angles ($0-3^\circ$), the polariton frequency in the hyper-Raman spectra of carbon tetrachloride shifts from 130 to 750 cm^{-1} on the lower branch and upward from 866 cm^{-1} on the upper branch.

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In principle, hyper-Raman scattering by vibrational polaritons is allowed in media either having or lacking a center of inversion. This scattering has been observed in crystals and glasses previously^{1,2}; in the present experiments we studied it in a liquid.

Observation of this effect in glasses showed that the absence of long-range order (the absence of translational invariance) does not rule out the existence of vibrational polaritons or their dispersive behavior in liquid. In a liquid there is a factor other than the absence of long-range order which must be taken into account: the thermal motion of the particles (molecules). The thermal motion involves translational motion and reorientations, i.e., types of motion for which the relaxation times are short, $\tau \sim 10^{-11}-10^{-12}$ s (in glasses, τ is $\sim 10^{13}-10^{14}$ times longer than in a liquid). The thermal motion of the particles of a liquid causes a rapid damping of transverse acoustic waves.^{3,4} In the case of optical vibrations in a liquid, for which the vibration period (10^{-14} s) is considerably shorter than τ , the effect of the thermal motion on the vibrational spectra is less important than for acoustic vibrations, although still significant.⁵

A necessary condition for experimental observation of the polariton effect (a dependence of the polariton frequency on the scattering angle θ) is the presence in the medium (in a liquid, in the present experiments) of both transverse and longitudinal dipole vibrations and the existence of a significant longitudinal-transverse splitting Δ_{LT} of these vibrations. The value of Δ_{LT} is determined by the oscillator strength for the dipole vibration. We have found no published report of the observation of a splitting Δ_{LT} in liquids, although it has been predicted.⁶

The thermal motion of the molecules in a liquid can give rise to a broadening of the polariton lines in both ω space ($\Delta\omega \sim 1/\tau$) and k space (Δk). The broadening Δk actually reflects the extent to which the polariton wave vector is not conserved in the hyper-Raman scattering, and it may be written as

$$\Delta k \sim \left(\tau \frac{d\omega}{dk} \right)^{-1},$$

where $d\omega/dk$ is the polariton group velocity. As long as the polariton frequency differs significantly from that (ω_T) of the transverse vibration, the group velocity $d\omega/dk$ will be approximately equal to the speed of light, and Δk may be very small. Near ω_T the polar-

iton group velocity falls off markedly, and for this reason we are interested in the shape of the polariton spectra in the ω_T -vibration region.

In the present experiments we studied the hyper-Raman scattering by polaritons in carbon tetrachloride (CCl_4) at small scattering angles, $\theta = 0\text{--}3^\circ$. To observe the scattering at small values of θ , we used the same arrangement with annular diaphragms as in Refs. 1 and 2. The angular interval ($\Delta\theta$), in which the scattered light transmitted through the annular diaphragms was collected, was $\sim 0.4^\circ$; the divergence angle of the exciting beam had the same value.

The hyper-Raman spectrum of CCl_4 at $\theta = 90^\circ$ consists of two lines, at ~ 310 and 780 cm^{-1} , of which the higher-frequency line is the more intense.⁷ Both lines correspond to dipole vibrations of the CCl_4 tetrahedron. The hyper-Raman spectrum obtained in a forward observation ($\theta = 0^\circ$, $\Delta\theta = 5^\circ$) (Fig. 1a) has a completely different structure: a continuous background which stretches down to low frequencies with an intensity that increases with the frequency. Only at $800\text{--}850\text{ cm}^{-1}$ do we see a dip in the background intensity. These structural differences in the hyper-Raman spectra at different values of the scattering angle θ indicate that the intensities of the CCl_4 lines depend on the wave vector of the vibrational states.

As the angular resolution is increased ($\Delta\theta \approx 0.4^\circ$), two bands appear in place of the continuous background (Fig. 1a); the positions at which these bands peak depend on θ (Figs. 1b-1d). With increasing θ the low-frequency band shifts from 130 to 750 cm^{-1} . The high-frequency band, at 870 cm^{-1} at $\theta = 0^\circ$, shifts rapidly in the high-frequency direction with increasing θ . These results are evidence that the high-frequency band corresponds to polaritons of the upper branch, and the low-frequency band to polaritons of lower branches. The increase in the polariton linewidth on the upper branch results

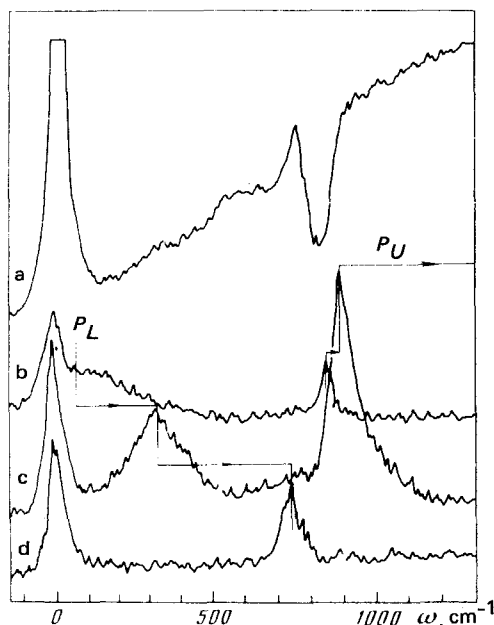


FIG. 1. Spectra of hyper-Raman scattering by polaritons in CCl_4 . a— $\theta = 0^\circ$ ($\Delta\theta = 5^\circ$); b— $\theta = 0^\circ$; c— $\theta = 0.9^\circ$; d— $\theta = 2.35^\circ$. Spectra b-d were recorded at an angular resolution $\Delta\theta = 0.4^\circ$. The arrows show the polariton shifts on the lower (P_L) and upper (P_U) branches with increasing scattering angle θ .

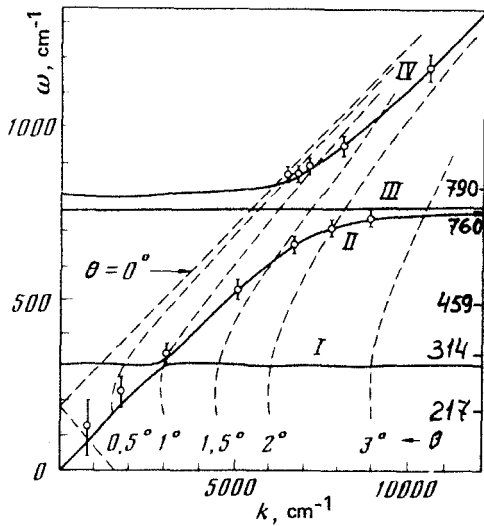


FIG. 2. Dispersion curves of polaritons in CCl_4 . Solid curves—Calculated curves of $\omega(k)$; points—experimental values of $\omega(k_i)$. I-III—Lower polariton branches; IV—upper branch. The dashed curves are a family of calculated $\omega_\theta(k)$ curves for the given angles $\theta = \text{const}$. The numbers at the right are the frequencies of the Raman lines in liquid CCl_4 (for “free” molecules).

from an increase in the width of the angular instrumental function. The angular interval in which the light was collected had to be chosen very small ($\Delta\theta = 0.4^\circ$) in order to reduce the contribution of the angular instrumental function to the apparent width of the polariton line. Nevertheless, the polariton bands on the upper branch at $\theta > 1.6^\circ$ are so broad that it is essentially impossible to determine their peak positions.

From the measured values of $\omega(\theta_i)$ we calculated the corresponding values of $\omega(k_i)$ for the polaritons of the lower and upper branches (the points in Fig. 2). To calculate the expected behavior of the polariton curves $\omega(k)$ (solid curves in Fig. 2), we used data on the IR spectra.⁸ The IR absorption band at $\sim 780 \text{ cm}^{-1}$ is known to be more than 100 times more intense than all the other bands, and it has two peaks of roughly equal intensity ($\omega_{T1} = 759 \text{ cm}^{-1}$, $\omega_{T2} = 783 \text{ cm}^{-1}$). From the data of Ref. 8 on the optical constants ($\hat{n} = n + ik$) of CCl_4 in the region $720\text{--}822 \text{ cm}^{-1}$ we found not only the transverse vibration frequencies (ω_{T1} and ω_{T2}) but also the longitudinal vibration frequencies ($\omega_{L1} = 769 \text{ cm}^{-1}$ and $\omega_{L2} = 803 \text{ cm}^{-1}$). We see from Fig. 2 that there is a satisfactory agreement of the calculated dispersion behavior $\omega(k)$ with the experimental points.

On most parts of the polariton curves, where the polariton group velocity is much smaller than the speed of light (on the lower part of the upper branch and the upper part of the lower branch), the polariton lines are quite narrow. On this basis it may be suggested that the thermal motion of the molecules in the liquid does not cause a significant nonconservation of the polariton wave vector in the light scattering.

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