

for steady state. The study made in the trajectory zone restricts the range for rigid monitoring of the additive concentration in the crystal. This is restricted further by the phenomena occurring at the interfacial zone pertinent to crystal quality (to be discussed in a separate publication).

Control of Cr(III) content in the powder is essential to a reproducible burnout. The kinetic study with powders show a stationary (maximum) concentration of Cr(VI).<sup>1</sup> It is possible that this is coincident with the occurrence of a maximum in the specific surface; the surface concentration of the additive serving as an

indicator. If so, this is desirable for optimizing the collision transfer of energy.

#### ACKNOWLEDGMENTS

For participation in the various supporting phases of this study, we are grateful to the following members: L. Podoksik (chemical analysis of powders and rubies); M. A. Pearson (preparation of, and host transformation experiments on the powders); R. Larson (design and construction of the pulsed-sound drive); L. Sims, J. Meyer, and R. Dean (crystal-growth instrumentation and operation).

### Laser-Induced Luminescence and Dissociation in Biphenyl

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(Received 11 February 1966)

The interaction of the radiation field of an unfocused ruby laser with molecules containing a phenyl-phenyl or benzyl-benzyl single bond is found to give rise to a new luminescence. This luminescence is linearly dependent on the molecular concentration and proportional to either the second or the third power of the laser intensity. Thus it appears that a multiphoton absorption is occurring. The absorption does not appear to involve the electronic states of the molecules. This luminescence occurs throughout the visible region and bears no resemblance whatever to either the normal fluorescence or phosphorescence. Because of the exceedingly high laser intensities or electric fields necessary for electronic dielectric breakdown it appears that this mechanism is not of importance. It is suggested that multiphoton vibrational excitation to a dissociative state of the molecule may occur which leads to molecular fragmentation. This process is followed by a chemiluminescent emission. A quantitative comparison of the experimental results with a theoretical treatment of multiphoton vibrational dissociation is made.

#### I. INTRODUCTION

WE have observed a short-lived ( $<10^{-6}$  sec) visible luminescence in biphenyl and other compounds which possess a phenyl-phenyl single bond under excitation by an unfocused giant pulsed ruby laser or focused nongiant pulsed ruby laser with peak powers of between 0.1 to 5 MW/cm<sup>2</sup> (i.e., peak field strengths of the order of  $10^4$  to  $10^5$  V/cm). That biphenyl should exhibit such behavior is surprising from a number of considerations. In the first place, the first singlet transition in biphenyl lies fully three photons away from the ground state and would not be expected to be accessible at this low laser intensity. Even the lowest-lying triplet state is fully two photons away from the ground state and the probability for a two-photon transition to a spin-forbidden state is very small. Furthermore, the luminescence, which is shown in Fig. 1, occurs throughout the entire visible range and is certainly not related in any simple way to either the

normal fluorescence from the first singlet or the normal phosphorescence from the first triplet state which are shown in Fig. 2.

With the advent of the ruby laser, a number of effects have been observed and are now well known in which the intense red light from the ruby laser is used to stimulate or effect some luminescence in materials at frequencies higher than the laser frequencies. These include two-photon excitation of the singlet state,<sup>1</sup> three-photon excitation of the singlet state,<sup>2</sup> the formation of triplet excitons followed by annihilation to form an excited single state,<sup>3</sup> stimulated anti-Stokes Raman emission,<sup>4</sup> and what is generally called "dielectric breakdown"—a phenomenon which has been observed in a number of gases and liquids upon the action of an

<sup>1</sup> W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, *Phys. Rev. Letters* **10**, 43 (1963); W. L. Peticolas and K. E. Rieckhoff, *J. Chem. Phys.* **39**, 1347 (1963).

<sup>2</sup> S. Singh and B. P. Stoicheff, *J. Chem. Phys.* **38**, 2032 (1963).

<sup>3</sup> R. G. Kepler, J. C. Caris, A. Anakian, and E. Abramson, *Phys. Rev. Letters* **10**, 400 (1963).

<sup>4</sup> G. Eckhardt, R. W. Hellwarth, F. J. McClung, S. E. Schwarz, D. Wiener, and E. J. Woodbury, *Phys. Rev. Letters* **9**, 455 (1962).

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intensely focused giant pulsed laser beam.<sup>5</sup> For reasons stated in detail below, each of these effects can be ruled out as the cause of the luminescence described here. Consequently, we believe that this effect in biphenyl is new and suggest that it may arise from a luminescence of molecular fragments created by dissociation of the molecule caused by multiphoton vibrational excitation. Such a process has been anticipated theoretically by Bunkin, Karapatyan, and Prokhorov<sup>6</sup> and Askar'yan.<sup>7</sup>

## II. EXPERIMENTAL

All of the chemicals used in this study were carefully purified. The purity of the materials was checked using thin-layer chromatography. The single laser pulse reached its maximum intensity in 20 nsec with an intensity of 0.1–5 MW. Figure 3 gives a diagram of the experimental setup. The luminescence was observed at right angles to the exciting beam and filtered to eliminate signals due to scattered laser radiation. The emission was detected by an EMI 6256 S/A photomultiplier and displayed on an oscilloscope. The laser signal was monitored by an RCA 925 diode and was displayed simultaneously with the luminescence signal on the oscilloscope. In the case of crystalline biphenyl the emission was photographed with an  $f/1.5$  prism spectrograph.

## III. DISCUSSION

Figure 1 shows the densitometer trace of the spectrum of laser-induced luminescence in biphenyl obtained from a crystalline sample. From a comparison with the normal fluorescence and phosphorescence

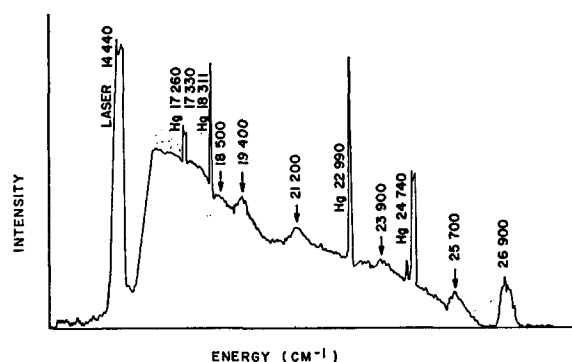


FIG. 1. Microdensitometer tracing of the laser-induced luminescence spectrum of the biphenyl crystal at 298°K.

<sup>5</sup> R. W. Terhune, *Solid State Design* **4**, 38 (1963); R. G. Meyerand, Jr., and A. F. Haught, *Phys. Rev. Letters* **11**, 401 (1963); W. I. Linlor, *ibid.* **12**, 383 (1964); R. G. Brewer and K. E. Rieckhoff, *ibid.* **13**, 344 (1964).

<sup>6</sup> F. V. Bunkin, R. V. Karapatyan, and A. M. Prokhorov, *Soviet Phys.—JETP* **20**, 145 (1965) [*Zh. Eksperim. i Teor. Fiz.* **47**, 216 (1964)].

<sup>7</sup> G. A. Askar'yan, *Soviet Phys.—JETP* **21**, 439 (1965) [*Zh. Eksperim. i Teor. Fiz.* **48**, 666 (1965)].

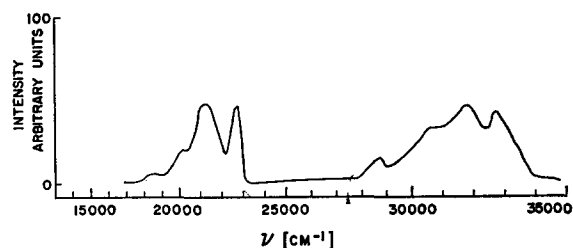


FIG. 2. The luminescence of biphenyl in an EPA glass at 77°K (see Ref. 9).

shown in Fig. 2, it is clear that the luminescence is not due to emission from these states. The fluorescence of biphenyl is well known and lies entirely in the ultraviolet while the laser-induced luminescence peaks in the red or near infrared. (Since the sensitivity of the film is very low below 6500 Å, the exact location of the luminescence maximum is difficult to determine.) Not only is the phosphorescence spectrum unrelated to the luminescence spectrum but phosphorescence is never observed in the crystalline form or in the liquid state at room temperature where we have readily observed the luminescence. Thus, by the nature of the spectrum of the luminescence we may rule out normal multiphoton excitation of either the singlet or the triplet state or any stimulated anti-Stokes Raman scattering.

The same considerations rule out triplet exciton formation and annihilation since this phenomenon is known to give the normal fluorescence spectrum changed only by its delay in time. However, to show that the luminescence is occurring on an essentially monomolecular level, measurements of the intensity of the luminescence as a function of concentration were made and are shown in Fig. 3. The linear relationship between the luminescence intensity and the concentration indicate that exciton effects or other effects involving two or more molecules are unlikely.

The broad spectrum of the luminescence resembles to some degree the spectrum obtained from dielectric breakdown in gases and other liquids. However, in every case where dielectric breakdown has been observed<sup>8</sup> the laser intensities have been much higher than those which we have used. Furthermore, dielectric breakdown should occur at approximately the same intensity threshold in biphenyl as in benzene since the ionization potential is approximately the same for these molecules. Yet although we have observed a laser-induced luminescence in benzene which resembles the well-known dielectric breakdown in other materials, this phenomenon in benzene occurs at  $10^3$ – $10^4$  times the intensity as in biphenyl. Since the effect in biphenyl is independent of path length down to paths of the order of 1 mm, it is apparent that there can be no unusual increase in intensity due to self-trapping or

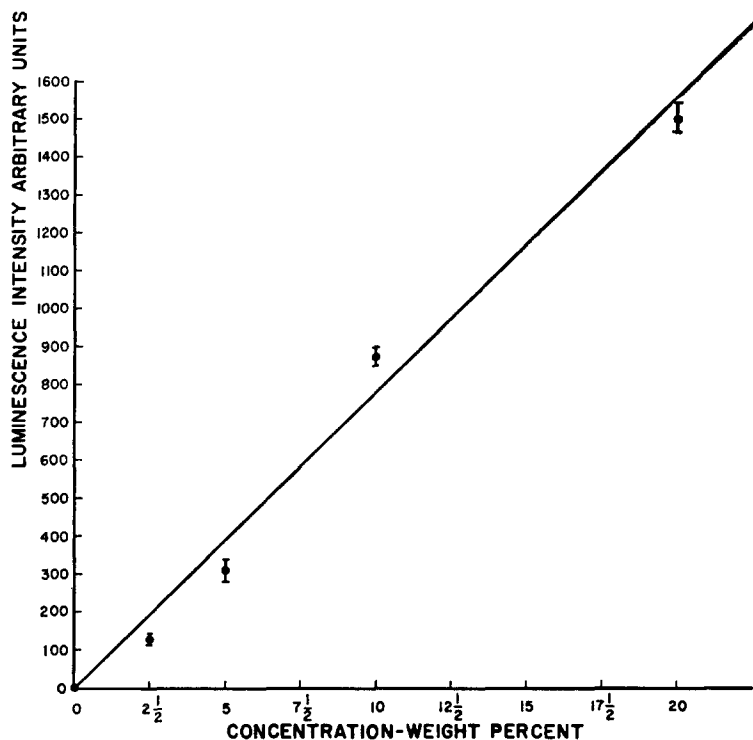


FIG. 3. The concentration dependence of the laser-induced luminescence of dibenzofuran in ether at 298°K.

self-focusing of the light,<sup>8</sup> so that our measured laser intensities must be the ones present in the media. Indeed, our laser intensities are so low that it is easy to obtain dc fields of comparable field strengths. To see if comparable dc fields had any effect, samples of biphenyl and related compounds were placed between electrodes and fields of  $10^4$  to  $10^5$  V/cm were applied. No dielectric breakdown was found to occur at  $10^5$  V/cm or below. Consequently, if the electric fields of the laser beam are, in fact, responsible for the luminescence, then it must be an ac effect because equivalent dc fields produce no effect whatever.

Although the experiments listed above tend to rule out involvement of both the singlet and triplet electronic states, an additional set of experiments were performed in which the compounds were subjected to irradiation with ultraviolet light equivalent in energy to two or three laser quanta. When this light fell within the first singlet state it was completely absorbed and led to the normal ultraviolet fluorescence. In no case was any luminescence of the type shown in Fig. 1 observed. Consequently, there appears to be no way to obtain the luminescence by excitation of the singlet electron state.

Involvement of the triplet state is unlikely for

<sup>8</sup> G. A. Askar'yan, *Zh. Eksperim. i Teor. Fiz.* **42**, 1567 (1962) [English transl.: *Soviet Phys.—JETP* **15**, 1088 (1962)]; V. I. Talanov, *Izv. Vysshikh Uchebn. Zavedenii Radiofiz.* **7**, 564 (1964) [English transl.: *Radiophysics* **7**, 254 (1964)]; R. Y. Chias, E. Garmire, and C. H. Townes, *Phys. Rev. Letters* **13**, 479 (1964).

reasons listed above. However, experiments were made on a series of halogen-substituted biphenyls and it was found that there was no correlation whatever between the magnitude of the observed luminescence with the well-known singlet-triplet transition probabilities in these compounds.

The intensity of the luminescence was found to be directly proportional to the  $n$ th power of the incident laser intensity with  $n$  being 2 or 3 depending on the compound in question as shown in Figs. 4 and 5. Thus, from these experiments, it is apparent that we have a two- or three-photon process leading to a broad visible luminescence completely unlike any normal luminescence coming from the well-known electronic transitions. The question naturally arises as to what could be the cause of this luminescence. We have observed that in the crystalline state, repeated excitation of the crystal leads to a darkening, indicating that some decomposition has taken place. Consequently, we have proceeded to examine the possibility that perhaps the laser beam is leading to dissociation of the molecules followed by some sort of luminescence. Thus, one might imagine that the ac electric field of the laser light is exciting higher vibrational levels in the electronic ground state of the molecule leading ultimately to dissociation followed by luminescence. This mechanism for photodissociation has been predicted theoretically by Bunkin, Karap'yan, and Prokhorov,<sup>6</sup> and Askar'yan.<sup>7</sup> According to the mechanisms proposed by these authors, higher vibrational modes in molecules

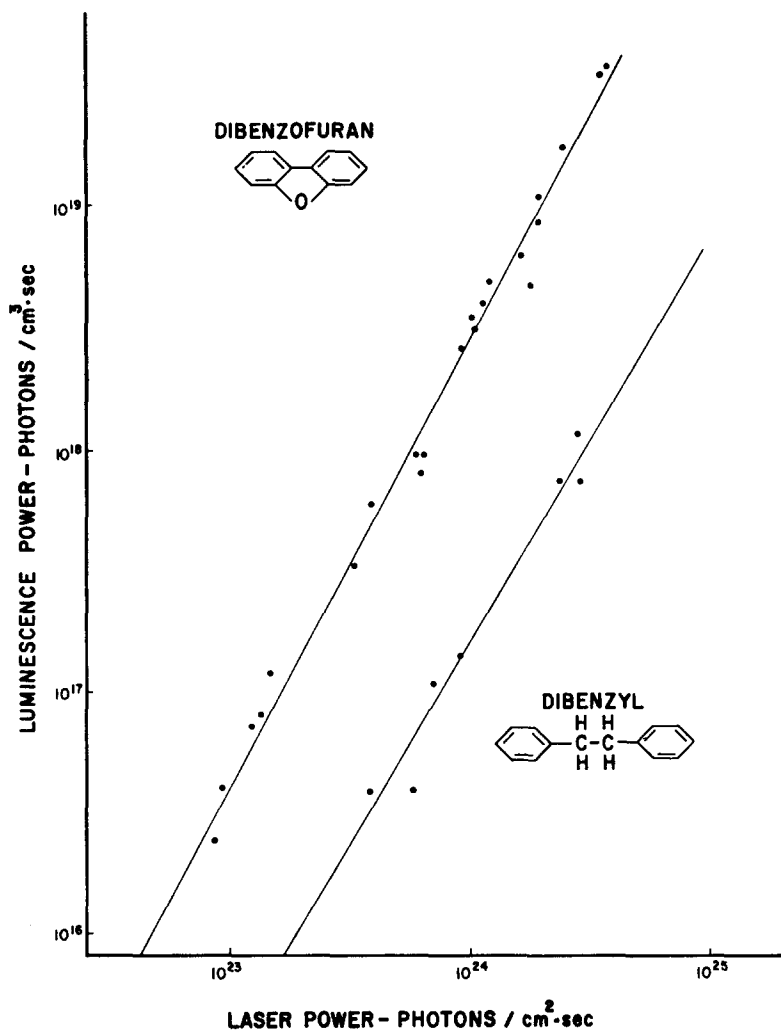
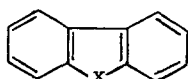


FIG. 4. Log-log plot of luminescence versus peak laser intensity. Dibenzofuran (liquid at 100°C). Dibenzyl (16% by weight in xylene). The observed slopes of 1.9 and 1.8, respectively, are satisfactorily close to the integer 2 expected for a two-photon process.

are connected with the ground vibrational level by means of the anharmonic terms in the potential-energy function.<sup>6</sup>

For a small diatomic molecule the anharmonicity of the vibrations is relatively small. Even so, theoretical calculations<sup>6,7</sup> show that there is sufficient probability for a diatomic molecule connected by a Morse potential to become dissociated under the influence of the laser beam. However, for single bonds connecting rigid bulky groups such as the phenyl-phenyl and benzyl-benzyl single bonds the anharmonicity must be much larger so that the probability of multiphoton vibrational dissociation must be greatly increased in these molecules. In fact, it is only in molecules containing a phenyl-phenyl or benzyl-benzyl single bond that we have been able to observe this luminescence at these correspondingly low laser powers. Thus, in addition to biphenyl, compounds of the formula



such as dibenzofuran (X=O), dibenzothiophene (X=S) show this effect while benzene and naphthalene do not, even if the laser power is increased a factor of 10 or more. Indeed, naphthalene fluorescence can be excited to its ordinary singlet by an intense laser beam by means of a three-photon process,<sup>9</sup> but shows no luminescence of the type shown in Fig. 1 with laser powers in the 0.1–10-MW range.

The weakest bond in dibenzyl and biphenyl are the center bonds which have dissociation energies of 17 000 and 39 000  $\text{cm}^{-1}$ , respectively.<sup>2,3</sup> Consequently, dibenzyl and biphenyl would require two and three photons of laser energy, respectively, to dissociate their weakest bonds. Bunkin *et al.*<sup>4</sup> have calculated the transition probability per unit time for two- and three-photon dissociation of diatomic molecules connected by a Morse potential using the dipole Hamiltonian. Using these calculations we have obtained a quantitative estimate of the effect and compared it with our measurements assuming unit quantum efficiency for the luminescence.

For two-photon nonresonance (not exact resonance)

<sup>9</sup> K. Kasha, *Radiation Res. Suppl.* **2**, 243 (1960).

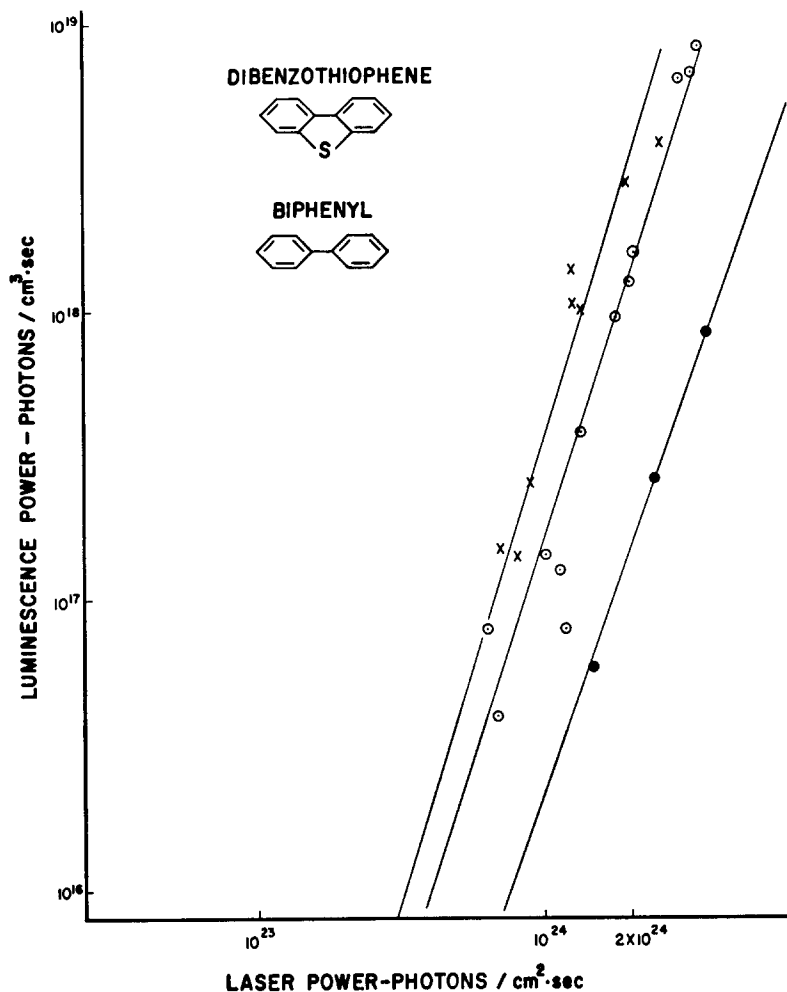


FIG. 5. Log-log plot of luminescence versus peak laser intensity. Dibenzothiophene (X) (15% by weight in xylene). Biphenyl (●) (10% by weight in xylene). Biphenyl (○) (liquid at 75°C). The observed slopes of 3.1, 3.1, and 2.9, respectively, are satisfactorily close to the integer 3 expected for a three-photon process.

processes, the transition probability per unit time,  $B_2$ , is given by<sup>6</sup>

$$B_2 = \left(\frac{M}{8\hbar\omega}\right)^{\frac{1}{2}} \left(\frac{e_1\bar{x}_{nE}E_0}{2\hbar}\right)^2 \left(\frac{\mu_{n0}E_0}{\hbar\Delta\omega_1}\right)^2, \quad (1)$$

while for three-photon nonresonance processes, the transition probability is given by<sup>6</sup>

$$B_3 = \frac{5}{16} \left(\frac{M}{8\hbar\omega}\right)^{\frac{1}{2}} \left(\frac{e_1\bar{x}_{nE}E_0}{2\hbar}\right)^2 \left(\frac{\mu_{n0}E_0}{\hbar\Delta\omega_1}\right)^2 \left(\frac{\mu_{nm}E_0}{\hbar\Delta\omega_2}\right)^2, \quad (2)$$

where  $\Delta\omega_1 = |\omega - \omega_{m,0}|$  and  $\Delta\omega_2 = |\omega - \omega_{mn}|$  and give the frequency mismatch of the laser line and the higher vibronic lines;  $\mu_{mn}$  is the dipole matrix element connecting the  $m$ th and the  $n$ th excited state of an anharmonic oscillator obeying the Morse potential;  $\bar{x}_{nE}$  is the matrix element from the  $n$ th level of the harmonic oscillator to the dissociated state of energy level  $E$  which was taken as a plane wave.

In order to obtain a measurable quantity from the transition moments we observe that for an  $n$ -photon dissociation,  $I = \alpha_n L^n N$ , where  $I$  is the luminescence

intensity in photons per cubic centimeter·second,  $L$  is the laser intensity in photons per square centimeter·second,  $N$  is the molecular concentration in molecules per cubic centimeter, and  $\alpha_n$  is a parameter characteristic of the molecule and independent of molecular concentration and laser intensity, given in units of centimeter<sup>2n</sup>·second<sup>+n-1</sup>. The transition probability per unit time for an  $n$ -photon process is related to the measurable  $\alpha_n$  by the relation  $\alpha_n = B_n/L^n$ .

The calculated values of  $\alpha_n$  for resonance and nonresonance are given in Table I along with our measured values.

For the cases of almost exact resonance, i.e.,  $\Delta\omega_1 \rightarrow 0$  and  $\Delta\omega_2 \rightarrow 0$ , Eqs. (1) and (2) can no longer be used. In this condition the molecule would be expected to oscillate back and forth between the two states with frequency  $f$ , given by<sup>10</sup>

$$f = 4\mu_{nm}(\omega_L^n/6\hbar)^{\frac{1}{2}},$$

where  $n$  is the number of laser photons per cubic

<sup>10</sup> L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 40.

TABLE I. Comparison of experiment and theory<sup>a</sup> for multiphoton vibrational dissociation.<sup>b</sup>

Molecular species	Theory							
	Experiment		First two absorptions are resonant		First absorption is resonant		Nonresonant	
	$n$	$\alpha$ (cm <sup>6</sup> ·sec <sup>2</sup> )	$n$	$\alpha$ (cm <sup>2</sup> )	$n$	$\alpha$ (cm <sup>4</sup> ·sec)	$n$	$\alpha$ (cm <sup>6</sup> ·sec <sup>2</sup> )
Three-photon dissociation								
Biphenyl (liquid at 75°C)	3.1	10 <sup>-76</sup>	1	10 <sup>-20</sup>	2	10 <sup>-55</sup>	3	10 <sup>-90</sup>
Biphenyl (10% by weight in xylene)	2.9	10 <sup>-76</sup>	1	10 <sup>-20</sup>	2	10 <sup>-55</sup>	3	10 <sup>-90</sup>
Dibenzothiophene (15% by weight in xylene)	3.1	10 <sup>-76</sup>	1	10 <sup>-20</sup>	2	10 <sup>-55</sup>	3	10 <sup>-90</sup>
Two-photon dissociation								
Dibenzofuran (liquid at 100°C)	1.9	10 <sup>-51</sup>			1	10 <sup>-20</sup>	2	10 <sup>-55</sup>
Dibenzyl (16% by weight in xylene)	1.8	10 <sup>-51</sup>			1	10 <sup>-20</sup>	2	10 <sup>-55</sup>

<sup>a</sup> Reference 1.<sup>b</sup>  $I = \alpha_n N L^n$  = number of photons per cubic centimeter·second.  $N$  is numberof molecules per cubic centimeter.  $L$  is laser intensity (number of photons per square centimeter·second).

centimeter. This corresponds to a frequency  $f$  of about  $10^7$  sec<sup>-1</sup> for resonant oscillation between the two states. However since the vibrational relaxation times for these molecules is well known to be of the order  $10^{-13}$  sec, it is highly unlikely that these resonance effects in fact take place. Furthermore, a resonance transition would give a more complicated power dependence than we have observed. However, calculations for resonant as well as nonresonant transitions are given in Table I, based on calculations by Bunkin *et al.* of the transition probabilities. However, we discuss below only the near-resonant case.

It should be noted that the two- and three-photon dissociation near resonance whose matrix elements are given by Eqs. (1) and (2) are similar to other two-photon and three-photon processes<sup>1,2</sup> and must be regarded as single elementary acts. Consequently, for these processes, the fast vibrational relaxation times of the molecules is of no consequence.

While the agreement in the two-photon case is probably within the uncertainties of the applicability of the theory, the measured values of  $\alpha$  for the three-photon case are 14 orders of magnitude greater than calculated for near resonance. The difference probably

arises from one of the following causes: (1) the vibrations of the polyatomic molecules are much more anharmonic than the diatomic molecules obeying the Morse potential, (2) the plane wave approximation of the wavefunction for the fragments is grossly in error, or (3) the  $A^2$  term was omitted and is of major importance. All three of these possibilities are being investigated both experimentally and theoretically.

We have also discovered that if one goes to a focused, Brillouin-amplified, giant pulse laser with three to four orders of magnitude greater intensity one obtains a similar luminescence from a large number of organic materials (such as benzene itself) which do not show this effect at the power levels described here. One is tempted to say that this is a higher-order photon effect of the same type. However, when the dissociation energy becomes of the same order of magnitude as the ionization potential, it is impossible with present techniques to distinguish between multiphoton ionization and MVE.

In conclusion, it should be pointed out that these photon-induced dissociations should be very hard to detect chemically since we observe only about  $5 \times 10^{11}$  photons emitted per giant pulse corresponding to about  $10^{-10}$  g of material.