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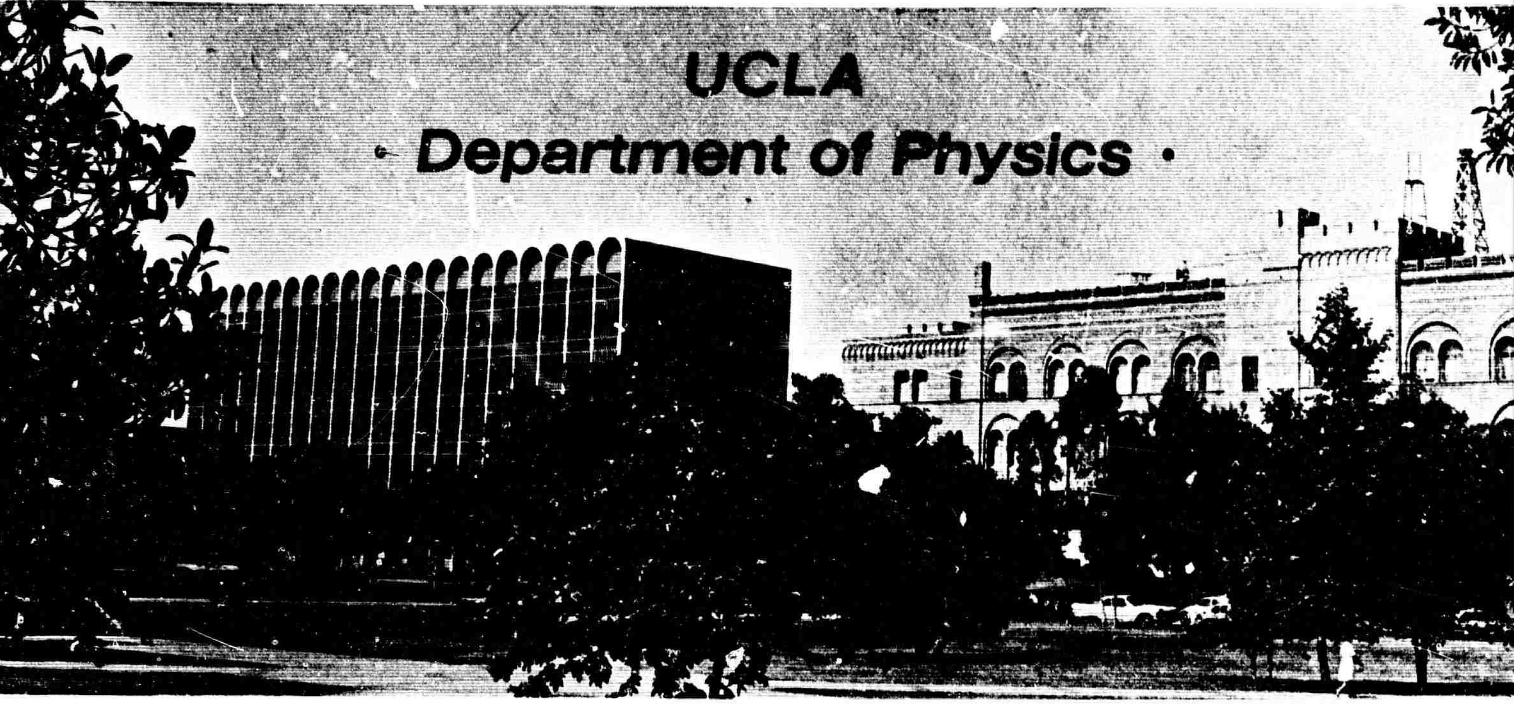

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STUDY OF OPTICAL INTERACTIONS IN SOLIDS

Contract: Nonr-233(93)

ARPA Order #306

Principal Investigator: Professor R. Braunstein
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Los Angeles, California

Final Technical Report

September 1, 1966 August 31, 1968

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CONTENTS

I. SUMMARY

The objective of the present program was a study of the interaction of intense optical radiation with matter so as to obtain a correlation of various nonlinear processes in terms of the band structure and lattice dynamics of the solid. These included a study of multiple-photon absorption, and Raman scattering. Concomittant with this program, the band structure and lattice dynamics of semi-conductors, metals and insulators were investigated by the use of conventional as well as laser sources of radiation. Since the major results of this work have been published, we include a series of reprints in this report, as well as high-light summaries of these contributions. The following is a summary of the specific accomplishments during this contract.

a) A theory for the reflection of neutral atoms from standing light waves was developed. It is indicated that it is experimentally feasible to spacially separate excited states in a beam of neutral atoms or molecules and hence, produce beam optical lasers.

b) A new type of He-Ne gas plasma oscillation was discovered, obtained by shunting the plasma with an external capacitor. The configuration works as well as an oscillator or regenerative amplifier.

c) A new multiple-phonon stimulated Raman line at 1.07μ in benzene was reported. This line is well understood in terms of a light feedback theory.

d) It was shown that multiple-photon absorption can set an intrinsic upper limit to the power density that can be propagated through a semiconductor. This yields an effective means of optically pumping semiconductor lasers, sets an intrinsic limit to the power density obtainable from such devices, as well as a means of fashioning power limiters.

e) A unique cyclic temperature dependence of the stimulated Raman effect in benzene was reported.

f) The first observation of infrared stimulation emission associated with optical phonons of a liquid was reported. This was seen at 5μ from benzene. In addition, induced transparency by coherent optical phonons was observed.

g) A new technique of frequency-modulated spectroscopy was developed which enables us to readily obtain the first or higher derivatives of any optical spectra. A change in reflectivity absorption or emission of a few parts per million are detectable by this technique. This technique was used to study critical points in band structure of semiconductors and metals.

h) A fine structure of 2.2°C period on the thermo-spectrum of the 8050Å stimulated Raman output in benzene was reported, in addition to the previously reported large period.

i) A double thermo-spectrum of the 8050Å line in benzene was discovered which yielded a double period of 2.2°C. The cyclic thermo-spectrum in benzene indicates that a specific molecular interaction is responsible for the effect.

II. BRAGG REFLECTION OF NEUTRAL PARTICLES BY OPTICAL STANDING WAVES

The possibility of observing Bragg reflection of electrons by standing light waves was predicted by Dirac and Kapitza in 1933. There has been recent experimental interest in observing this phenomena. The Dirac-Kapitza analysis has been generalized to show that any neutral particle, including neutral atoms, capable of scattering photons can be Bragg scattered by standing light waves. This phenomena is analogous to ordinary scattering of light waves by periodic structures such as diffraction gratings and crystals.

The above calculations showed that a neutral particle will be defected through twice the Bragg angle given by $\hbar\omega/Mcv$ where c is the frequency of the standing light wave and M and v are the mass and velocity of the scattered neutral particle. If this condition is not satisfied, there is essentially no scattering. If a neutral atom of mass 20 and kinetic energy 1 ev is incident within a ruby laser cavity, the angle of deflection will be of the order of 10^{-5} radians. Although it is experimentally feasible to measure such deflection angles, much larger angles will be obtained if sub-thermal beams could be employed.

This phenomena opens up the possibility of using an optical cavity to spatially separate excited atomic states and so produce a whole class of optical beam lasers similar to the ammonia microwave maser. A note on this calculation was published in Phys. Rev. Letters 17, 231 (1966); a reprint of this publication is included in this section. This work was done in collaboration with S. Aultshuler and L. M. Frantz of TRW Systems, Redondo Beach, California.

REFLECTION OF ATOMS FROM STANDING LIGHT WAVES

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(Received 16 May 1966)

It was predicted in 1933 by Dirac and Kapitza[1] that electrons could undergo Bragg reflection from standing light waves. This phenomenon of electron-wave scattering is analogous to the ordinary scattering of light waves by periodic structures such as diffraction gratings and crystals. Recent interest[2] has been stimulated by the increased possibility of observing the effect using the intense light beams now available as a result of laser technology.

We wish to point out that Bragg reflection by standing light waves is not restricted to electrons, but should occur for all particles capable of scattering photons, including neutral atoms. The Dirac-Kapitza analysis results in the expression for the scattering probability per unit length k of the electron traversing the region occupied by the standing waves,

$$k = \frac{4\pi^3 n^2 c^4}{\omega^2 \gamma v} \frac{d\sigma(\pi)}{d\Omega}, \tag{1}$$

where n is the photon number density, ω is the angular frequency, γ is the spectral width of the electromagnetic radiation, v is the electron velocity, and $d\sigma(\pi)/d\Omega$ is the Thomson differential cross section for backscatter of a photon by a free electron. Although the original analysis and all of the subsequent references have been concerned explicitly with electrons, it is of considerable interest to note that the same analysis applies regardless of the nature of the incident particle. Equation (1) remains valid provided only that $d\sigma(\pi)/d\Omega$ be interpreted as the differential cross section for backscatter of a photon from the particle in question.

Dirac and Kapitza regard the standing wave as a superposition of two traveling waves. The essence of their analysis is then the computation of the stimulated backscatter rate, viz., that corresponding to scattering a traveling-wave photon from a mode associated with one propagation direction into the mode associated with the opposite direction. Because photons obey Bose statistics, this rate is proportional not only to the radiation density in the mode from which the photon is absorbed, but also to the radiation density in the mode into which the photon is emitted.[3] It is to be emphasized, however, that this proportionality to the photon density in the final-state mode is a consequence of only the Bose statistics obeyed by the photons, and is independent of the nature of the scatterer. It is for this reason that the Dirac-Kapitza analysis is directly generalizable from electrons to arbitrary scatterers.

Equation (1) applies only if the Bragg condition is satisfied, i.e., the particle must be incident at an angle θ_B relative to the direction normal to the photon-propagation vector. The Bragg angle is given by $\theta_B = \hbar\omega/Mcv$, where M is the particle mass. The particle is deflected through an angle $2\theta_B$; however, if the Bragg condition is not satisfied, there is essentially no scattering.

As an illustration of the magnitude of the effects, let us consider the scattering of a neutral atom of atomic mass of about 20 and kinetic energy of 1 eV. We shall choose the radiation frequency to be that appropriate to a ruby laser ($\omega = \pi \times 10^{15}$ sec^{-1}), a power density of one megawatt per cm^2, and a typical cavity loss rate γ of 10^7 sec^{-1}. For the back-scattering cross section, $d\sigma(\pi)/d\Omega$, we choose a typical value of 10^{-28} cm^2 corresponding to Rayleigh scattering. It should be observed, however, that $d\sigma/d\Omega$ for atoms is strongly frequency dependent, and at or near resonances can be many orders of magnitude larger than the value for Rayleigh scattering. For the numbers we have chosen, the deflection angle is quite small, namely, $2\theta_B = 2\times 10^{-5}$ rad. However, the interaction is quite strong; the scattering probability per unit length is $k = 0.2$ cm^{-1}, and, as we have just indicated, it can be enormously greater near a resonance. This strong interaction suggests that a large net scattering angle may be attainable with a succession of individual Bragg scatterings by an appropriate arrangement of successive standing-wave cavity orientations.

Finally, it should be mentioned that the above reasoning can be readily extended to multiple-photon events. That is, to every N-photon scattering process occurring in free space there corresponds an N-photon stimulated scattering process for which the Bragg angle is $N\hbar\omega/Mcv$, the scattering angle is $2N\hbar\omega/Mcv$, and the scattering probability per unit length is proportional to the $2N$th power of the photon density n^{2N}.

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III. He-Ne PLASMA OSCILLATOR AND REGENERATIVE AMPLIFIER

While several He-Ne gas lasers were being placed in operation, plasma oscillations in the frequency range from 200 kHz to 430 kHz were encountered whose frequency could be changed by external conditions. This new type of gas plasma oscillation was investigated in a He-Ne plasma. The frequency and the amplitude of these oscillations depends essentially on the external capacitor connected to the ends of the plasma tube and on the current of the discharge. Many spontaneous oscillations have been previously reported in the literature; however, all these former instabilities depend on the plasma internal conditions and are also difficult to control whereas in this experiment all the parameters are easily controlled.

The results of this study were reported in Physics Letters 22, 430 (1966). A reprint of this publication is included in this section.

ERRATUM

He-Ne plasma oscillator and regenerative amplifier,
J. P. Biscar, Physics Letters 22 (1960) 430

The heading of this letter should read:

He-Ne plasma oscillator and regenerative amplifier [*]

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[†] C.N.R.S. and NATO Fellow.

case ν_0 = 132 Mc/s. Fig. 1B (5 nsec/div) is a beat display corresponding to ν_0 for the TEM$_{00}$ transverse mode. (The upper curve 1A is the "dark" display obtained by merely covering the photomultiplier). Fig. 1C (5 nsec/div) is a display of ν_0 and $2\nu_0$ combined, also for the TEM$_{00}$. The presence of $2\nu_0$ (which is obtained by increasing the driving power level) is an indication of the simultaneous oscillation of at least three longitudinal modes. The frequency response of the photomultiplier falls off around 350 Mc/s. For that reason $3\nu_0$ was not observed. Upon transition to higher transverse modes (i.e. changing $m+n$ in eq. (1) beat frequencies corresponding to $\Delta(m-n) \neq 0$ were observed. Curves D, E, F in fig. 1 are the examples of the displays corresponding to $\nu_0(0+f)$ = 28 Mc/s (1D), $\nu_0(1+f)$ = 160 Mc/s (1E), $\nu_0(1-f)$ = 104 Mc/s (1F). In a first attempt frequencies corresponding to $(0+f)\ \nu_0$, $(0+2f)\ \nu_0$, $(1-f)\ \nu_0$, $(1+0)\ \nu_0$, $(1+f)\ \nu_0$, $(2+0)\ \nu_0$, and $(2+f)\ \nu_0$ were observed. It should be noted that the various frequencies are obtained as "clean" displays by suitably varying both the driving power level and the angular position of the concave mirror.

It is noted that in addition to the above frequencies one gets some times the frequencies corresponding to $(1-f)\ \nu_1$, $(1+0)\ \nu_1$, $(1+f)\ \nu_1$, $(2+0)\ \nu_1$, and $(2+f)\ \nu_1$ where ν_1 = 128 Mc/s.

The significance and meaning of ν_1 is being studied and a more detailed account of the present research will be published in a forthcoming publication.

The author is indebted to Drs. P.A. Forsyth and R. Mitalas for reading the manuscript and to Mr. W. Heinrich for skillful technical assistance.

This work was supported by grants from NRC and DRB of Canada.

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He-Ne PLASMA OSCILLATOR AND REGENERATIVE AMPLIFIER

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A new type of gas plasma oscillations is reported, obtained by shunting the plasma with an external capacitor. This configuration can work as an oscillator or as a regenerative amplifier.

This letter reports the conditions and the main data of peculiar plasma oscillations. The frequency and the amplitude of these oscillations depend essentially on the external capacitor connected to the ends of the plasma tube and on the current of the discharge. Many spontaneous oscillations have been reported [1-2] on direct current glow discharges in noble gases, and in the frequency range lower than 50 kHz. As Donahue and Dicke [2] have demonstrated, moving striations are almost always present in d.c. discharge, and they have been studied [3-5]. Ion sound waves in plasmas have been reported too [6-7] and also unexplained waves [8] in r.f. discharge. All of these former instabilities depend on plasma internal conditions and are also difficult to control whereas in this experiment all the parameters are easily controlled.

The experiment is carried out with a plasma obtained through a d.c. discharge in a tube 60 cm length and 5 mm in diameter. The tube is filled with a 5:1 (by pressure) helium neon gas mixture to a total pressure of 1.22 Torr. A resistor of 60 kΩ is always used as ballast. The plasma oscillations are detected with a very light electrostatic coupling to the plasma of a 10 MΩ probe and are displayed in an oscilloscope.

The plasma obtained under these conditions

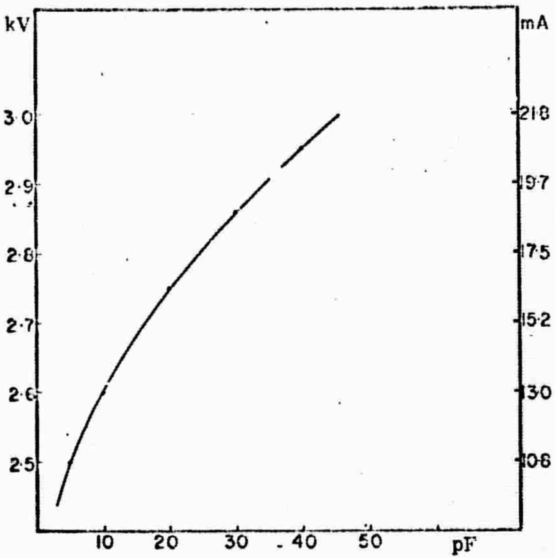

Fig. 1. Current (and voltage) threshold versus external capacitor C.

has a linear negative characteristic between 8 and 22 mA. However, any type of oscillant circuit shunted by this element of negative resistor cannot oscillate, but a simple capacitor for a very precise current is successful. With this configuration, briefly, three different kinds of oscillations are:

1) Some instability of frequency lower than 50 KHz, similar to the oscillations reported by Donahue [2].

2) With a capacitor $C > 50$ pF, there are strong relaxation oscillations whose frequency changes (100-150 KHz) with the voltage of the power supply, but whose amplitude remains constant.

3) The most interesting and completely different oscillations were found with $C < 50$ pF.

The output is always perfectly sinusoidal and, after some thermalisation, is stable in amplitude. The frequency stability is $\Delta f/f \approx 3 \times 10^{-4}$.

An important point, is that, for a given value of the external capacitor, these oscillations start at a very precise voltage or current threshold. For example, using a power supply of 3000 volt, the precision of this threshold is about one volt, demonstrating that the negative characteristic does not explain the mechanism of these plasma instabilities. Fig. 1 shows the variation of this threshold versus the capacitor value.

When you find the threshold, by decreasing the voltage of the power supply the amplitude of these oscillations increases linearly. (They can also produce some output power and if they become too great they can extinguish the plasma). However, the control of their amplitude is made by the set voltage of the power supply.

The frequency also depends on the external conditions. With the same plasma tube one can cover the frequency range from 200 kHz to 430 kHz by changing only external conditions.

At each of these preceding frequencies, this plasma oscillator works as a regenerative amplifier, but only if the set voltage is very close to the threshold voltage. For a difference over 2 V, there is no further amplification; the oscillator is autonomous. We use an electrostatic coupling of the external h.f. generator to the plasma tube (in the opposite side of the output). The set voltage must be adjusted at the beginning of the proper oscillations at the frequency f_0. By changing the frequency of the external generator, one sees a great maximum for the precise frequency f_0 of the plasma oscillator. It is difficult to know the exact input in the plasma, because of the extremely light coupling. However, a gain superior to 20 dB was found with a band pass of 4 kHz.

A longitudinal magnetic field decreases linearly the amplitude of the oscillations, whereas a transverse magnetic field increases them. The force behind these plasma instabilities is the existence of atoms in metastable state which are also sensitive to a precise near infrared wavelength. In another paper, we will report this optical property with the "plasma mechanism".

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IV. MULTI-PHOTON ABSORPTION

Calculations have shown that the double-photon absorption cross-sections in a number of III-V semiconductors is sufficiently large to set an intrinsic upper limit to the power density that can be propagated through such media using presently available lasers. In addition, it should be possible to observe double-photon stimulated emission in such systems and so produce difference frequencies by this process. The large cross-sections for this process indicates that double photon absorption is also an effective mechanism for optical pumping of semiconductor lasers, can limit the power density obtainable from such devices, or can enable one to fashion nonlinear optical power limiters.

The fact that these compounds have been used as laser sources further dictated the desirability of obtaining these cross-sections, since the power density obtainable from these materials will be limited by this quadratic loss process. In addition, these results can be used for calculating the double-photon stimulated emission cross-sections in the case of a population inversion and so obtain coherent emission or amplification in new regions of the spectrum.

The previous theory, developed for the double-photon absorption in semiconductors utilized a three-band model for the band structures and took into acco the parity of the virtual transitions. However, application of s theory to allowed-forbidden two photon absorption in a two-band mod reveals simple generalizations regarding the underlying band paramete ch determine the cross-sections for all the III-V and II-VI compoun so enables one to succintly set a lower band for this cross-section for this class of materials. The results of this calculation together with the estimates of the cross-sections for selected III-V compounds are discussed in the following section. Although a reprint of the resulting publication is also included, the following discussion contains material not included in the publication.

Saturable Transmission by Multiphoton Absorption in Semiconductors*

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Multiphoton absorption can set an intrinsic upper limit to the power density transmittable through semiconductors. This mechanism is an effective means of optically pumping semiconductor lasers, can limit the power density from such devices, or can enable the fashioning of nonlinear optical power limiters.

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*This research is part of Project Defender Contract NONR 233(93) from the Office of Naval Research, the Advanced Project Agency and the Department of Defense of the United States of America.

Recent measurements of double-photon absorption in a number of semiconductors such as CdS,[1,2] GaAs,[3] PbIe,[4,5] and InSb[4] have shown that the theory[1,6] developed for the two-photon excitation of interband transitions is adequate to account for the observed cross-sections. It is of some interest, because of this agreement between theory and experiment for the above semiconductors, to consider the calculation of the double-photon absorption for all the III-V compounds since such multiphoton processes can set an intrinsic upper limit to the flux density that can be transmitted through such media using presently available laser sources. Since the absorption coefficient for this process obeys a nonlinear transmission law, the multiphoton absorption mechanism can serve as an efficient agent for multiphoton optical pumping of semiconductor lasers,[3,5,7] set an intrinsic upper limit to the power density obtainable from semiconductor lasers, or enable one to fashion nonlinear optical power limiters.

The previous theory,[1,6] developed for the double-photon absorption in semiconductors utilized a three-band model for the band structure and took account of the parity of the vertical transitions. However, the application of this theory to allowed-forbidden two photon absorption in a two band model, reveals simple generalizations regarding the underlying band parameters which determine the cross-section for all the III-V-II-VI compounds and so enables one to succinctly set a lower bound for this cross section for this class of materials. Using the framework of the theory[1,6], it can be easily shown that the double photon absorption coefficient for a two-band model is given by:

$$K_2 = \frac{(2)^{9/2} \pi N_2 \alpha_c^2 |P_{vc}|^2 e^4}{c n_1 n_2^2 m^{3/2} (\alpha_c + \alpha_v)^{5/2}} \left[\hbar\omega_1 + h\omega_2 - E_g\right]^{3/2} \left[\frac{1}{\hbar\omega_1} + \frac{1}{\hbar\omega_2}\right]^2 \tag{1}$$

where $\hbar\omega_1$ and $\hbar\omega_2$ are the photon energies, n_1 and n_2 are the indices of refraction for photon one and two respectively, E_g is the energy gap, α_c and α_v are the inverse effective masses of the conduction and valence bands, and $|Pvc|^2$ is the square of the momentum matrix element for the inter-band transition. This expression is essentially similar to that previously obtained[1] using the three-band model, with the simplification that only one matrix element, the inter-band matrix element remains to be specified since we have performed the integration over the intra-band matrix element of zeroth order in $\vec{k}$ which vanishes at an extreme and is equal to the group velocity times the free electron mass.[8]

In order to evaluate the above expression for a specific substance, a knowledge of α_c, α_v, Eg and $|Pvc|^2$ is necessary. However, it can be shown, using $\vec{k}\cdot\vec{p}$ perturbation theory,[9] that the valence and conduction band effective masses at $\vec{k}=o$ can be accounted for by assuming that $|Pvc|^2$ is a constant[10] for all the III-V compounds and is equal to 11.5 eVm. It is instructive to re-express the absorption coefficient in equation (1) in terms of a nonlinear absorption cross-section; taking the above value for the square of the matrix element and assuming $\hbar\omega_1$ and $\hbar\omega_2$ are approximately equal to Eg , one obtains

$$\sigma_2 = \frac{2.6 \times 10^{-48} \alpha_c^2}{n_1 n_2^2 (\alpha_c + \alpha_v)^{5/2}} \cdot \frac{1}{E_g^{5/2}} \ \mathrm{cm.^4 \, sec.} \tag{2}$$

The conduction band effective masses for the III-V compounds are given by $\vec{k}\cdot\vec{p}$ theory as

$$\alpha_c = \frac{m}{m_c} = 1 + \frac{2}{3}\left|P_{vk,ck}\right|^2\left(\frac{2}{E_g} + \frac{1}{E_g+\Delta}\right) \tag{3}$$

where Δ is the spin-orbit splitting at $\vec{k}=0$. Using the experimentally determined values[10] of α_c, E_g, and Δ or the calculated values of α_c from equation (3), and assuming $\alpha_v \simeq 1$, explicit values for the double-photon absorption cross-sections from equation (2) can be calculated. The values σ_2 for some representative compounds are shown in Table I. It is seen that σ_2 increases as the band gap decreases. In the derivation of equation (1), it was explicitly assumed that the absorption occurs via a single intermediate state which allows coupling between the initial and final state. In fact, it is necessary to sum over all possible intermediate states; consequently, this calculation represents a lower bound for σ_2.

Let us now consider the transmission laws obeyed for a medium within which a linear and a quadratic loss process can simultaneously take place. In the steady state, the transmitted flux is given by the continuity equation:

$$\nabla\cdot F = -\sigma_1 F N_1 - \sigma_2 F^2 N_2 \tag{4}$$

where σ_1, is the linear absorption cross-section in units of cm^2, σ_2 is the double-photon absorption cross-section in $cm^4 sec$, N_1 and N_2 are the density of centers responsible for the single and double-quanta process, respectively, and F is the flux in photons/cm^2/sec.

We shall assume that N_1 and N_2 are independent of F, i.e., the lifetime for recombination to the ground state is short compared to duration of the light pulse. For a plain parallel state of thickness r and neglecting reflection losses, the transmission = F/F_0 is given for:

$$\text{Plane:} \quad \frac{F}{F_0} = \frac{\sigma_1 N_1 r}{\exp(\sigma_1 N_1 r)\left[\sigma_1 N_1 r + \sigma_2 N_2 r F_0\right] - \sigma_2 N_2 r F_0} \tag{5}$$

Similar results can be obtained for spherical and cylindrical geometry where for simplicity we neglect σ_1 in these cases:

$$\text{Spherical:} \quad \frac{F}{F_0} = \frac{1}{\sigma_2 N_2 \frac{r^2}{r_0^2} F_0 + \frac{r^2}{r_0^2} - \sigma_2 N_2 \frac{r}{r_0} F_0} \tag{6}$$

$$\text{Cylindrical:} \quad \frac{F}{F_0} = \frac{1}{\sigma_2 N_2 r F_0 \ln r + \frac{r}{r_0} - \sigma_2 N_2 r F_0 \ln r_0} \tag{7}$$

It is seen from equations (5), (6), (7), that for high incident intensities the transmission saturates for all geometrics.

Figure 1 shows a plot of the absorption $A = 1 - F/F_0$ for the plain geometry for a medium having linear and quadratic lows processes simultaneously present. When the parameter $\sigma_2 N_2 r\ F_0$, the quadratic loss process becomes dominant and the transmission ultimately saturates, showing that there is an intrinsic upper limit to the power density that can be transmitted for a multiphoton process. It should be noted that only the linear absorption process yields an exponential fall-off of the intensity with distance, while the quadratic and higher order processes will fall off inversely proportional to the product of the distance and intensity.

It is of interest to consider the regime of intensity where the double-photon process will become dominant in semiconductors. Although semiconductors injection lasers have less power output compared to most optically pumped solid state lasers, they are relatively small area devices so the flux per unit area are still quite high at the emitting junctions. Furthermore, the emitted frequencies lie slightly below the band-gap, satisfying the threshold conditions for double-photon absorption. Considering a GaAs diode of length 0.1 cm and using σ_2 , the intrinsic upper limit to the power output from GaAs should not exceed 10^9watts/cm^2; similar results were obtained for GaAs[11] using a theory of Keldysh[12] even if an electron-hole pair created by double-photon absorption subsequently recombines and re-emits a photon, two quanta will be annihilated to produce one subsequently re-emitted quantum. Since $\sigma_2 \sim 1/E_g^{5/2}$, this process will set in at lower power densities for the lower gap materials. Q-switching, in the attempt to yield higher power densities, will not circumvent the double-photon loss mechanism.

The fact that double-photon absorption is proportional to the product of the intensity and length of path in the medium, indicates that it is an effective means of volume generation of electron-hole pairs to induce laser action as opposed to single-quanta pumping of semiconductors where high generation rates are limited to surface regions of semiconductors as was experimentally demonstrated for CdS[7], GaAs[3], PbTe[5]. The results of the above calculation show that the appropriate semiconductor can also be used as an effective nonlinear optical power limiter.

Although the considerations in this rate were directed to the case of double-photon inter-band transitions similar considerations apply to transitions between discrete levels in a solid, gas, or liquid. In the case of the propagation of a laser beam through a gaseous atmosphere, if care is not taken so that no state exists at twice the laswer frequency to which double-quanta absorption can take place, there is an intrinsic upper limit to the power density that can be transmitted through such an atmosphere. Although we would normally consider only multiphoton absorption in cases where high intensity lasers are available, the fact that absorption for this process is proportional to the length of path and the intensity, such nonlinearities may manifest themselves in a number of astronomical cases where exceedingly long paths are involved such as the case of a planetary nebula or propagation through inter-stellar hydrogen.

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Figure Captions

Figure 1. Tranmission law for a medium with linear and quadratic losses simultaneously present.

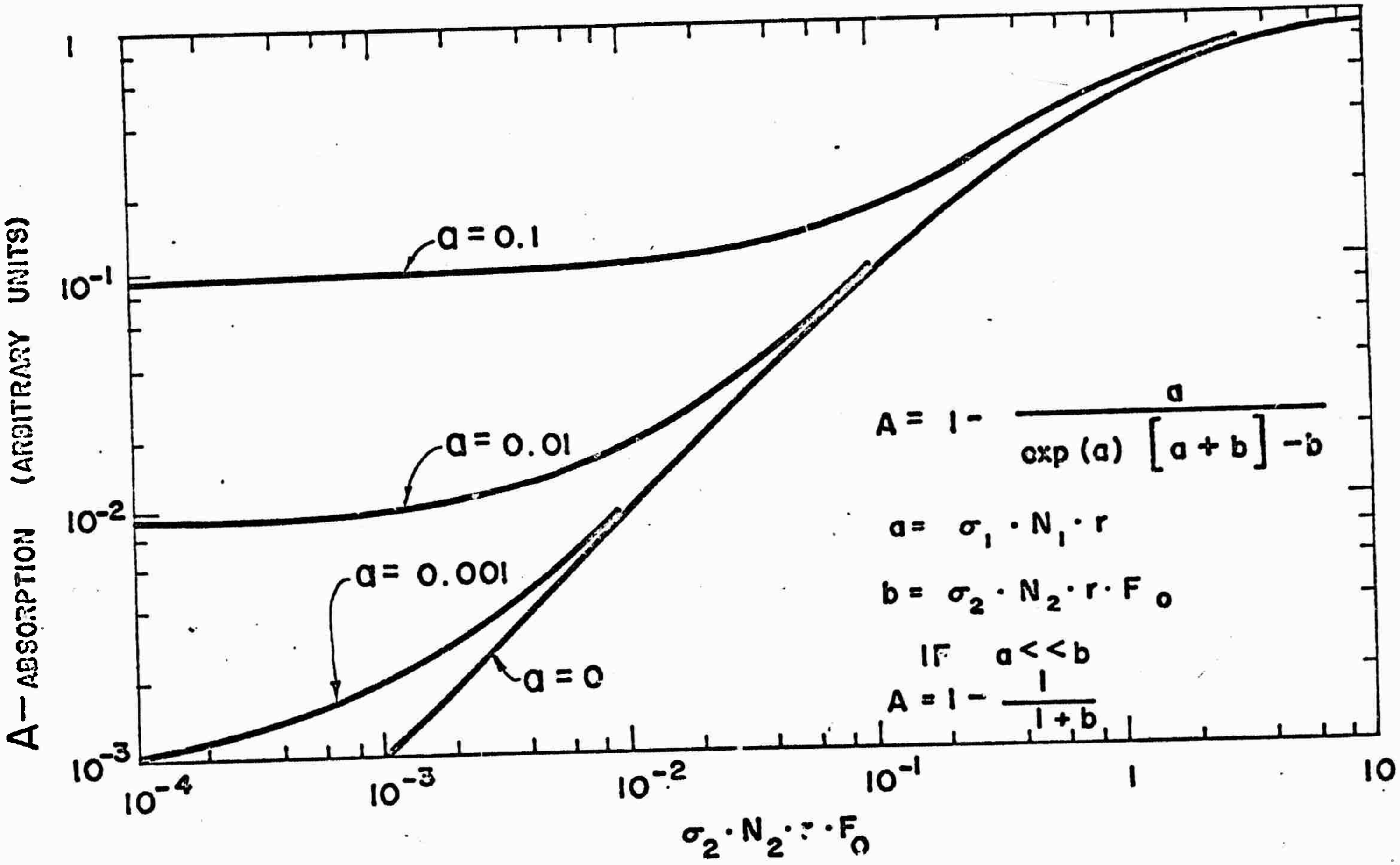
A — ABSORPTION (ARBITRARY UNITS)
1
10^-1
10^-2
10^-3
10^-4
10^-3
10^-2
10^-1
1
10
$\sigma_2 \cdot N_2 \cdot r \cdot F_0$
a = 0.1
a = 0.01
a = 0.001
a = 0
$A = 1 - \frac{a}{\exp(a)\left[a+b\right]-b}$
$a = \sigma_1 \cdot N_1 \cdot r$
$b = \sigma_2 \cdot N_2 \cdot r \cdot F_0$
IF $a << b$
$A = 1 - \frac{1}{1+b}$

Table I

Band parameters and calculated double-photon absorption cross-sections.

	GaAs	InP	InAs	InSb
E_g – eV	1.53	1.34	0.45	0.25
a_c –	13.3	15.2	38.5	65.5
Δ –	0.33	0.24	0.43	0.84
σ_2 – $cm^4 sec$	2.8×10^{-49}	3.7×10^{-49}	4.0×10^{-48}	1.4×10^{-47}

V. DOUBLE-PHOTON PUMPING OF A GaAs LASER

Preliminary measurements were made of the two-photon absorption cross-section in GaAs ($E_g = 1.51$ ev) using a Q-switched neodymium blass laser ($\hbar\omega = 1.17$ ev). The fluorescence excited by the 1.17 ev photons absorbed in GaAs centered at 8365 Å. The sample of GaAs was a rectangular slab 5 mm x 5 mm x 9 mm with end surfaces polished flat to form a plane-parallel cavity and was directly immersed in liquid nitrogen. The unfocused laser beam was incident normal to the polished faces and longitudinal to the long direction of the sample. An incident power densities of 50 megawatts/cm^2, the line narrowed to < 10 Å at 8365 Å and yielded a power output of one megawatt/cm^2; this beam seemed to have very little divergence. These manifestations indicated that we were obtaining double-photon pumping and subsequent laser action in GaAs. At these power levels excitation was probably occurring throughout the volume of the sample through which the laser beam was passing. The incident neodymium laser pulse width was ~ 40 nsec., while the output pulse at 8365 Å from GaAs was < 40 nsec. wide.

The photoconductivity of the GaAs sample was measured as a function of incident intensity. This was evidence that a double-photon absorption was the exciting mechanism; this alone is not conclusive evidence for double-photon absorption since the lifetime of the generated carriers can be a function of incident intensity. However, the superlinearity of the flourescence and evidence of laser action induced by photons of energy $\hbar\omega = 1.17$ ev in a material of $E_g \approx 1.51$ ev are all good circumstantial evidence for double-photon pumping.

Since the double-photon cross-sections seemed encouragingly large, it was decided to concentrate effort in the direction of trying to observe double-photon stimulated emission at the difference frequency 1.51 ev - 1.17 ev = 0.34 ev. It was also decided to turn our attention to the use of stimulated Raman lines produced in benzene so as to obtain pairs of convenient lines, one for single quanta primary of GaAs to obtain a population inversion, the other to induce double-photon stimulated emission at the frequency differences between the energy gap and the line below the energy gap.

While this work was in progress an extremely interesting temperature dependent anomally of the threshold for stimulated Raman in benzene was observed. Since such a temperature anomaly was not previously reported, it was decided to investigate this phenomena in some detail, before returning to the problem of double-photon stimulated emission. The results of the temperature dependent anomaly in benzene are discussed in Section VI.

VI. STIMULATED RAMAN EMISSION IN BENZENE AND ITS TEMPERATURE BEHAVIOR

A new temperature anomaly of the threshold for stimulated Raman emission in liquid benzene was discovered and investigated. The results of this work are presented in the accompanying reprints in this section.

Since the publications only contain cursory reference to the experimental set-up used in these investigations a more detailed description will now be presented.

Experimental Conditions

To perform the present research, an unfocused output from a giant pulse ruby laser is used. The dimensions of the ruby crystal are 6" long by 9/16" in diameter. The laser is Q-switched by a rotating prism, providing a two joules pulse with a 25 nanosecond half-width. Inclusion of a sapphire mode selector in the cavity insured a single longitudinal mode output. The cavity is generally 50 cm. long. For the present experiment, we used a diaphragm of 4.2 mm located inside the cavity just in front of the rotating prism.

The Raman cell used in this experiment is 67 cm long, terminated by two optically flat quartz windows. A water jacket surrounding the cell enabled the setting of very precise and stable temperatures. The temperature was varied between 15°C and 40°C. At each temperature setting, a very long time was allowed to elapse so as to attain thermal uniformity throughout the cell. Even at uniform temperatures, the laser shots were separated by an interval of two minutes for absolute reproducibility (a lot of molecules, broken by the laser filaments, must be removed by dilution). However, the temperature wasn't measured directly inside the benzene, but in the water jacket. There could be a slight difference between these values.

The normal optical setup is shown in Figure 7A for the detection of the 8,050 Å and 1.07μ lines. The fluorescence of the filters (7-56 or 7-69) was avoided by using part of the beam reflected by a concave glass reflector, which is the equivalent of a neutral density filter of 2.0. Additionally, the dispersion of the quartz prism gave us the possibility of focusing the laser and all of the anti-Stokes lines far form the slit of the monochromator, where the line of interest was focused. This technique improves the performance of the monochromator, which has a scattered light value of 10^{-5}.

The monochromator is a vacuum model Jarrell-Ash and it is absolutely light tight. In the output of the monochromator, we used two different detectors: an RCA 7102 photomultiplier or an SD-100 photodiode (for maximum time resolution). The coupling from the photomultiplier to a 93 ohm cable is made by a transistorized total feedback, high impedance, and low capacitance input element. A Tektronix 547 oscilloscope, triggered by the laser pulse, is used to display the output signal.

To be sure that possible temperature dependent effects on the stimulated Raman lines are not due to some interferential pattern of the cell output, we have been using a large area detector (Photomultiplier 7102) in the configuration shown in Figure 7C, both close to and far from the output of the cell. The results were the same.

The photodiode has been used, in the configuration shown in Figure 7B, for maximum time resolution.

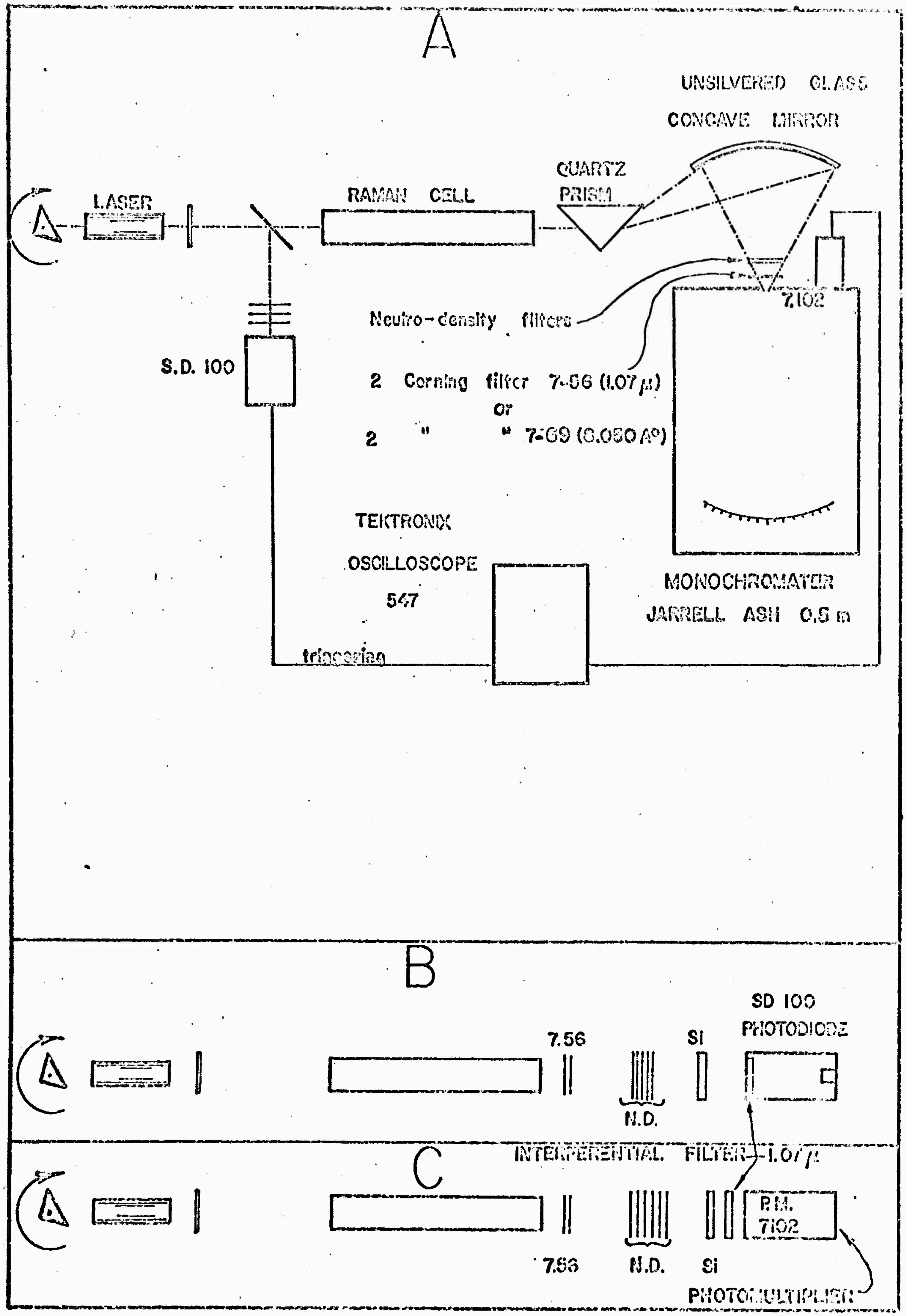
A
UNSILVERED GLASS
CONCAVE MIRROR
QUARTZ
PRISM
LASER
RAMAN CELL
7102
Neutro-density filters
S.D. 100
2 Corning filter 7-56 (1.07 μ)
or
2 " " 7-69 (6.950 A°)
TEKTRONIX
OSCILLOSCOPE
547
MONOCHROMATER
JARRELL ASH 0.5 m
triggering
B
SD 100
PHOTODIODE
7.56
Si
N.D.
INTERFERENTIAL FILTER 1.07 μ
C
P.M.
7102
7.56
N.D.
Si
PHOTOMULTIPLIER

FIG. 7

A NEW MULTIPHONON STIMULATED RAMAN LINE IN BENZENE *

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Received 21 August 1967

A new multiphonon stimulated Raman line at 1.07μ in benzene is reported. Its critical power is about 100 MW cm^{-2}. This line is better understood in terms of light feed-back theory than in terms of self-focusing.

We have observed a new stimulated Raman line at 1.07μ in benzene. Since the discovery of the stimulated Raman effect by Woodbury [1], benzene has been extensively studied. A Raman cell of 67 cm length and an unfocused laser beam (single mode Q-switched ruby) of 4.2 mm in diameter were used in our experiments. Under these conditions, the threshold power of the first and second Stokes of the 992 cm^{-1} phonon is around 15 MW/cm^2. At higher laser power, a new stimulated Raman line appears at 1.07μ. Involved in this line, together with the laser photon of 6943 Å, are two phonons of 992 cm^{-1} and one phonon of 3064 cm^{-1}. The main characteristic of this line is that the laser threshold power is as high as 130 MW/cm^2. The presence of two stimulated Raman processes in the same liquid occurring at two well separated power thresholds is an indication of the failure of the self-focusing theory to explain the stimulated Raman threshold.

It has been predicted [2, 3] that above a critical power level, because of self-focusing in a medium, a laser beam can be trapped in a diameter of a few microns independently of the original beam diameter. A photograph of Hauchecorne and Mayer [4] shows the existence of some high intensity filaments of very short lifetime in liquids. If the laser beam is trapped, a power density could be reached of such magnitude that the threshold for all lines would be attained simultaneously; but that is not the case in the present experiment. While it is believed [5-7] that self-focusing could explain most of the puzzles of the stimulated Raman effect, Maier, Stein and Kaiser [8] found two lines at two different thresholds in single crystal naphthaline without any self-focusing. Even in liquids there is some doubt about its validity, especially in mixtures where it has been reported [9] that stimulated Raman takes place at a higher threshold power than is required by the self-focusing in the mixture.

On the other hand, if the "Woodbury laser" is really a stimulated effect having a positive light feedback, the general properties of the feedback theory should be verifiable. For an amplifying medium having a nominal gain $G_0(\lambda, T)$ and a

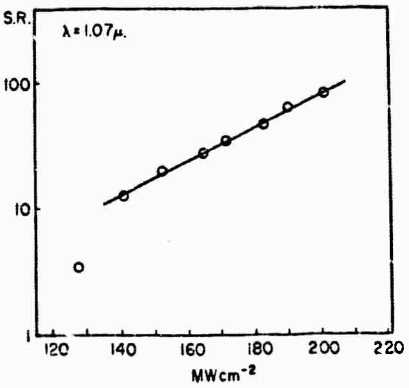

Fig. 1. Semi-log plot of the stimulated Raman line (1.07μ) output power versus incident ruby laser power density.

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feedback β, the total gain of the medium is

$$G(\lambda, T) = G_0(\lambda, T)\,[1-\beta G_0(\lambda, T)]^{-1}. \qquad (1)$$

For $1-\beta G_0(\lambda, T) > 0$, we have a regenerative Raman amplifier. The threshold for the amplifier to become a Raman oscillator is $1-\beta G_0(\lambda, T) = 0$.

In a simplified approach we can say that the nominal gain $G_0(\lambda, T)$ of a Raman cell is proportional to: the laser power density P, the length of the cell, l, a function $F(\lambda, T)$ which describes the stimulated Raman behavior of each line at different temperatures and a coefficient, A, relating the interaction of the laser beam and the liquid. The feedback β is expressed as $\beta = Bl$, since the probability for a photon to stimulate another one is proportional to the distance it travels in the active medium. The threshold condition gives the threshold power (P_{th}) of the stimulated Raman effect in the cell and we have:

$$P_{th}^{\frac{1}{2}}(\lambda, T) = (ABF(\lambda, T))^{\frac{1}{2}}\, l^{-1}. \qquad (2)$$

Since for an infinite length cell, the onset of the stimulated Raman, as opposed to the normal Raman, needs a critical power density (P_{cr}) for the threshold, the last expression should be completed as follows:

$$P_{th}^{\frac{1}{2}}(\lambda, T) = P_{cr}^{\frac{1}{2}}(\lambda) + [ABF(\lambda, T)]^{\frac{1}{2}}\, l^{-1}. \qquad (3)$$

Each stimulated Raman line may have a different critical power depending on the exact mechanism taking place inside of the molecule. The 1.07μ line has a very high critical power density (about 100 MW/cm^2). Eq. (3) is the type of relation verified by Wang [6]. Kelly's equation [5] for self-focusing is similar to eq. (3) but a criterion other than the stimulated Raman onset [6] should be used in attempting to verify it.

Below the threshold, according to eq. (1) the gain of the regenerative Raman amplifier is

$$G(\lambda, T) = \frac{APl\; F(\lambda, T)}{1-ABPl^2\; F(\lambda, T)}\,. \qquad (4)$$

For constant laser power density and varying cell length, data [10] fit expression [4] better than the exponential gain dependence reported [10].

Above the threshold, the stimulated Raman output, W, can be calculated taking into account the stimulation effect. For a uniform laser power density P, in a cell of length l, S being the stimulation coefficient, α relating the laser power to the density of particles in excited states and being a constant depending upon units, the stimulated Raman output is given by

$$W = K\exp(\alpha SPl)\,. \qquad (5)$$

Fig. 1 shows a semi-log plot of the output of the 1.07μ line vs. laser power; a straight line between 130 MW/cm^2 (threshold) and 210 MW/cm^2 is obtained, indicating that the output of this line is controlled by the light feedback above the threshold.

The stimulated Raman output and threshold, and even the regenerative amplifier, are better understood in terms of a feedback amplifying medium than in terms of self-focusing for this line. Elsewhere, we will report on the temperature behavior of the stimulated Raman lines of benzene and the associated mechanism.

The authors wish to thank D. Fink and M. Welkowsky for their assistance in these experiments.

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CYCLIC TEMPERATURE DEPENDENCE OF THE STIMULATED RAMAN EFFECT IN BENZENE*

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(Received 5 September 1967)

The cyclic temperature dependence of two stimulated Raman lines of benzene is reported. These data are inconsistent with the self-focusing theory for the anomalous gain.

We report an unprecedented cyclic temperature dependence of the 1.07-μ and the 8050-Å stimulated Raman lines in benzene. The 1.07-μ is a Stokes line, previously reported,[1] which is created by the interaction of the parallel ruby laser beam with two phonons of 992 cm^{-1}, and one phonon of 3064 cm^{-1}. The 8050-Å is the second Stokes line of the 992-cm^{-1}. Figure 1 shows the characteristic cyclic temperature dependence of the aforementioned lines.

An unfocused beam of a single-mode Q-switched ruby laser was used in these experiments. The laser-beam diameter was 4.2 mm. The 67-cm-long Raman cell was terminated by two optically flat quartz windows. A water jacket, surrounding the cell, enabled the setting of precise and stable temperatures. Sufficient time was allowed to attain temperature uniformity throughout the cell and the laser shots were separated by an interval of 2 min for reproducibility. The lines were separated from the transmitted ruby by a combination of quartz prism and uncoated concave mirror before entering a half-meter monochromator to which the detector was attached.

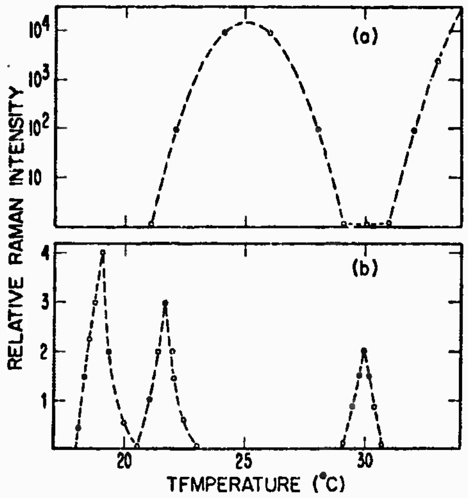

FIG. 1. (a) The relative intensity at 8050 Å as a function of the benzene cell temperature; incident power density at 6943 Å is 70 MW/cm^2. (b) The relative intensity at 1.07 μ as a function of the benzene cell temperature; incident power density at 6943 Å is 140 MW/cm^2.

We summarize here the results for the two lines of benzene mentioned above. The output at 8050 Å shows a maximum between 25 and 26°C and a minimum around 30°C. The intensity change between the maximum and minimum has been measured to be as high as four magnitudes. The data of Fig. 1(a) were taken with a constant laser power density of 70 MW/cm^2. Upon the increase of the laser power density up to 100 MW/cm^2, the position and amplitude of the maximum and minimum of the output remained the same as shown in Fig. 1(a), only the area under the curve increases. Upon the decrease of the laser power to 60 MW/cm^2, the only change is that the area under the curve decreases and the peak becomes sharper, but its position and amplitude remain unchanged.

The temperature behavior of the above line is an indication of a precise molecular mechanism being responsible for the stimulated Raman generation. A careful study of the 1.07-μ line underlines this assertion. Indeed, the 1.07-μ line showed a very specific and different temperature dependence. The data of Fig. 1(b) were taken with a constant laser power density of 140 MW/cm^2, just above the threshold for this line. Figure 1 shows the cyclic temperature dependence of the intensity at 1.07 μ, completely different from the curve of Fig. 1(a) in the amplitude, separation, and position of the maxima.

The fundamental problem in understanding the stimulated Raman processes in liquids is to account for the anomalies in the observed gain for this process. That the observed Raman gain is one or two orders of magnitude greater than the theoretical estimates[2] obtained from spontaneous-Raman-scattering data has led to a number of investigations by several groups[2-5] with several proposed explanations for this discrepancy. It was first suggested that the anomalous gain might be the result of the multimode structure[6-8] of the laser pumping beam. However, experiments[2] with a single-mode laser beam still revealed the presence of anomalous gain. Experiments[9] have shown the presence of high-intensity filaments during the propagation of a laser beam through Raman-active liquids. The formation of such filaments by the self-focusing[10,11] of the laser beam is believed to be responsible for the lowering of the threshold for stimulated Raman emission.[12] Since the stimulated Raman emission takes place only after the laser beam has traveled some distance in the medium, Kelley[13] proposed that there is a self-focusing distance. The experiments of Wang[14] have indicated the existence of such length-dependent thresholds. Most of the experiments and their theoretical interpretation up to now seem to indicate that the observed thresholds for stimulated Raman emission are determined by the changes in the structure of the laser beam due to self-focusing[11-14] or other beam deterioration interactions[15] rather than the value of the Raman susceptibilities.

The following salient features of the present experiments seem to be inconsistent with the self-focusing explanation for the anomalous gain in Raman oscillators:

(1) We have found the threshold power of the 8050-Å line to be about 15 MW/cm^2 at 25°C, while even with filaments existing, the 1.07-μ line has a power threshold[1] of at least 130 MW/cm^2.

(2) Even with an input power density of 70 MW/cm^2, the condition at which the data of Fig. 1(a) were taken, there is no stimulated Raman output at 20 and 30°C, while the 1.07-μ data of Fig. 1(b) show a minimum at a different temperature.

It is clear that each of these temperature dependences reflects a precise molecular behavior of the benzene molecule for each of these lines. It is impossible to include such different temperature behaviors on the self-focusing capabilities of benzene since its governing equation must be unique.

The authors wish to thank D. Fink and D. Hon for their assistance in these experiments.

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FINE STRUCTURE PERIOD OF THE THERMO-SPECTRUM OF THE STIMULATED RAMAN 8050 Å LINE IN BENZENE *

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Received 12 August 1968

A fine structure of 2.2°C period on the thermo-spectrum of the 8050 Å stimulated Raman output in benzene is reported, in addition to the previously reported large period.

We have previously reported evidence of a cyclic temperature dependence of the stimulated Stokes lines of benzene [1]. In that report it was shown that the 8050 Å output which is the Stokes line of the ruby laser and 2 × 992 cm^{-1} phonons, had a large period of about 8°C. The 1.07 μ multi-phonon Stokes [2] **, output which involves, in addition to the aforementioned phonons, the 3064 cm^{-1} phonon of benzene, had a 2.7°C period in the region of 20°C [1]. In another investigation, the output of the stimulated infrared emission from optical phonons as a function of the temperature of benzene again showed a peak at 25°-26°C and another at 17°C indicating that this large period is associated with the 2 × 992 cm^{-1} optical phonons [3]. Now, having refined our experimental arrangement, we have found evidence of a shorter periodicity of 2.2°C on the 8050 Å output, in addition to the previously reported large period.

The experimental setup was the same as in ref. 1 except that the laser stability had been improved to be better than 2%, and the addition of a precision temperature control unit which allowed the rate of temperature change to be precisely controlled. The ruby laser pump power density was maintained at 60 MW/cm^2, the cell length was reduced to 38 cm. The temperature of the cell was raised at a constant speed of one degree centrigrade every six minutes. The laser shots were separated by two minute intervals, that is 0.3°C.

If we assume the period is proportional to wavelength, a linear extrapolation of the 1.07 μ output temperature period gives 2.18°C as the temperature tuning period for 8050 Å line. Experimentally, fig. 1 shows several periods that at the precision of the data have a value of 2.1°C to 2.2°C, which is in good agreement with the predicted value.

In the data of fig. 1, one could distinguish two parts: a constant level of the stimulated Stokes

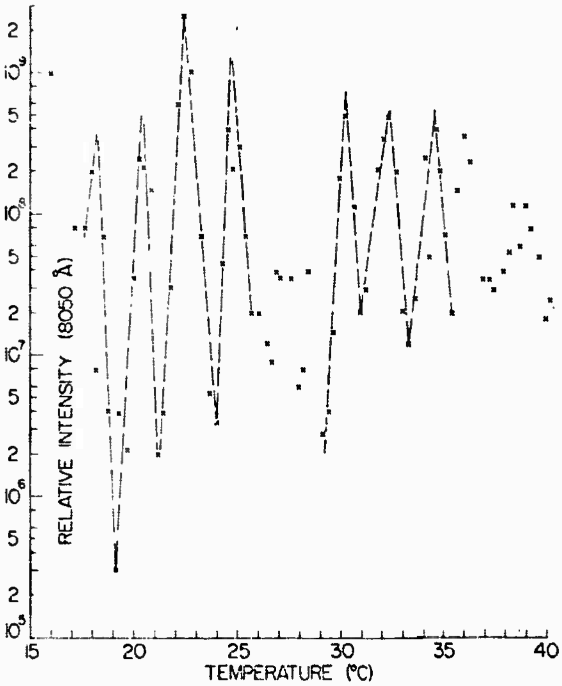

Fig. 1. Relative stimulated Raman intensity versus temperature in benzene, cell length: 38 cm; laser power: 60 MW/cm^2.

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** In ref. 2 a minus sign has been omitted in eqs. (2) and (3), they should read

$$P_{\mathrm{th}}^{\frac{1}{2}}(\lambda, T) = [ABF(\lambda, T)]^{-\frac{1}{2}}\, l^{-1} \qquad (2)$$

$$P_{\mathrm{th}}^{\frac{1}{2}}(\lambda, T) = P_{\mathrm{cr}}^{\frac{1}{2}} + [ABF(\lambda, T)]^{-\frac{1}{2}}\, l^{-1} \qquad (3)$$

line of about 5×10^6 on the scale of relative amplitude and a temperature dependent output from 5×10^6 to about 5×10^8. The temperature behavior could be viewed as the manifestation of a regenerative amplifier with the constant Stokes power as its input. In the range of our investigation the line shape of the thermo-spectrum depends upon the total gain of the regenerative amplifier [2], while the position of the peak depends only on the temperature dependent mechanism taking place in the molecule of benzene. In this experiment the maximum of the total gain was estimated from the experimental data to be of the order of 100.

In order to observe the present temperature dependent phenomenon, it is absolutely necessary to maintain amplifier below saturation. Thus after choosing the ruby pumping power density (60 MW/cm^2 in this case) we still have the possibility of reducing the cell length, decreasing at the same time the Stokes input level and the gain of the amplifier. In this experiment, the cell length was reduced to 38 cm (as compared to larger lengths in previous work [1, 3]. If one increases the cell length, all the other parameters being the same, the temperature variation of the output is drastically reduced, or annihilated, by saturation effects. In the low gain regime, as for the 1.07 μ line [1] and especially the 5 μ line [3] the temperature dependent phenomenon was observed even though the cell was 80 cm long.

The present observation of a fine structure period of 2.2°C on the thermo-spectrum of the 8050 Å (laser - 2 × 992 cm^{-1}) stimulated Raman line in benzene, in addition to the large period of 8°C, as well as the previously observed period of 2.7°C for the 1.07 μ (laser - 2 × 992 cm^{-1} - 3064 cm^{-1}) line further indicates that a precise molecular mechanism is responsible for the thermo-spectrum.

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DOUBLED THERMO-SPECTRUM OF THE 8050 Å STIMULATED RAMAN LINE IN BENZENE *

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A doubled thermo-spectrum of the 8050 Å stimulated Raman output in benzene is reported. The observed doubled period of 2.2°C indicates that a specific molecular interaction is responsible for the cyclic temperature dependence of the stimulated Raman output.

We have previously shown [1] that the 8050 Å (laser - 2×992 cm^{-1}) stimulated Raman line of benzene exhibits a cyclic temperature dependency with a peak at 25° - 26° in its thermo-spectrum. The thermo-spectrum of the stimulated emission output at 5μ (2×992 cm^{-1}) from optical phonons has shown the same peak [2]; consequently it appears that the 2 × 992 cm^{-1} optical phonons are responsible for this peak. Further investigation [3] of the thermo-spectrum of the 8050 Å line revealed a fine structure period of the order of a 2.2°C. Even though a fine period can be clearly distinguished in this previous work [3] it appeared that either there was too much scatter in the data or that there was even more detail which would be revealed with a higher temperature resolution. The present work has indeed revealed a doubled period of 2.2°C of the 8050 Å line.

The general experimental setup used in this work was the same as in ref. [1]. The call length was 38 cm and the ruby laser pumping power density had a stability of better than 2%. The temperature of the benzene cell was raised at a constant speed by equidistant steps of 0.025°C. The laser shots were separated by two minute intervals. As usual in our technique of thermo-spectrometry, after choosing the cell length and ruby laser pumping power density, we recorded the straight forward intensity of the stimulated Stokes Raman output as a function of the temperature of the benzene cell.

Fig. 1 shows the spectrum taken at a power density of 60 MW cm^{-2} and an 0.3°C temperature interval. The data of fig. 2 were obtained with an 80 MW cm^{-2} pump power density and an 0.2°C interval. One can distinguish a 2.2°C period in the data of fig. 1 with some scatter or possibly partially resolved lines. The spectrum of fig. 2 looks much more complicated than the 2.2°C period of fig. 1. However, a careful examination of fig. 2 shows that there is the same periodicity though now for every other peak. It seems we are now getting, under these experimental conditions, a doubled spectrum. At the same time, the deeper

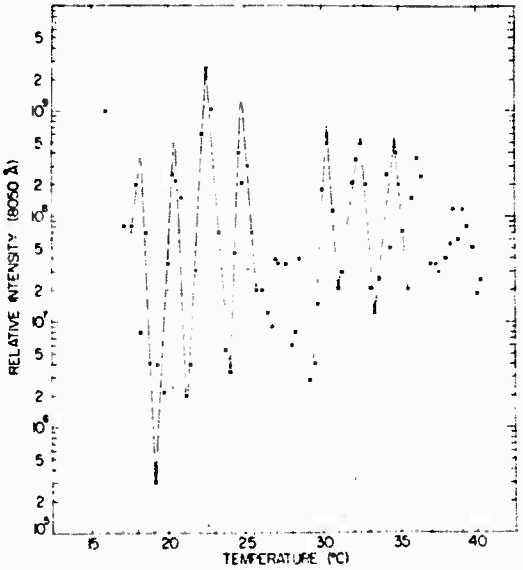

Fig. 1. Relative stimulated Raman intensity at 8050 Å in benzene, cell length: 38 cm: laser power: 60 MW cm^{-2}. Data taken at 0.3°C intervals.

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* This research was supported by the U.S. Office of Naval Research under Contract No. NONR-233(93).

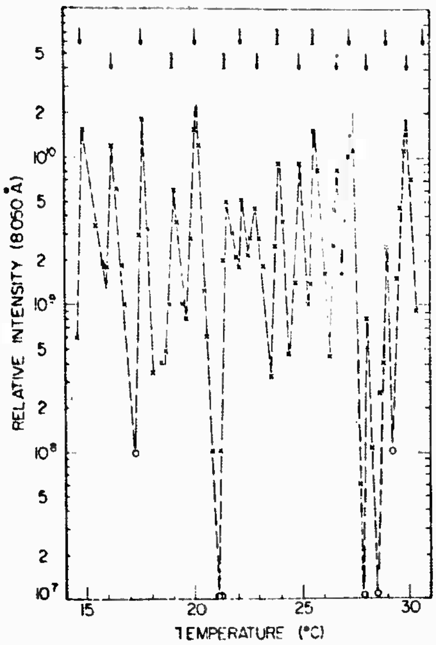

Fig. 2. Thermo-spectrum of 8050 Å line in benzene, cell length: 38 cm: laser power: 80 MW cm^{-1}. Data taken at 0.2°C intervals. (Each line of arrows indicates the fine temperature period of the alternating peaks.)

minima at 21°C and 28°C look very familiar since it is exactly there that the minima [1, 2] of the 2×992 cm^{-1} emission occur, independent of cell length and laser power. The loss of periodicity in the intensity of the spectrum between 21° and 23°C in fig. 2 is due to an accidental temperature backlash of 0.5°C that disturbed the temperature homogeneity.

For the 1.07μ multiphonon stimulated Stokes line [4], we found a period of 2.7°C in the 20°C region. It is interesting to note that the three peaks of the 1.07μ (laser - 2×992 - 3064 cm^{-1}) reported in ref. [1] are in good periodical position if one assumes that two peaks are missing in the 25°C region where the maximum of the strong 2×992 cm^{-1} mode [1, 2] occurs. It appears that the period of the 2×992 cm^{-1} line manifests itself even in the 1.07μ line by suppression of the expected peaks at 25°C and 17°C.

So far, the thermo-spectrum of benzene at different wavelengths follows a consistent pattern. The different temperature periods have been: 2.7°C at 1.07μ, 2.2°C at 8050 Å, and 2.0°C at 7456 Å [5], with no detectable dispersion of the successive peaks within our experimental precision, in the temperature range of these experiments; however, there is some dispersion for the 7° to 8°C period of the 5μ [2]. These periods are defined between 20° and 30°C, below 20°C there is an increase of the thermo-period.

The results of these experiments are a very strong argument against explaining the temperature behavior by any mixing, traveling wave generation, or phase matching theory, but are in favor of a localized interaction; whereby the vibrational mode generated in each molecule interacts with electrons in the benzene bonds and modulates the density of the π-electron streamers. The hydrogen-carbon vibrations (3064 cm^{-1}) in the plane of the molecule seems to be less efficient than the carbon-carbon vibrations (2×992 cm^{-1}) in this process; the higher critical power [4] of the 1.07μ line is an argument for the less efficient interaction of the 3064 cm^{-1} phonons.

The observation of a doubled thermo-spectrum of the 8050 Å line in benzene leads us to believe that the overtone on the thermo-spectrum of this Stokes line is associated with a very precise molecular mechanism. It could be a new type of molecular orbital electronic resonance. We have chosen benzene in our investigation because of the symmetry of the molecule and the known overlapping of the π-orbitals. One would expect to see a thermo-spectrum for benzene derivatives, enabling further study of intra-molecular interactions. Very possibly, other types of molecules could also yield such thermo-spectra.

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VII. Infrared Emission from Coherently Driven Optical Phonons

A great many of the studies of stimulated Raman scattering have been concerned with the anomalies associated with such parameters as the Raman gain, the anti-Stokes and Stokes emission angles, the importance of regeneration and the ratio of forward to backward output. The practical application of the process has been as a source of intense, pulsed monochromatic radiation over a wide range of wavelengths derivable from a single laser wavelength. The fact that in addition a high level of excitation of the optical branch of the lattice vibrations occurs during stimulated Raman scattering has hardly been exploited. The existence of such intense sources of coherent optical phonons leads one to consider their utilization in a number of subsidiary interactions. The possibility of observing infrared emission from these coherently driven optical phonons has been discussed at various times in the literature. However, up to the present work no experimental observation of this effect had been reported.

One may consider the process of the emission of infrared radiation from optical phonons as a parametric interaction in which the laser frequency serves as the pump, the Raman scattered frequency as the idler and the generated difference frequency as the signal. Since the stimulated Raman scattering results in a highly efficient conversion of laser photons to Stokes photons, a high level of generation of optical phonons accompanies the process. If the substance lacks a center-of-inversion infrared emission at appropriate phonon frequencies should be observable provided the momentum matching conditions between the incident laser frequency, the Stokes frequency and the generated infrared difference frequency can be satisfied.

Our previous work on the temperature dependence of the stimulated Raman output in benzene indicated that we were observing a parametric type of interaction where the phase matching was obtained by temperature control of the Raman cells. It was consequently decided to look for infrared emission at appropriate Raman frequencies, despite the fact that many of the vibrational modes of liquid benzene are Raman-active but infrared-inactive

Accompanying the stimulated Raman process in benzene, infrared emission at 5 microns was observed and the variation of intensity with temperature was measured. The thermospectrum of the 8050Å stimulated Raman line, which involves a shift of 2 x 992 cm^{-1} from the laser frequency peaks at the same temperature as the 5 micron line, indicating that both lines involve the 2 x 992 cm^{-1} plasma.

The results of this work are described in the accompanying reprint in this section.

Symmetry arguments indicate that the 992 cm^{-1} mode and its harmonic are Raman-active, but infrared-inactive and hence should not couple to the radiation field. However, benzene has a strong infrared absorption band at 1955 cm^{-1}, which is due to a combination of the 985 – and the 970 cm^{-1} vibrations. The limited resolution of our detecting system precluded the possibility of distinguishing between 1955 cm^{-1} and 1984 cm^{-1}. The experimental arrangement for this work has been previously described in the section in the temperature behavior of the stimulated Raman thresholds.

A point of considerable interest is the observation that the emission at 5 microns was observed despite the fact that the absorption coefficient is $K \sim 40$ cm^{-1} for this wavelength and for a cell 60 cm long one would normally expect self-absorption to obviate the observation of the radiation.

This would indeed have been the case for spontaneous emission generated along the laser beam path. However, during stimulated Raman scattering coherent phonons are generated and by virtue of the temperature dependency of the above lines appropriate phase matching conditions are obtained. One might say we have established a condition of "induced transparency" engendered by the coherently driven optical phonons.

Benzene is not the ideal choice to study the generation of infrared emission from coherently driven optical lattice vibrations since most of the vibrational modes which are Raman-active are infrared-inactive. A more appropriate choice would be one of the large band-gap III-V compounds. In single crystal material, it should be possible to obtain phase matching by appropriate orientation with respect to the crystal-axes. In addition it would be desireable to use appropriate independent pairs of probe beams to measure the dispersion of the generator infrared difference frequency, rather than depend upon the mixing between the laser and the Stokes frequency.

The present work indicates that the utilization of the coherent phonons generated in the stimulated Raman process should be a fertile area of research. Aside from the observation of infrared emission from these phonons, considerations such as the study of phonon-phonon interactions and phonon lifetimes should be rewarding.

STIMULATED INFRARED EMISSION FROM OPTICAL PHONONS*

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(Received 27 May 1968)

The first observation of infrared stimulated emission associated with the optical phonons of a liquid is reported at 5 μ from benzene. The variation of the 5-μ output, as a function of the temperature of the benzene, is the same as the large period of the thermospectrum of the 8050-Å stimulated Raman line, which involves the same optical phonons.

We report the generation of stimulated infrared radiation at 5 μ by phonons from benzene excited by a Q-switched laser. The radiation observed corresponds to 1984 cm^{-1}. The carbon-carbon vibration in the plane of the molecule, 992 cm^{-1}, and its harmonic, 1984 cm^{-1}, have been shown to be strongly active in second order[1-3] and multiphonon[4] stimulated Raman generation.

The experiments were performed with a ruby laser Q switched by a rotating prism. The single pulse output had a half-width of 40 to 50 nsec. We used two different configurations in these experiments. In all runs, the parallel output beam of the laser was used. The temperature of the benzene was controlled by temperature-regulated water circulating in a jacket surrounding the Raman cell.

The first set of runs were performed with a cell, 69 cm long, having a quartz input window and a sodium chloride exit window. The infrared radiation was separated from the laser and stimulated Raman output by a sodium chloride prism, passed through a germanium filter, and was detected by a liquid-helium-cooled Ge:Hg detector. The response time of the detector was about 500 nsec.

The variation of intensity of the 5-μ line as a function of the temperature of the liquid was measured. Figure 1(a) shows the thermospectrum of the 5-μ line for a constant laser-pumping-power density (90 MW cm^{-2}). As a comparison, Fig. 1(b) shows the thermospectrum of the 8050-Å stimulated Stokes line of benzene taken at a slightly lower pump-power density (60 MW cm^{-2}). Both spectra show a peak at about 25-26°C. In previous work,[5] a similar thermospectrum of the 8050-Å line was observed. It should be noted in this comparison that the change in infrared amplitude in this temperature interval is less than an order of magnitude, while the amplitude variation of the 8050-Å line is over four orders of magnitude when measured under proper conditions.

In the second set of experiments, we used an 80-cm long cell with an input window of quartz, but having a barium fluoride output window. The radiation out of the cell passed through a calcium fluoride prism, set in total reflection for the ruby and the Raman lines, while transmitting from 3 to 9 μ. The infrared radiation was focused by a rotatable, 37-cm focal length, front-surface aluminum mirror through a germanium filter to a Ge:Au detector cooled to 65°K. The range of the temperature control unit had been increased to check the validity of the amplitude increase below 20°C as seen in Fig. 1(a). It was necessary to use a higher laser power density (100 MW cm^{-2}) to overcome the lower detectivity of the Ge:Au detector.

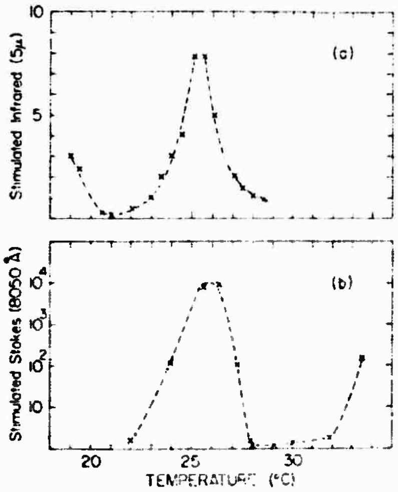

FIG. 1. (a) Relative stimulated infrared output at 5 μ as function of the temperature of benzene. Cell length = 69 cm; laser power density = 90 MW cm^{-2}. (b) Relative stimulated Raman output (Stokes line, 8050 Å) as a function of the temperature of benzene. Cell length = 69 cm; laser power density = 60 MW cm^{-2}.

We again found the maximum of the 5-μ line at 25°C, though broader (the same occurs in the thermospectrum of 8050 Å at increased laser power density[4]). We found, repeatedly, another peak at 17°C with another minimum at 13°C. The 8050-Å Stokes line was found to have a similar structure just above its threshold. In the thermospectrum of the 5-μ line, the amplitude of the 17°C peak is larger than that of the 25°C peak. Similar behavior, i.e., larger amplitude at lower temperature, was noted for the 8050-Å line especially on the runs to reveal a 2.2°C-period fine structure[6] together with the aforementioned large period.

The possibility of observing the process of generation of far-infrared radiation concurrent with stimulated Raman generation has been considered by a number of authors.[7-11] These proposals have considered the situation in which, under stimulated Raman scattering, large-amplitude coherent vibrations will be produced, and if these molecules have an electric dipole moment, infrared radiation will be emitted at the vibrational frequencies.

The idealized benzene molecule is nonpolar and has centro-symmetry D_{6h}. This configuration allows five major operations of symmetry which define the various classes of motion for different fundamental vibrations of the molecule and whether they can be active in infrared or Raman processes. Both 992 cm^{-1} and its harmonic belong[12] to the symmetry class A_{1g} and so are Raman active but infrared inactive. There is experimental evidence which implies that in the liquid, because of intermolecular forces, the structure is slightly changed and the D_{6h} symmetry is not absolutely perfect.[12-14] At low light intensities, as are employed in normal Raman and infrared spectroscopy, the point groups of the molecular vibrational modes are of prime importance in determining the optical properties. But at coherent and high light intensities needed for stimulated Raman generation induced phenomenon may take over producing a radiating dipole moment corresponding to 1984 cm^{-1}.

The infrared stimulated emission is observed despite the absorption ($K \sim 40$ cm^{-1}) of the medium[15] due to background absorption and a strong neighboring absorption band at 1955 cm^{-1}, which has been identified[13] as a combination of the 985- and 970-cm^{-1} vibrations. The large absorption of the medium at 5 μ must first be saturated to allow the stimulated infrared radiation to propagate.

That the thermospectrum of the 8050-Å stimulated Raman line, which involves a shift of 1984 cm^{-1} from the laser frequency, and the thermospectrum of the stimulated-emission line at 5 μ peak at the same temperature indicate that both are due to phonons of 1984 cm^{-1}. Although we have observed optical-phonon-stimulated emission from benzene, such emission should be observable from many liquids, gases, and solids.

We wish to thank Mr. J. Hoover of the Aerojet General Corporation of Azusa, California, for kindly providing us with one of their newly developed, excellent Ge:Hg detectors.

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VIII. DERIVATIVE SPECTROSCOPY

There are a number of applications for which it is desirable to sweep the frequency of a monochrometer at relatively rapid rates. In the case of signal averaging using multi-channel analyzer techniques for detecting weak spontaneous Raman lines, the signal to noise is enhanced proportional to the square root of the number of sweeps through the line. In order to detect very weak narrow absorption lines out of a background of relatively smooth absorption, it would be desirable to obtain the derivative of the absorption since conventional techniques require a highly stable optical detecting system. We have developed a technique which enables us to frequency modulate a spectrometer in any desired spectral range. This technique has rather wide applicability in a number of areas. Since there has been a number of developments in derivative techniques for the study of band structure of solids, we shall describe the present technique in some detail in the context of band structure studies. However, the same methods can be used to measure small narrow absorption bands in liquids and gases.

During the past few years, several new techniques[1-7] have been developed which have made it possible to determine the singularities in the density of states for optical transitions in solids. These techniques are essentially derivative techniques which allow the detection of very small changes in optical absorption or reflectivity in an otherwise flat background. The common denominator of all these techniques is that some material parameter is modulated and the derivatives of the corresponding optical absorption or reflectivity is measured by a phase sensitive detector. The advantage of these new techniques is that they give rise to large effects at critical points such as band edges or saddle points, resulting in converting otherwise continuous-like spectra into line-like spectra with the consequent ease in measuring the positions of these singularaties. The electro-optical technique[1-5] may be used on insulators and semi-conductors, while the piezo-optical[6,7] technique may be used for insulators or metals. The recently developed thermal-derivative technique can be used on most materials.[8] However, all these methods are necessarily restrictive in their applicability since they require appropriate sample preparation to which stress, electric fields, or thermal rise in temperature is to be applied. In additional, all these techniques yield line shapes which are not completely understood.

It would be desirable in this field to have a method of obtaining the derivative of the absorption or reflectivity as a function of waveleng without recourse to the actual modulation of the optical properties of the material. In this manner, it would then be possible to locate the singularities and then to separately study the effects of stress, electric fields, or temperature. Essentially, what is needed is a frequency modulated spectrometer, so that appropriate phase sensitive of the detection signal would yield first or higher derivatives. We have developed such means of frequency modulation anywhere from the ultra-violet to the far-infrared at depths of modulation of $\frac{\Delta\lambda}{\lambda} \approx 10^{-3}$ at frequency rates up to a kilocycle/sec. We have demonstrated that such a device is capable of measuring changes in absorption or reflectivity at levels of one part per million for narrow lines out of a continuous background.

Several methods have been reported for producing derivative spectra.[9-13] In one class,[9,10] differentiation is obtained by electrical differentiation of the output signal with respect to time in an analogue fashion. This method has the disadvantage that the value of the derivative is a function of the scanning speed. However, differentiating the independent variable, such as the wavelength, is not subject to this disadvantage. The wavelength of a spectrometer may be modulated by varying the wavelength of the light incident on the detector. This may be done by the vibration of one of the slits[11,13] or by oscillating the deflection of the beam through the exit-slit by the use of a refractor plate.[12] Both of these methods require a modification of the spectrometer and in addition, the latter is limited by the transmission characteristics of the refractor plate. A more universal method which requires a minimum of interference with an existing spectrometer and requires very little auxiliary equipment is to oscillate a deflecting mirror within the spectrometer.

Figure 1 shows the experimental arrangement for obtaining the derivative of an optical quantity. The only modification within the spectrometer is an additional structure upon which the exit mirror is mounted which enables it to be oscillated at a frequency and amplitude determined by the voltage applied to a piezo-electric element connected in a bimorph configuration. The mounting of the exit-slit diagonal mirror in Perkin-Elmer 99G, 210 and 301 monochromonators was so modifield the frequency of oscillation of the mirror can be from 30/1000 cycles/sec. and yield an amplitude of oscillation so that the depth of modulation was at $\frac{\Delta\lambda}{\lambda} \approx 10^{-3}$ in the wavelength range 3000Å-20,000Å.

The intensity of the light falling on the detector after transmission through a sample is given by:

$$I(\lambda) \approx \frac{[1-R(\lambda)]^2 \exp[-K(\lambda)d]}{1-R^2(\lambda)\exp[-2K(\lambda)]} \cdot I_o(\lambda) \qquad (1)$$

where K, R and d are the absorption coefficient, reflectivity and thickness of the sample and $I_o(\lambda)$ is the incident intensity on the sample. In regions where the transmission is not too great, i.e., $K(\lambda)d > 1$, we can let the denominator equal unity and:

$$I(\lambda) = (1-R)^2 \exp[-K(\lambda)d]\, I_o(\lambda) \qquad (2)$$

If we neglect the spectral dependence of R

$$\frac{dI}{d\lambda} = (1-R)^2 \frac{dI_o}{d\lambda} e^{-K(\lambda)d} - \frac{dK(\lambda)}{d\lambda}(1-R)^2, d, I_o e^{-K(\lambda)d} \qquad (3)$$

If the slits of the monochromator are adjusted so as to keep the light intensity falling on the detector a constant, we obtain:

$$\frac{\frac{dI(\lambda)}{d\lambda}}{I} = \frac{\frac{dI_o(\lambda)}{d\lambda}}{I_o} - \frac{dK(\lambda)}{d\lambda} \cdot d \qquad (4)$$

Thus we see if the contribution to $\frac{dI(\lambda)}{d\lambda} / I$ from atmospheric absorption, the wavelength response of the detector, and the light source is small compared to that of the sample, it is possible to obtain the derivative of the absorption coefficient with respect to wavelength. If the contribution from the source background is comparable to that of the sample, a separate run without the sample will yield $\frac{dI_o}{d\lambda} / I_o$ and the derivative of the absorption coefficient can be calculated. A separate run to obtain the background derivative can be obviated by the use of a double-beam optical system such as the Perkin-Elmer 301 where the derivative of the signal through the sample and that of the background are simultaneously measured and the background correction made by an electric analogue circuit.

It should be noted that by this method of direct differentation, i.e., by frequency modulating the macrochromater, the line shapes at the singular points are obtained unambiguously. This is in contrast to the electro-optical piezo-optical, or thermo-optical technique where a material parameter is modulated and so the observed line shape of the derivative must be unfolded from the raw data by theoretical considerations.

The experimental arrangement for obtaining the derivative of a spectra is shown in Figure 1. The light signal incident on the sample is amplitude modulated at 13 c.p.s. by a chopping wheel and the rectifield d.c. component is fed to a servo control which adjusts the slits of the manochromater to keep a constant incident intensity on the detector so as to maintain a fixed d.c. operating point on the detector. The exit-slit mirror is driven at ~ 200 c.p.s. and this a.c. component of the transmitted beam is detected synchronously with the voltage driving the piezo-electric bimorph. The frequency of oscillation is chosen as high as possible to overcome the $^1/f$ noise in the detecting system. The frequency of modulation depends upon the mass resonance frequency of the mirror system. Although maximum amplitude occurs at 200 c.p.s. frequencies up to 1000 c.p.s. can be obtained with somewhat decreased modulation.

In order to demonstrate the operation of the derivative spectrometer, the following data was taken using the green-line of a Hg-arc as the source. A Perkin-Elmer 210 monochromator was used, with an RCA 1P28 Photomultipier as the detector, in conjunction with a PAR HR-8 lock-in-amplifier. Figure 2a shows the amplitude of the green line, Figure 2b and Figure 2c show the first and second derivative of this line at a modulation voltage which did not cause any appreciable broadening of the line. Figures 2b and 2c also show the same sequence of data taken with larger modulating voltage where the line widths of the derivative spectra are modulation broadening caused by the fact that the depth of frequency modulation is comparable with the instrumental line width.

Phonon-assisted indirect transitions in transmission and the singulariites in the reflectivity of semiconductors were investigated using the above techniques. Figure 3 shows the phonon-assisted indirect transitions in silicon at room temperatures. This figure shows the actual chart recording of both the derivative of silicon and the derivative of the background I_0. One should note the small structure in the $dI_0/d\nu$ signal. The net result of interest, $\frac{dK}{d\nu}$, is derived by taking the difference of these two signals, but as the $dI_0/d\nu$ signal is roughly constant, the main structure of is apparent in the $dI/d\nu$ signal.

The plasma edges of the noble metals silver and gold have been investigated using this method in reflection and transmission using aluminum as a standard. Figure 4 shows the derivative of the reflectivity of silver in the region of the plasma absorption. In this region the derivative of the aluminum reflectivity is practically flat so that this figure represents the net result $dR/d\nu$.

Although in this report we have illustrated the use of derivative spectroscopy in emission, transmission and reflection in solids, it was possible to detect very weak atmospheric absorption in moderately short laboratory paths by this technique. This derivative technique should prove very useful in measuring single and double-photon absorption in gases and solids.

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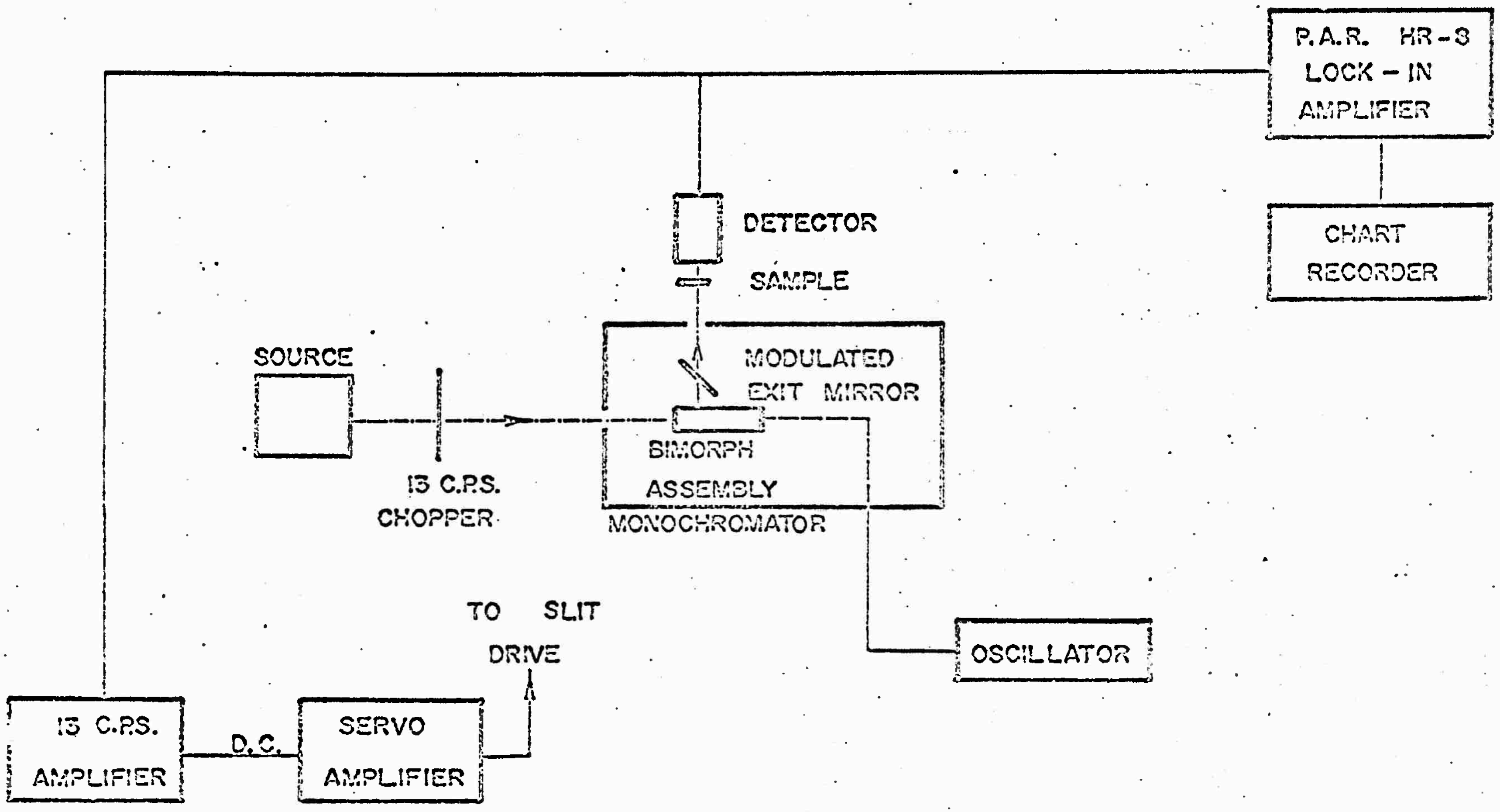
FIGURE CAPTIONS

1. Schematic diagram of optical set-up used to obtain the derivation of a spectrum.

2. Emission of the green-line of H_g, together with the first and second derivative. Also are shown the same spectra taken under conditions where the depth of modulation is comparable to the instrumental line width showing the effects of modulation broadening.

3. Derivative of the phonon-assisted indirect transitions in silicon at room temperatures.

4. Derivative of the plasma edge of silver in reflection.


P.A.R. HR-8
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MONOCHROMATOR
13 C.P.S.
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TO SLIT
DRIVE
OSCILLATOR
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D.C.
SERVO
AMPLIFIER

Figure 1

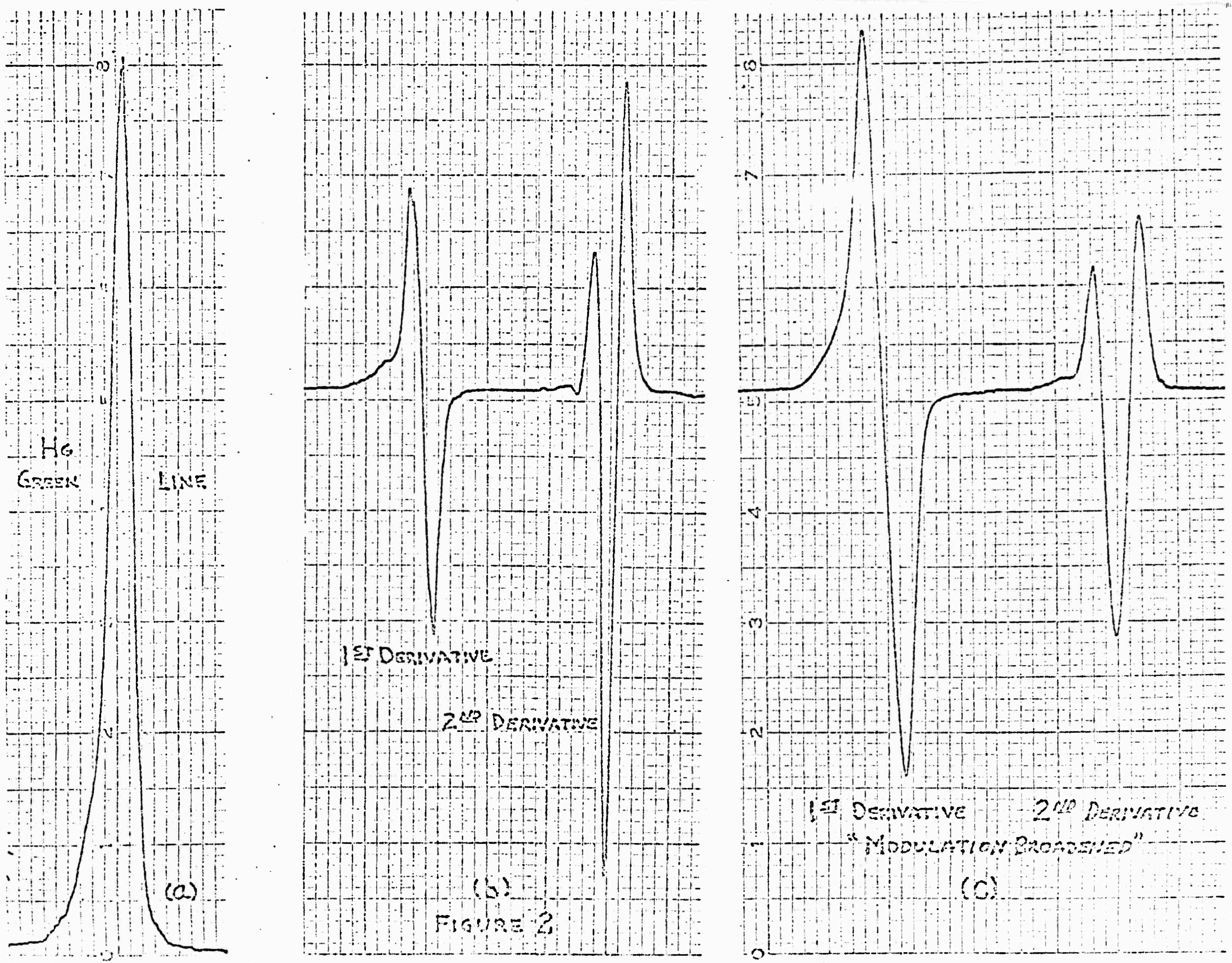Hg
Green
Line
(a)
1st Derivative
2nd Derivative
(b)
1st Derivative
2nd Derivative
"Modulation Broadened"
(c)
0
1
2
3
4
5
6
7
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Figure 2

DERIVATIVE OF SILICON TRANSMISSION:
REGION OF INDIRECT PHONON TRANSITIONS

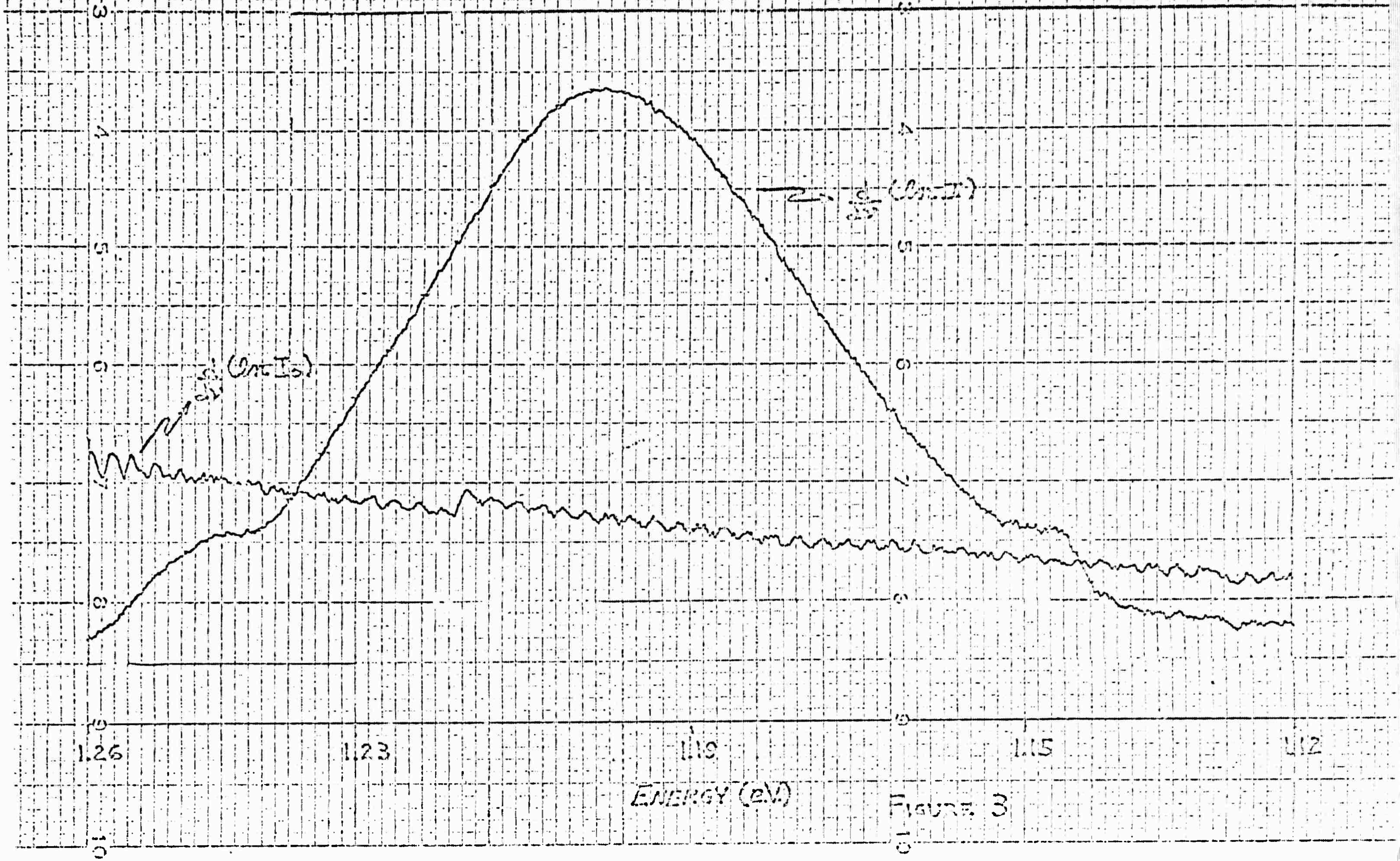
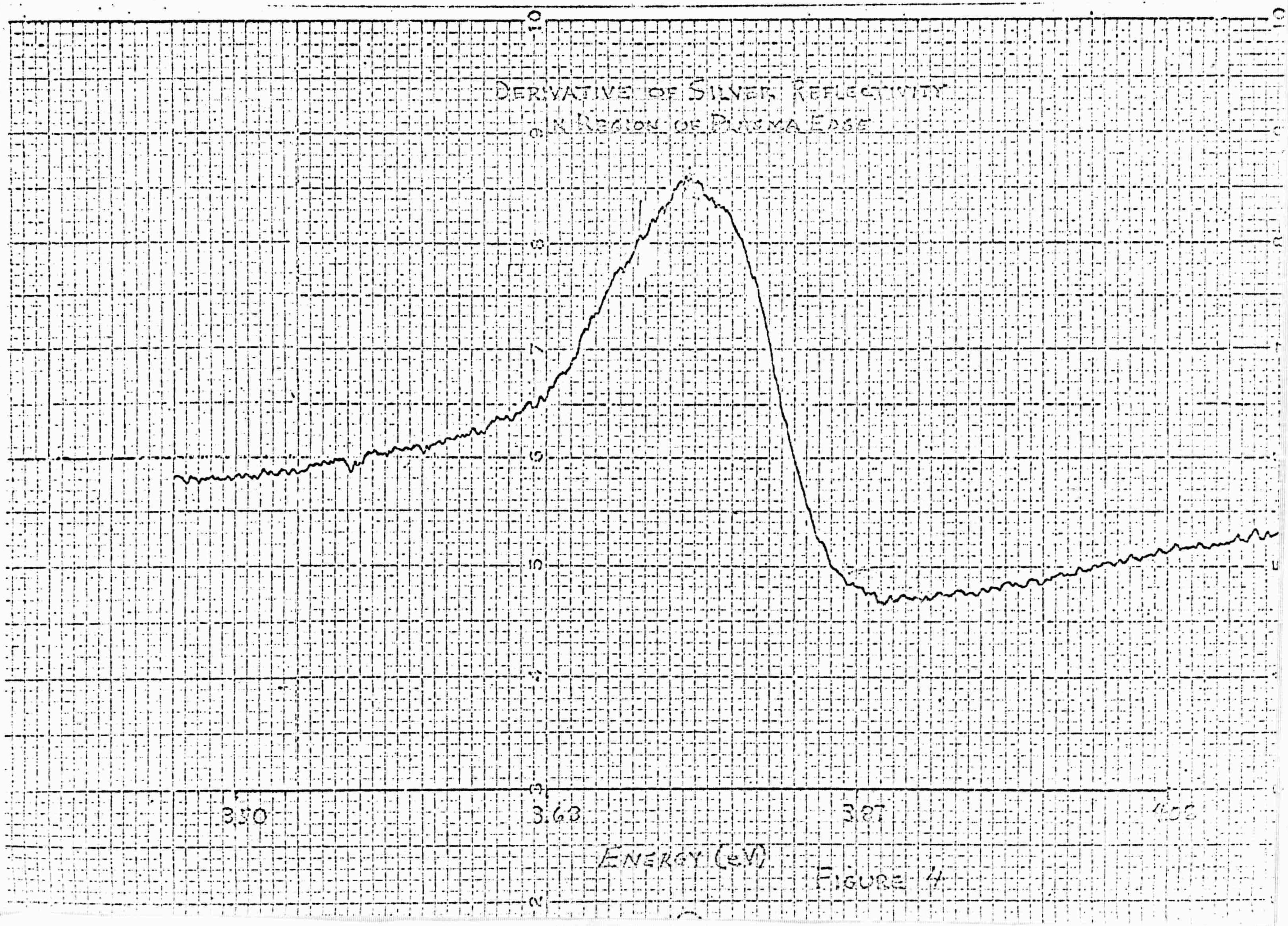


FIGURE 3



DERIVATIVE OF SILVER REFLECTIVITY IN REGION OF PLASMA EDGE

FIGURE 4

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CRITICAL POINT DETERMINATION BY DERIVATIVE OPTICAL SPECTROSCOPY*

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The singularities of phonon-assisted transitions in Si and the reflectivity in the neighborhood of the plasma edge in Ag were determined by a method of derivative spectroscopy. The use of this technique of frequency-modulated spectroscopy enables one to readily obtain the first or higher derivatives of any optical spectra.

THE SINGULARITIES of the phonon-assisted transitions in Si and the reflectivity in the neighborhood of the plasma edge in Ag were determined by a method of derivative spectroscopy. This technique of frequency-modulated spectroscopy enables one to readily obtain the first and higher derivatives of optical spectra and is of general utility in problems involving the detection of very weak narrow absorption, reflection or emission lines out of a relatively smooth background spectra. In particular, this technique is of general utility in determining the critical points in interband transitions in solids.

During the past few years, several new derivative techniques[1-5] have been developed which have made it possible to determine the singularities in the density of states for optical transitions in solids. The common denominator of all of these approaches is the modulation of a material parameter and the subsequent detection of the derivative of the optical transmission or reflectivity by phase sensitive detection. However, all of these methods are necessarily restrictive in their applicability since they require appropriate sample properties so that stress, electric fields, or temperature changes can be applied. In addition, all of these techniques yield line shapes which are difficult to interpret.

A more desirable method is to frequency modulate a spectrometer and then to obtain the first or higher derivatives of the spectra by phase sensitive detection. In this manner, it is possible to locate the singularities and then to separately study the effects of stress, electric fields or temperature. Several methods have been reported for producing derivative spectra.[6-10] However, they all are unnecessarily restrictive in some manner.

We have used a method which requires a minimum of interference with an existing spectrometer: this was accomplished by oscillating a deflecting mirror before the exit slit in a conventional spectrometer. A somewhat similar technique has been reported in another context.[11] In this manner, we have converted Perkin-Elmer 99G, 201 and 301 monochromators to frequency modulated spectrometers. The only modifications were additional structures upon which the exit mirrors were mounted which enabled them to be oscillated by a piezo-electric element connected in a bimorph configuration. The frequency and amplitude were determined by the applied voltage, resulting in a depth of modulation of $\Delta\nu/\nu \simeq 10^{-3}$.

The transmitted intensity, neglecting internal reflection, from a sample of absorption

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coefficient k, thickness d, and reflectivity R is given by:

$$I(\nu) = I_0(\nu)\,(1-R)^2 \exp[-k(\nu)\cdot d]\ .$$

If the output of the spectrometer is frequency modulated while the average light intensity on the detector is kept constant, we obtain:

$$\frac{\frac{d\,I(\nu)}{d\nu}}{I} = \frac{\frac{d\,I_0(\nu)}{d\nu}}{I_0} - \frac{dk}{d\nu}\cdot d$$

where we have neglected the spectral dependence of R. If $(dI_0/d\nu)/I_0$ is small, it is possible to directly obtain the derivative of the absorption coefficient with respect to wavelength. If $(dI_0/d\nu)/I_0$ is not small, a separate normalization run without the sample must be made. The latter can be obviated by the use of a double-beam optical system such as the Perkin-Elmer 301. We have used both systems under the appropriate conditions.

It should be noted that by the use of this method of direct differentiation, the line shapes at the singular points are obtained unambiguously. This is in contrast to the electro-optical,[1-3] piezo-optical,[4] or thermo-optical[5] techniques where a material parameter is modulated requiring an unfolding of the true line shape of the derivative from the raw data by theoretical considerations.

Since the background was small in the results we are reporting, we used a single-beam configuration. A fixed d. c. operating point was maintained on the detector by a feedback network which controlled the slit-width of the monochromator. The exit-slit mirror was driven at ~ 200 c/s and this a. c. component of the transmitted beam was detected synchronously with the voltage driving the piezo-electric bimorph.

As an illustration of the operation of the derivative spectrometer, Fig. 1 shows the data taken using the green-line of a Hg-arc as the source. Included is the amplitude of this line and its first and second derivatives. Also shown are the modulation broadened derivatives caused by an excessive modulation, which is comparable to the instrumental line width.

Phonon-assisted indirect transitions in transmission in semiconductors and the singularities in the reflectivity of semiconductors and

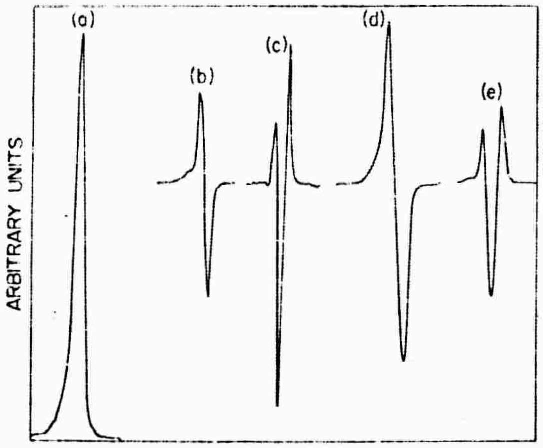

FIG. 1

Emission of the green-line of Hg, together with the first and second derivatives; (a) shows the amplitude modulated signal, (b) the first derivative, (c) the second derivative, (d) and (e) show the same sequence as (b) and (c), but taken under conditions where the depth of modulation is comparable to the instrumental line width revealing the effects of modulation broadening.

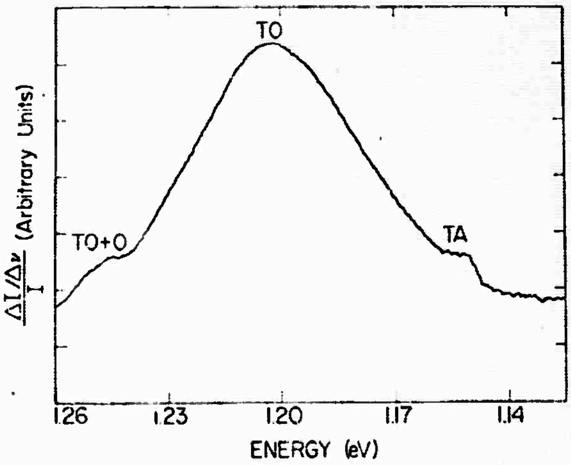

FIG. 2

Derivative of the phonon-assisted indirect transitions in silicon at room temperatures; TO = transverse optical phonon, TA = transverse acoustical phonon, O = optical phonon of zero momentum.

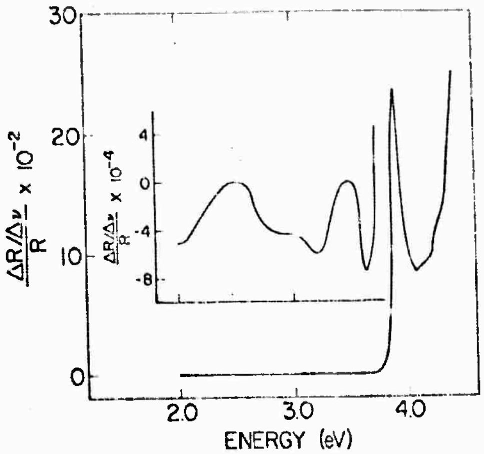

FIG. 3

Derivative of the reflectivity in the neighborhood of the plasma edge of evaporated silver.

metals were investigated using the above techniques. Figure 2 shows the phonon-assisted indirect transitions in silicon at room temperature. Identified in the figure are the TO, TA, and TO + O phonon-assisted transitions. The energy separations of these phonon bumps agree with the results of electro-absorption,[2] but of course the line shapes are different.

Figure 3 shows the derivative of the reflectivity of evaporated Ag using Al as a standard. The prominent features in the derivative spectra are a peak which occurs at the steep plasma edge at 3.88 eV which is displaced from the calculated free-electron value by the $L_{32} \rightarrow L_2$,[12] interband transition. The smaller structures between 2.0 and 3.5 eV which are shown in the insert in Fig. 3, expanded by two orders of magnitude, are reproducible from sample to sample; structure in this region has been seen by electro-optical[3] and piezo-optical[4] techniques. The beginning of structure starting beyond 4.0 eV may be the precursor of another interband transition which is expected around 5 eV.

It also was possible to detect very weak atmospheric absorption in moderately short laboratory paths by this technique. In addition to the study of critical points in the band structure of solids, this technique has great utility in all areas of spectroscopy requiring the detection of weak lines out of broad background spectra.

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Les singularités des transitions assistées par phonons dans le Silicium et le coefficient de réflection au voisinage d'un front d'absorption de plasma dans l'argent ont été mesurés grâce à une methode de dérivation spectroscopique. L'utillisation de cette technique spectroscopique, à modulation de fréquence, donne la possibilité d'obtenir les dérivées première et d'ordre supérieur de n'importe quel spectre optique.

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13. ABSTRACT

Multiphoton absorption in semiconductors was investigated with emphasis on the III-V compounds. It was shown that this mechanism can set an intrinsic upper limit to the power density transmittible through semiconductors. Laser action in a large volume of GaAs was excited by double-photon pumping using a Q-switched neodymium laser, yielding output power of the order of a megawatt/cm^2 at 8365 Å at liquid nitrogen temperature.

A new temperature anomaly of the threshold for stimulated Raman emission in liquid benzene was discovered and investigated.

The first observation of infrared stimulated emission associated with optical phonons of a liquid was reported. This was seen at 5μ from benzene. In addition, induced transparency by coherent optical phonons was observed.

A new technique of frequency-modulated spectroscopy was developed which enables ~~us~~ to readily obtain the first or higher derivatives of any optical spectra.

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