Multiple-photon light scattering*

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(Received 25 October 1973; revised manuscript received 14 October 1974)

Triple- and double-photon inelastic and elastic scattering is observed from diamond upon the passage of intense picosecond laser pulses. The spectrum and intensity of the nonlinear scattering is measured. The triple-photon scattering is interpreted in terms of the hyper-Raman and hyper-Rayleigh effects. The value for the three-photon Raman hyperpolarizability is estimated from the experiment.

About a decade ago, Terhune *et al.*[1] first observed second-harmonic generation (SHG) and the hyper-Raman effect in isotropic media (e.g., liquids and fused quartz) which lack a center of symmetry in the individual molecules. The effect was attributed to a cooperative scattering of the individual dipoles induced in the molecules. Recently, Kielich *et al.*[2] observed SHG in liquids whose molecules possess a center of inversion. Although the inversion symmetry does not allow dipole moment at $2\nu_L$ for the molecules, the center of inversion may be destroyed because of temporal and spatial fluctuations of the local molecular fields in regions of short-range ordering. The symmetry properties and selection rules for the hyper-Raman polarizability tensor have been studied in detail by Cyvin *et al.*[3] The theory of second-order nonlinear Rayleigh scattering has been treated by Kielich.[4] Acoustically induced SHG has been observed in GaAs[5] and its theory has been presented by Nelson and Lax.[6,7]

This paper reports the first measurements of three-photon hyper-Raman effects in a crystal. Scattered light at frequency $3\nu_L - \nu_p$, as well as $3\nu_L$, is observed upon the passage of intense picosecond laser pulses of frequency ν_L through diamond, where ν_p is the optical-phonon frequency of the diamond lattice. Scattered light at frequencies $2\nu_L$ and $2\nu_L - \nu_p$ from diamond, which cannot be produced from the rank-three susceptibility tensor because of the inversion symmetry of the lattice and even parity of the phonon, is also observed. New experimental characteristics of the three-photon nonlinear scattering process are presented and interpreted in terms of the theory of hyper-Raman and Rayleigh light scattering. The observation of the light scattering of three- and two-photon inelastic and elastic scattering provides a new spectroscopic tool for studying interactions of phonons in crystals and molecular vibrations in liquids on a picosecond time scale.

Diamond is particularly suitable for the study of the Raman effect because the lattice has three optical vibrational branches which are degenerate at the center of the Brillouin zone. The optical-phonon modes at $|\vec{K}| \sim 0$ have frequency $\nu_p = 1332$ cm^{-1} and are described by the irreducible representation F_{2g} of the crystal point group O_h. The parity of F_{2g} modes is even. The acoustic-phonon modes have odd parity about $|\vec{K}| \sim 0$. In first order the 1332-cm^{-1} optical phonon is Raman active and infrared-absorption inactive. For a crystal having a center of inversion and an even-parity phonon mode, symmetry requires susceptibility tensors of odd rank and their derivatives with respect to the even-parity phonon mode to be zero. Therefore, the hyper-Raman effect in diamond should be observed at $3\omega \pm \omega_p$. However, SHG and hyper-Raman Stokes generation at $2\omega - \omega_p$ cannot be produced by terms like $\chi^{2\omega}_{ijk} E^{\omega}_j E^{\omega}_k$ and $\chi^{2\omega\pm\omega_p}_{ijkl} E^{\omega}_j E^{\omega}_k q^{\omega_p}_l$, but possibly from terms involving the gradient of the field $\chi_{ijkl} E^{\omega}_j \nabla_l E^{\omega}_k$ (quadrupolar effect) or terms involving the large local molecular fields,[8] $\chi^{2\omega}_{ijkl} E^{\omega}_j E^{\omega}_k F^0_l$. The observation of SHG from calcite has previously been attributed to terms like $\chi_{ijkl} E_j \nabla_l E_k$.[9,10] When an intense field is applied (ac, dc, or optical), the symmetry of the crystal is altered and corresponding modes which are inactive can become active and electric field dependent.[11]

In the experiment intense picosecond light pulses of wavelength 1.06 μm are generated by a Nd:glass mode-locked laser with a spectral width of ~80 cm^{-1}. The laser output typically consists of about 80 pulses, of peak power ~10^{+9} W, spaced ~7 nsec apart. The average pulse width is about 8 psec as measured by the two-photon fluorescence technique.[12] The laser beam is focused with a 20-cm focal length lens into a 3-mm-long sample of type II-b diamond. The beam diameter at the sample is about 400 μm. The symmetry axes of the diamond sample ($\langle 001\rangle, \langle 010\rangle$) are oriented parallel to the propagation vector and polarization direction of the 1.06-μm laser electric field. Scattered light emitted from the diamond is collected at an angle of 90° to the propagation direction of the 1.06-μm beam into a solid angle of 0.8 sr by a 10-cm-focal-length lens and passed into a 1-m Czerny-Turner

spectrometer for spectral analysis. An RCA 7265 photomultiplier tube is used to detect the light at the exit slit of the spectrometer. A Corning 1-75 filter is placed at the entrance slit to reduce any 1.06-μm scattered light. Stimulated Raman scattering (SRS) from diamond and SHG created in a quartz sample by the 1.06-μm beam are measured for use as reference signals for normalizing the data. The SHG from quartz is detected by an S-20 TRG 105B photodiode filter combination. The SRS reference signal is filtered and measured by a $\frac{1}{2}$-m Jarrel-Ash spectrometer and an RCA 7102 photomultiplier. The four signals—laser input reference, SHG from quartz, SRS from diamond, and signal from diamond—are delayed using appropriate lengths of cables and simultaneously displayed on a dual-beam Tektronix 555 oscilloscope and photographed on Polaroid film.

A correlation study shows that the intensity of the scattered light at frequencies $3\nu_L - \nu_p$, $3\nu_L$, $2\nu_L - \nu_p$, and $2\nu_L$ varies with the laser intensity as $I_{3\nu_L-\nu_p}$, $I_{3\nu_L} \propto I_{\nu_L}^3$ and $I_{2\nu_L-\nu_p}$, $I_{2\nu_L} \propto I_{\nu_L}^2 \propto I_{2\nu_L}$ (quartz). Limited by the damage threshold of the crystal a decade variation in laser intensity is used in the correlation study. In Fig. 1, the normalized average light intensity of 20 or more laser shots $I_{3\nu_L-\nu_p}/I_{\nu_L}^3$ and $I_{2\nu_L-\nu_p}/I_{\nu_L}^2$ is separately plotted as a function of wave number ν. The peaks correspond to the frequencies of third-order and second-order hyper-Raman Stokes light created from the optical phonon at $\nu_p = 1332$ cm^{-1}, and corresponding hyper-Rayleigh light. Since the laser spectral width (~80 cm^{-1}) is much wider than the thermal-acoustic-Brillouin-phonon frequencies (<1 cm^{-1}), Brillouin shifts are not readily observed in this experiment. The signal peaks will therefore be denoted by $2\nu_L$, $3\nu_L$, $2\nu_L - \nu_p$, and $3\nu_L - \nu_p$. It should be noted here that the intensity of the four observed signals are comparable in size. (The average laser intensity in Fig. 1 is $\langle I_L \rangle \approx 5$.) In order to estimate the relative size of the nonlinear susceptibilities, the intensity of the observed signals are compared with the signals from other well-studied nonlinear media, e.g., rhodamine 6G ethanol solution (2×10^{-4} M), quartz crystal, and BK-7 glass. The intensity of the signal from diamond at $2\nu_L$ is about 10^{-3} of SHG emission from quartz, and at $2\nu - \nu_p$ is ~10^{-7} of the two-photon fluorescent emission from the Rhodamine 6G solution at $2\nu_L - \nu_p$; and the third-harmonic signals (THG) from the diamond and the BK-7 glass are of comparable size. The absolute intensity of the hyper-Raman signals arriving at the spectrometer entrance slit is estimated at 10^{-8} W. No detectable anti-Stokes hyper-Raman light is observed under our experimental conditions. The polarization ratios of the light signals at frequencies of $2\nu_L$ and $2\nu_L - \nu_p$ have also been measured by inserting a rotatable polarization analyzer between the sample and detector. Each polarization direction is separately tested then averaged over many laser shots. After taking into account the polarization sensitivity of the Jarrel-Ash 1-m spectrometer, the emission at $2\nu_L$ is observed to be polarized favorably in the direction parallel to the incident $\vec{K}$ vector by ~20%, while at $2\nu_L - \nu_p$ no appreciable polarization is observed. Both directions for the polarization of the incident laser beam have been tested.

The signals observed at frequencies of $3\nu_L - \nu_p$ and $3\nu_L$ can be attributed to the dipole-allowed susceptibility $\chi_{ijkl}^{3\omega}$ and $\chi_{ijkl,m}^{3\omega-\omega_p}$. Inversion symmetry prohibits the production of hyper-Raman light at $3\omega_L - \omega_p$ from three-wave mixing by the observed $2\omega_L - \omega_p$ signal with the incident laser light, or by SHG and SRS signals. In principle, four-wave mixing of two incident photons and SRS light is allowed. Since the intensity of the SRS signal is less than 0.1% of the laser intensity, any production of $3\omega_L - \omega_p$ by mixing waves at ω_L, ω_L, and $\omega_L - \omega_p$ should be 0.1% smaller than the third-harmonic generation. In Fig. 1, the observed intensity at $3\omega_L$ and $3\omega_L - \omega_p$ is comparable in size. Furthermore, the multimode effect and self-focusing should not favor the four-wave mixing mechanism by a factor of 10^3. Therefore, in this experiment the four-wave mixing of SRS and laser light is not a dominant mechanism for the production of $3\omega_L - \omega_p$ light. Comparing intensities with the third-harmonic generation from BK-7 glass, and SHG of quartz, $\chi^{3\omega} \approx 4\times10^{-16}$ esu is estimated.[13] The hyper-Raman polarizability tensor per unit cell $\chi_{ijk,l}^{3\omega-\omega_p}/N_v$ is estimated to be 4×10^{-34} esu/unit cell.[14] Previously, only the ordinary Raman polarizability per unit cell, $\chi_{ij,k}^{\omega-\omega_p}/N_v$, has been

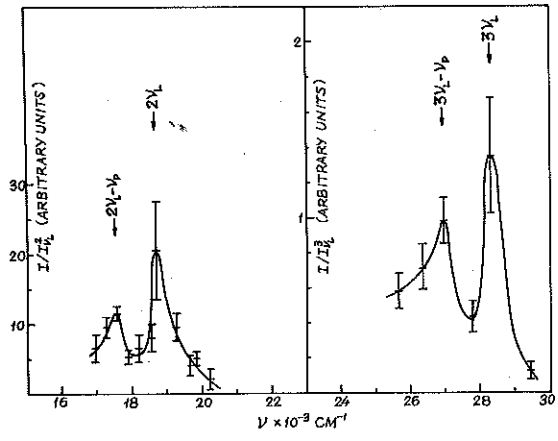

FIG. 1. Normalized scattered light intensity vs frequency.

reported[15-17] to be $\approx 4\times10^{-16}$ cm^2.

The mechanism for the production of SHG and $2\omega_L - \omega_p$ light in diamond is unknown at this time. We suggest the following possible mechanisms: (a) a field-gradient effect involving terms like $\chi^{2\omega}_{ijkl} E_j \nabla_k E_l$ and $\chi^{2\omega-\omega_p}_{ijkl,m} E_j \nabla_k E_l q_m$ (for the field-gradient effect to be operative, the second-harmonic light should be polarized in the direction parallel to the propagation vector of the incident beam; our measurement on polarizations has indeed favored this polarization direction), (b) the effect of a local molecular field at a low frequency on a picosecond time scale,[18] (c) scattering from substructure of the lattice, e.g., tetrahedral, which is noncentric,[19] and (d) other symmetry-breaking mechanisms, such as impurity or surface scatterings. It should be noted that mechanisms (a) and (b) invoke the existence of a field gradient (or quadrupolar effect), but (b) differs from (a) in the time domain. To pin down the exact mechanism (or mechanisms) of this scattering process, we believe two-orders-of-magnitude improvement in signal-to-noise ratio is essential.

We thank Dr. R. Caveney of De Beers Diamond Research Laboratory of South Africa for the loan of a diamond crystal, and Professor M. Lax and Dr. S. Kurtz for many discussions.

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*Supported in part by a City University of New York Faculty Award, a Cottrell Research Grant, and an NSF grant.

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[13]The intensity of a dipolar radiation $I_{\alpha\omega}$ is proportional to $k^4_{\alpha\omega} p^2 \prod_{i=1}^{3} \langle \sin^2[\frac{1}{2}(\Delta k^{\alpha})_i l_i]/[\frac{1}{2}(\Delta k_i) l_i]^2 \rangle$, where p is the dipole moment, $\vec{k}_{\alpha\omega}$ is the propagation wave vector of angular frequency $\alpha\omega$, $\alpha = 2$ or 3, $\Delta\vec{k}^{\alpha} = \vec{k}_{\alpha\omega} - \alpha\vec{k}_{\omega}$, and l_i is the dimension of the sample. The average of the phase-coherence factor $\langle \sin^2[\frac{1}{2}(\Delta k^{\alpha})_i l_i]/[\frac{1}{2}(\Delta k^{\alpha})_i l_i]^2 \rangle$ is $\sim 1/\frac{1}{2} l_i (\Delta k^{\alpha})_i$, for $l_i(\Delta k^{\alpha})_i \gg 1$ [see D. A. Kleinman, Phys. Rev. 128, 1761 (1962)]. In the experiment $\vec{k}_{\omega}$ is in the z direction, and the observed signal direction $\vec{k}_{\alpha\omega}$ is in the y direction; then $I_{\alpha\omega} \sim (n^2_{\alpha\omega} \alpha^2 / l_y l_z) p^2$. By comparing intensities of THG from diamond and BK-7 glass, $\chi^{(3)}_{\rm dia} \sim \chi^{(3)}_{\rm BK-7} (n_{\rm BK-7}/n_{\rm dia}) (I^{3\omega}_{\rm dia}/I^{3\omega}_{\rm BK-7})^{1/2} \sim 6\times10^{-16}$ esu, where $\chi^{(3)}_{\rm BK-7} \sim 10^{-15}$ esu is obtained from the measurement of $n_2 = 3\times10^{-14}$ esu by M. A. Duguay and J. W. Hansen [in *Damage in Laser Materials*, NBS special publication 341 (U.S. GPO, Washington, D.C., 1970), p. 47]. Also, by comparing intensity of THG from diamond and of SHG from quartz, $\chi^{(3)}_{\rm dia} = \chi^{(2)}_{\rm qua} (1/E) \frac{2}{3} (n_{\rm qua}/n_{\rm dia}) (I^{3\omega}_{\rm dia}/I^{2\omega}_{\rm qua})^{1/2} \sim 2\times10^{-16}$ esu, where $E = 8\times10^4$ esu and $\chi^{(2)}_{\rm qua}$ is taken to be 10^{-9} esu [see A. Yariv, *Quantum Electronics* (Wiley, New York, 1967), p. 345].

[14]In case of Raman Stokes emission, the quasimomentum conservation is satisfied, i.e., $\Delta\vec{k} = 0$. Intensity $I_{3\omega-\omega_p} \propto k^4_{3\omega-\omega_p} p^2$. Therefore, knowing $I^{3\omega}_{\rm dia} \sim I^{3\omega-\omega_p}_{\rm dia}$, $\chi^{(3)}_{\rm eff} \sim \chi^{(3)} (\alpha q k_{\omega})^{-1} (l_y l_z)^{-1/2} \sim 4\times10^{-11}$ esu and $\chi^{(3)}_{\rm eff}/N_v = 4\times10^{-34}$ esu, where $q = (\hbar/2M\omega)^{1/2} = 3\times10^{-10}$ cm, $N_v = 8.9\times10^{22}$ cells/cm^3, $l_z = 0.1$ cm, $l_y = 0.04$ cm, and M is the effective mass of the carbon atom.

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