PHYSICAL REVIEW
LETTERS

VOLUME 14 | 26 APRIL 1965 | NUMBER 17

MEASUREMENTS OF NONLINEAR LIGHT SCATTERING

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(Received 23 February 1965)

We have found that when the beam of a giant-pulsed ruby laser is brought to a focus inside liquids or fused quartz, about 10^{-13} of the incident energy emerges as scattered radiation near twice the laser frequency. The amount of scattered radiation was found to vary as the square of the laser intensity. Further, it was observed to occur only in the focal region of the laser beam. Inelastic scattering, with frequency displacements characteristic of the material, as well as elastic scattering occurred. Both types of scattering depend upon different properties of the material than their linear counterparts, Rayleigh and Raman scattering. Thus, this nonlinear scattering provides an important new tool for the study of molecular structures and their interactions in liquids.

The experiment is diagrammed in Fig. 1. A pulsed ruby laser having a plane-polarized, 1-MW peak power, 80-nsec half-width, 1-mrad divergence output beam and two-per-minute repetition rate was used. The laser was focused at $f/10$ and the scattering collected at $f/1$. The transmission efficiency of the detection system varied from 10 to 25% with wavelength and polarization. All measurements were carried out just below threshold for dielectric breakdown or Raman laser action in the sample. High-purity samples which had been filtered through 0.5-μ Millipore filters were used. As well as having lower breakdown thresholds, contaminated samples often produced spurious signals.

The nonlinear scattering spectra obtained for water and fused quartz are shown in Fig. 2. The intensity distribution is seen to be different in the nonlinear inelastic scattering and infrared absorption spectra, particularly in the 1000-

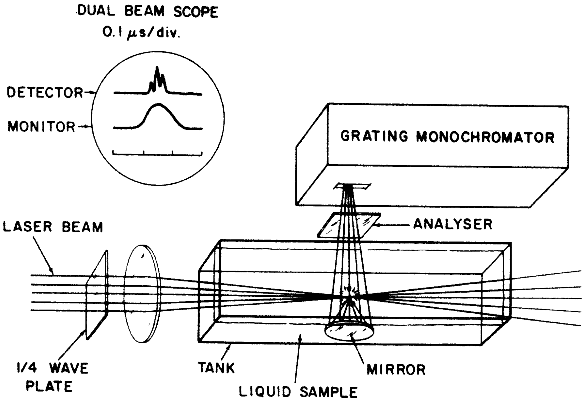

FIG. 1. Arrangement for observation of nonlinear scattering. The polarization properties of the scattered light were determined with the laser both plane and circularly polarized. The signal from a 1P28 phototube which measured the scattered radiation through the monochromator, along with that from a monitor of the laser beam, was displayed on a dual-beam oscilloscope. Individual photoelectrons could be detected. Spurious signals occurred during the laser pulse about once in every 200 pulses.

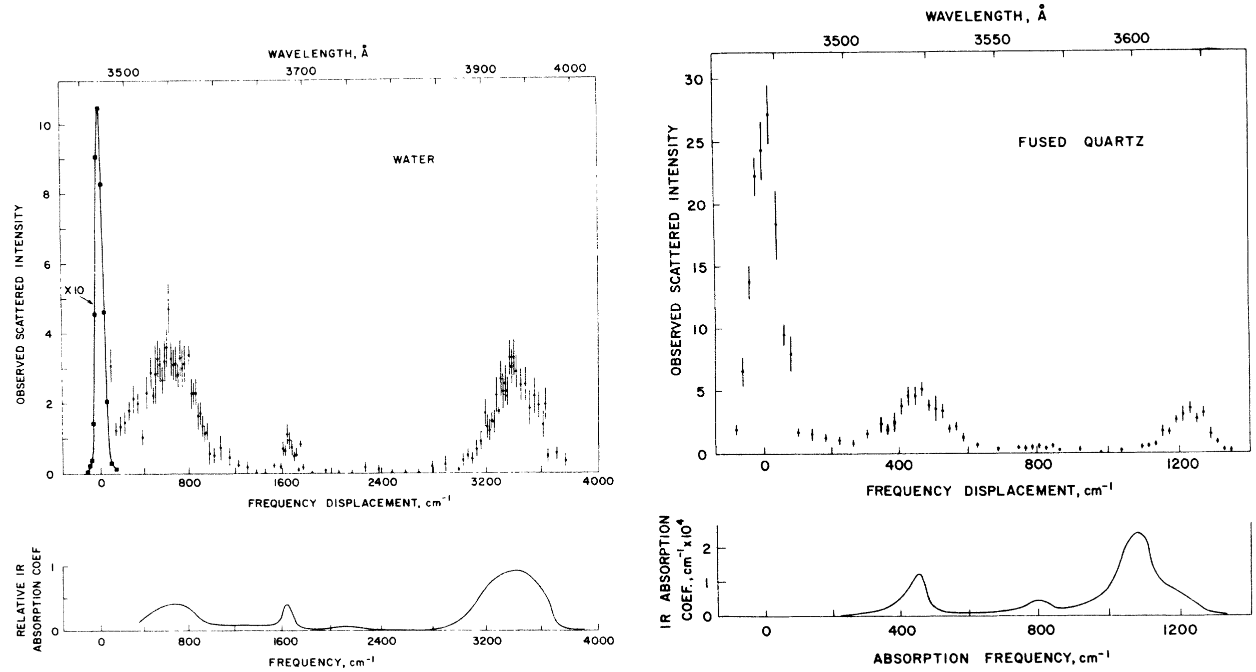

FIG. 2. Observed unpolarized nonlinear scattering spectra and infrared absorption spectra for water and fused quartz. The scattering intensity is given in photoelectrons per laser pulse ($\frac{1}{2}$-MW peak power in the case of water, 1-MW for fused quartz) averaged over approximately 25 pulses. Standard errors are indicated. When no signal was observed, the 70% probability limits using Poisson statistics are shown. The spectrometer band pass was 80 cm^{-1}.

to 1300-cm^{-1} region of fused quartz.

The theory for second-order nonlinear elastic scattering has been treated by Li[1] and Kielich.[2] Li also discusses the symmetry requirements for allowed molecular transitions in inelastic nonlinear scattering. The brief treatment given below, which emphasizes measurable quantities, parallels that used by Landau and Lifshitz[3] for first-order scattering.

The dipole approximation will be made and a scattering tensor I_{ij} introduced,

$$I_{ij}(2\omega)=\langle E_i(2\omega)E_j^*(2\omega)\rangle_{\text{av}}=\frac{(2\omega)^4}{c^4R_0^2}\iint\langle P_{i,1}(2\omega)P_{j,2}^*(2\omega)\rangle_{\text{av}}dV_1dV_2, \tag{1}$$

where $\text{Re}[\vec{\text{E}}(2\omega)e^{i2\omega t}]$ is the electric field strength of the scattered wave and $\langle\ \rangle_{\text{av}}$ indicates time averaging over the motions of the particles. R_0 is the distance from the scattering region. $\vec{\text{P}}_{,1}(2\omega)$ is the complex Fourier amplitude of the induced dipole moment per unit volume at point 1. The contribution to $\vec{\text{P}}_{,1}(2\omega)$ associated with second-order nonlinear scattering will be assumed of the form

$$P_{i,1}(2\omega)=d_{ikl,1}(-2\omega,\omega,\omega)E_{k,1}(\omega)E_{l,1}(\omega). \tag{2}$$

In isotropic media the average value of d_{ikl} is zero. Assuming that the values of d_{ikl} at two different points are correlated only over distances small compared to a wavelength,[3] one can write

$$I_{ij}(2\omega)=\frac{(2\omega)^4}{c^4R_0^2}\int\langle d_{ikl,1}(-2\omega,\omega,\omega)d_{jmn,2}^*(-2\omega,\omega,\omega)\rangle_{\text{av}}dv\int E_k(\omega)E_l(\omega)E_m^*(\omega)E_n^*(\omega)dV. \tag{3}$$

In the case of isotropic media such as liquids, symmetry requires that[3]

$$\int \langle d_{ikl,1}(-2\omega,\omega,\omega)d_{jmn,2}{}^*(-2\omega,\omega,\omega)\rangle_{\rm av}dv$$

$$=a(-2\omega,\omega,\omega)[\delta_{ij}\delta_{km}\delta_{ln}+\delta_{ij}\delta_{kn}\delta_{lm}]+b(-2\omega,\omega,\omega)[\delta_{im}\delta_{kj}\delta_{ln}+\delta_{in}\delta_{kj}\delta_{lm}+\delta_{im}\delta_{lj}\delta_{kn}+\delta_{in}\delta_{lj}\delta_{km}]$$

$$+c(-2\omega,\omega,\omega)\delta_{ij}\delta_{kl}\delta_{mn}+d(-2\omega,\omega,\omega)[\delta_{ik}\delta_{lm}\delta_{jn}+\delta_{ik}\delta_{ln}\delta_{jm}+\delta_{il}\delta_{km}\delta_{jn}+\delta_{il}\delta_{kn}\delta_{jm}]$$

$$+e(-2\omega,\omega,\omega)[\delta_{ik}\delta_{lj}\delta_{mn}+\delta_{il}\delta_{kj}\delta_{mn}]+e^*(-2\omega,\omega,\omega)[\delta_{im}\delta_{kl}\delta_{jn}+\delta_{in}\delta_{kl}\delta_{jm}], \qquad (4)$$

where a, b, c, and d are real constants.

These formulas for elastic nonlinear scattering can be extended by analogy to cover the inelastic case by replacing 2ω with $2\omega-\omega_f$ and $d_{ikl}(-2\omega+\omega_f,\omega,\omega)$ with $\langle g|d_{ikl}(-2\omega+\omega_f,\omega,\omega)|f\rangle$. $I_{ij}(2\omega-\omega_f)$ is now to be interpreted as the scattering tensor for the transition to state f integrated over the band.

Results of the polarization studies are given in Table I. The column headings include symbols indicating the quantities measured and the constants deduced using Eq. (3) and (4). K^{-1} is given by

$$\frac{(2\omega_l-\omega_f)^4 n_{2\omega_l-\omega_f}\Omega}{8\pi c}\int\int[E_i(\omega_l)E_i{}^*(\omega_l)]^2dVdt$$

where $n_{2\omega_l}$ is the index of refraction at $2\omega_l$ and Ω the collection solid angle. In the data reduction, the approximation

$$\int\int[E_i(\omega_l)E_i{}^*(\omega_l)]^2dVdt=\left(\frac{8\pi}{n_{\omega_l}c}\right)^2W_l{}^2\frac{l}{t_{\rm eff}A_{\rm eff}}=1.6\times10^{-8}W_l{}^2/n_{\omega_l}{}^3(\rm esu)$$

was made. Here W_l is the total laser energy per pulse and l the demagnified spectrometer slit length. $t_{\rm eff}$ and $A_{\rm eff}$ were measured by probing the laser beam in the region of a focus. The uncertainties in this approximation and in the evaluation of $t_{\rm eff}$ and $A_{\rm eff}$ lead to an estimated probable error of a factor of two in the absolute values of the entries in Table I.

Table I. Second-order nonlinear scattering constants in units of cm^6 erg$^{-1}\times10^{42}$. Here $W_{x,x}{}^y$ is the scattered energy collected per laser pulse integrated over the band at $(2\omega_l-\omega_f)$. The superscript y denotes the direction of observation; the first subscript x (or z) gives the direction of polarization of the scattered radiation; the second subscript x (or +) indicates that the laser beam was plane polarized in the x direction (or circularly polarized and traveling in the z direction). The frequency dependence of the constants has been omitted. Each entry includes the average and standard error of at least 25 measurements.

Material	$\frac{\omega_f}{2\pi c}$ (cm^{-1})	$KW_{x,x}{}^y$ $2a+4b+c+4d+2e+2e^*$	$KW_{z,x}{}^y$ $2a+c$	$KW_{x,+}{}^y$ $2a+2b+2d$	$KW_{z,+}{}^y$ $2a$	$\frac{W_{x,+}{}^y}{W_{z,x}{}^y}$	$\frac{W_{x,x}{}^y}{W_{z,x}{}^y}$
H_2O	0	34±1	4.0±0.4	9.6±0.6	1.7±0.1	2.5±0.3	8.6±0.9
	660	2.5±0.3	1.15±0.1	2.1±0.2	0.7±0.1	1.8±0.3	2.1±0.3
	3420	6.1±0.4	0.6±0.1	1.7±0.2	0.4±0.1	3.2±0.9	10±2.5
Fused quartz	0	0.31±0.01	0.26±0.01	0.56±0.03	0.31±0.01	2.15±0.15	1.2±0.1
	470	0.16±0.03	0.09±0.01	0.15±0.01	0.043±0.005	1.7±0.3	1.8±0.4
	1240	0.030±0.005	0.094±0.007	0.115±0.010	0.031±0.005	1.2±0.15	0.32±0.07
CCl_4	0	100±5	34±3	95±5	50±4	2.8±0.3	2.9±0.3
	770	27±3	1.5±0.4	6±1	1.02±0.04	4.3±1.3	19±5
CH_3CN	0	145±7	14±1	31±3	7.5±1.0	2.2±0.3	10±1

The last two columns are included to exhibit the extent to which the assumption $d_{ikl}(-2\omega + \omega\ , \omega, \omega) = d_{kil}(-2\omega + \omega_f, \omega, \omega)$ is valid. In this case, a becomes equal to b and $c = d = e = e^*$. Thus only two constants are needed to fully characterize the scattering, and the measurements made provide three checks on their ratio. In particular, entries in the second-last column should be 2, and those in the last column should fall between the limits 1 and 9.

Considering the standard errors, only the fused quartz band at 1240 cm^{-1} is clearly not describable in this way.

Next, in order to compare the results with other calculations and experiments, the approximation that the scattering centers are randomly oriented individual molecules will be made. It will be assumed that $p_i(2\omega) = \frac{1}{4}\beta_{ijk}(-2\omega, \omega, \omega)E_j(\omega)E_k(\omega)$, where $\vec{p}(2\omega)$ is the second-order contribution to the induced dipole moment for an isolated molecule fixed in space.[4] Then

$$\int \langle d_{ijk,1}(-2\omega, \omega, \omega) d_{lmn,2}{}^*(-2\omega, \omega, \omega)\rangle_{\text{av}}\, dv = \left(\frac{n_\omega{}^2 + 2}{3}\right)^4 \left(\frac{n_{2\omega}{}^2 + 2}{3}\right)^2 \left(\frac{N}{16}\right) \langle \beta_{ijk}(-2\omega, \omega, \omega)\beta_{lmn}{}^*(-2\omega, \omega, \omega)\rangle_{\text{av}}, \tag{5}$$

where N is the molecular density and an approximate local field correction[5] has been included. For the CCl_4 molecule, only one constant, β_{123}, occurs. Averaging over all molecular orientations,[2] $\langle \beta_{iii}\beta_{iii}{}^*\rangle_{\text{av}} = (12/35)|\beta_{123}|^2$. From the data, $|\beta_{123}(-2\omega_l, \omega_l, \omega_l)|$ for the CCl_4 molecule equals 0.35×10^{-30} $\text{cm}^{9/2}$ $\text{erg}^{-1/2}$. Buckingham and Stephen[4] have computed a value of 0.24×10^{-30} esu for the electronic contribution to β_{123} for methane. Kielich[2] associated $\beta_{ijk}(-2\omega, \omega, \omega)$ with estimates near 10^{-29} esu for similar coefficients deduced from the depolarization of Rayleigh scattering due to molecular interactions in liquids. The latter, however, should probably be associated with the larger coefficients of $\beta_{ijk}(-\omega, 0, \omega)$.[6] Also, if all the CCl_4 molecules were aligned, one would obtain coherent second-harmonic generation with $d_{123}(-2\omega_l, \omega_l, \omega_l) = 1.4 \times 10^{-9}$ $\text{cm}^{3/2}$ $\text{erg}^{-1/2}$. This is within the range of values measured for piezoelectric crystals.[7]

In addition, with the above model elastic scattering of $2\omega_l$ could occur only for liquids of molecules lacking inversion symmetry. In support of this, 20 times as much scattering was observed from a liquid of cis-dichloroethylene, which lacks a center of inversion, than from a liquid composed almost entirely of the trans isomer, which is centrosymmetric. However, the effect of molecular interactions on the local symmetry is apparent in the elastic-scattering data for CCl_4. If the scattering were from individual molecules, the entry in the last column of Table I, 2.9 ± 0.3, should be $\frac{3}{2}$.[2]

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[1] Li Yin-Yuan, Acta Phys. Sinica 20, 164 (1964).

[2] S. Kielich, Bull. Acad. Polon. Sci. 12, 53 (1964).

[3] L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media (Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1960), p. 377.

[4] A. D. Buckingham and M. J. Stephen, Trans. Faraday Soc. 53, 884 (1957).

[5] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).

[6] P. A. Franken and J. F. Ward, Rev. Mod. Phys. 35, 23 (1963).

[7] R. C. Miller, Appl. Phys. Letters 5, 17 (1964).