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The Study of Laser-induced Absorption of a Secondary Light Beam in Molecular Liquids and Solutions

Abstract: New techniques are shown for determining the change in absorption spectrum of molecular liquids when a laser beam is passed through the sample. Two-photon absorption measurements are shown for α-chloronaphthalene. The experimental arrangement (Fig. 3) features a high signal-to-noise ratio and permits study of explicit time dependence of the absorption signal.

This communication describes newly developed techniques for measuring the change in the absorption spectrum of a molecular liquid while it is subjected to an intense pulse of laser energy. There are a number of uses for such apparatus, such as: (1) two-photon spectroscopy, (2) the study of the spectrum of plasmas or ions produced in a material by the laser beam, and (3) the study of triplet-triplet or singlet-singlet absorption after the saturation of a lower triplet or singlet level by the laser pulse. The techniques and equipment used here have been able to measure each of these effects for the first time. In particular, we have been able to achieve true two-photon absorption in a molecular liquid (α-chloronaphthalene). This type of measurement is very important because it allows for the first time the observation of singlet molecular levels whose molecular orbitals are antisymmetric (the so called "g" states). Such observations cannot be made by two-photon absorption in molecular solids because of electronic and vibrational coupling between adjacent molecules.

In fact, before the solid molecular exciton two-photon spectrum can be properly understood the molecular spectrum must be known, and this can be obtained only in a medium where the interaction between molecules is weak; it is most easily obtained in a fluid phase.

Experimental arrangement

In each of these experiments the physical set-up is very much the same. A beam of light from a broadband source (usually a xenon lamp) is passed through a small volume of the sample through a monochromator and into a photomultiplier tube which monitors the beam. During the time of exposure to the xenon lamp, a beam of light from a high-energy pulsed laser is passed through the sample. Coincident with the brief ($\sim 10^{-8}$ sec) laser pulse there is a decrease in intensity of the broadband source because of an increase in its absorption brought about by the presence of the laser light.

Although a few two-photon spectroscopic measurements have been made using equipment of other design,[1–4] the apparatus which is described here has the advantage that it can be assembled quickly from readily available commercial components and achieves a signal-to-noise ratio an order of magnitude higher than previously reported.[4]

Furthermore all previous experimental set-ups have used a high-pass electronic filter to permit only high-frequency signals of the time duration of the laser pulse to come through. Our procedure looks at the explicit time dependence of the absorption signal. As we shall show, the exact time dependence is of the utmost importance in determining the nature of the absorption process.

The main problems that are involved in studying the laser-induced absorption of a secondary beam are: (1) obtaining a sufficiently high signal-to-noise ratio so that it is possible to measure the very small fractional decrease in absorption when the laser is flashed, (2) obtaining precisely the time dependence of the absorption, and (3) preparing the samples so that a very long path length of laser light in the sample is possible without dielectric breakdown. To our knowledge no other workers have overcome each of the problems sufficiently to allow two-photon molecular spectra to be obtained.

To obtain a high signal-to-noise ratio in the photomultiplier which monitors the secondary light beam, it is neces-

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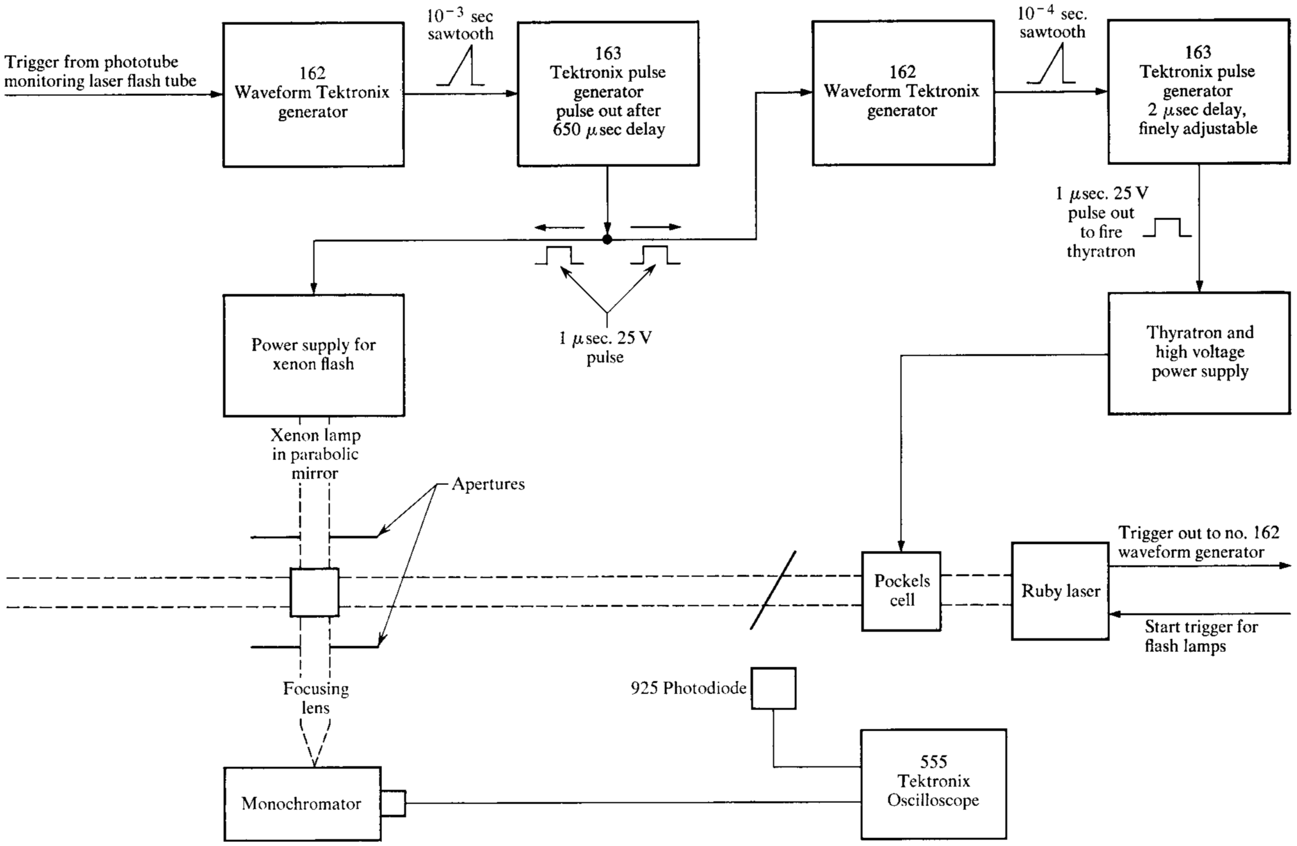


Figure 1 Timing circuit for the study of laser-induced absorption. The sequence is started by firing the trigger for the ruby laser flash lamps (lower right). When the flash is sufficiently intense a trigger is sent to the Tektronix 162 wave form generator (top left). The complete sequence is described in the text.

sary to increase the intensity of the secondary light beam since the signal-induced shot noise current increases with the square root of the light intensity while the signal current increases linearly with intensity.[5] However, each photomultiplier tube on the market has a rated maximum cathode current which limits the intensity of a continuous signal at a given frequency. Consequently, one must go to a pulsed secondary source, which is most conveniently a xenon flash lamp. The shorter the pulse of the secondary source, the more intense it may become before nonlinearities or damage to the photomultiplier tube results, and therefore a higher signal-to-noise ratio is obtained.

Use of a pulsed second source requires synchronization of the xenon flash and the laser pulse. The apparatus must then be made to work in the following order: (1) The xenon flash lamps which pump the laser are activated. (2) After a certain length of time (in our case 650 μsec), the xenon flash lamp which serves as a source of secondary photons is fired. (3) In another microsecond or so when the intensity of the secondary light has reached its maximum, the Pockels (or Kerr) cell Q-switch is opened so that a giant laser pulse is obtained. As mentioned above, the absorption is measured during this laser pulse.

To carry out such an experiment we have used the following commercially available equipment. For the secondary xenon flash source we have found that a General Radio Strobotac Model 1538-A with a type 1538-P4 high-intensity flash capacitor booster serves quite satisfactorily. The Strobotac is fitted with an EGG FX-GA bulb covered with Corning uv transmitting glass.

The laser we used is a Model 130 Optics Technology ruby laser with a Pockels cell Q-switch. Any 100–200 megawatt ruby laser fitted with a Kerr or Pockels cell would be satisfactory.

Since the Strobotac puts out about a 5 μsec pulse, it is necessary to quite accurately time the laser to coincide within 1 μsec of the peak of the xenon flash pulse. This is accomplished by means of a bank of Tektronix 160 series waveform and pulse generators.

Measurement technique

The apparatus is shown in Fig. 1. It works in the following way. The starter trigger on the laser is fired to activate the xenon flash lamps which pump the ruby. When the intensity of the flash lamps reaches a predetermined level, a photodiode monitor sends a signal to the trigger of a Tektronix

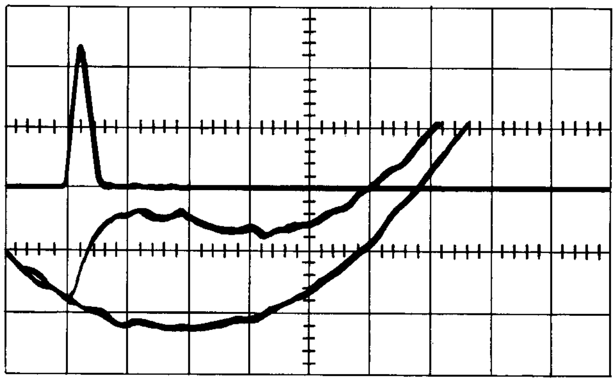
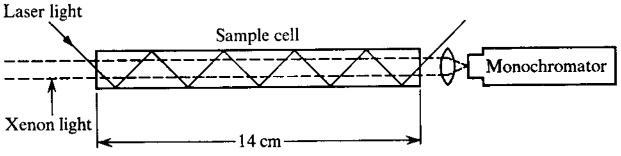


Figure 2 Tracing of typical oscilloscope photograph of laser-induced absorption in unfiltered liquids. Double exposure showing laser pulse on upper beam and the broad peak of the xenon flash, negative going, on the lower beam. The undeflected lower trace shows the secondary beam intensity in the absence of the laser pulse. The deflected lower trace shows a decrease in the intensity of the xenon flash of about 30 mV. The major part of the xenon intensity (650 mV total) was balanced off in the Tektronix type W plug-in differential amplifier. The decrease shown represents approximately 4% attenuation of the 4500 Å radiation in a solution of phenanthrene in benzene. The time scale is 100 nsec/division.

Figure 3 Configuration of laser and xenon flash for measuring absorption in liquids and solutions in 14 cm path length cell. The angle of the sample cell to the laser is adjusted by means of a He-Ne 6328 A gas laser whose beam is co-linear with the ruby laser so the total internal reflection of the laser beams is obtained at the glass-air interface.



#162 waveform generator. The waveform generator then puts out a 1000 μsec sawtooth which is fed into the input of the Tektronix Model 162 pulse generator. The pulse generator is delayed until 0.65 of the sawtooth has passed, time required to pump the ruby, (a 650 μsec delay) and it then emits a 25-V pulse of 10μsec duration. This pulse simultaneously initiates the firing of the external xenon lamp which is the source of the absorbed nonlaser photons as well as another waveform generator which produces a 100 μsec sawtooth. This sawtooth is fed into the second #163 generator equipped with a fine adjustment on the "fraction-sawtooth-delay" knob. Using this knob the timing of the output of a second 1 μsec, 25-V pulse can be adjusted within a few tenths of a μsec. This pulse fires the thyratron, which then fires the Pockels cell, which is the Q-switch for the cavity of the giant pulse laser. The timing of the external xenon flash and the giant laser pulse is adjusted so that the xenon flash is just reaching its peak when the laser fires; this can be done with considerable accuracy.

The light from the xenon flash passes through the sample and then through the monochromator and onto a Type 1P28 phototube, wired in the following special way. As mentioned above, in order to increase as much as possible the signal-to-noise ratio, a short (1–2 μsec) but very intense xenon source is used in order to obtain the maximum cathode current which is still linearly proportional to the lamp intensity. However, since the cathode current is very large, the full amplification of the eight dynodes would lead to an intolerably large anode current. Consequently, the tube is wired so that only three dynodes are used. The fourth serves as the anode, and the remaining dynodes and the anode are shorted to the third dynode so as to give them a repulsive negative potential. The fourth dynode is wired across a 93-Ω load to ground and the voltage developed across this load is fed into a 93-Ω BNC cable and then into a type W plug-in unit in a Model 555 Tektronix dual beam oscilloscope. The signal is generally about −1000 mV, which corresponds to ~10 mA in the 90-Ω load, about the maximum anode current allowable if the response is to remain linear. This −1000 mV signal is then balanced off with about +950 mV and displayed on the 10 mV/cm scale. Thus, a 5 mV decrease in the xenon signal, corresponding to 1/2% absorption, can be easily measured.

Two-photon absorption measurements

In two-photon absorption experiments some difficulty is encountered if the laser induces a fluorescence in the sample. When a strong collimated xenon light source is used, this difficulty is minimized. By measuring the laser-induced fluorescence independent of the xenon source, a correction can be made to the absorption.

This apparatus has been used for the study of dielectric breakdown in liquids.[6] If the liquids contain dust or other particulate matter, the laser appears to create very loosely bound electrons in the liquid (perhaps a type of plasma) which absorbs for a μsec or more after the laser shot. This phenomenon is shown in Fig. 2. It is present in almost all liquids but can be minimized by successive filtration through increasingly fine filters.

This apparatus has also been used for the study of two-photon absorption in aromatic molecules, notably α-chloronaphthalene.[7] In two-photon absorption studies very long path lengths are often required. We have found that cells made of a square pyrex tubing, 0.394 in. on a side, made by Fisher & Porter, work very nicely. Figure 3 shows our set-up for measuring two-photon absorption in α-chloronaphthalene. The total cell length is 14 cm and the red laser light enters at an angle such that total internal reflection off the glass-air interface along the flat sides of the cell is obtained. This whole apparatus including the angle for total internal reflection can be aligned by using a He-Ne cw laser.

When true two-photon absorption is obtained, the os-

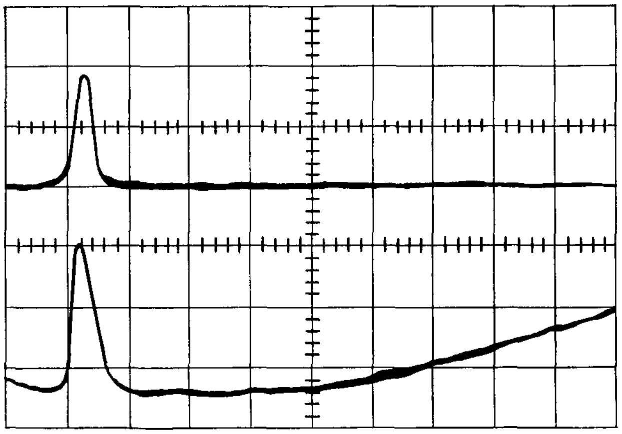


Figure 4 A tracing of an oscilloscope photograph showing laser-induced absorption in highly purified and filtered α-chloronaphthalene. The conditions are similar to those in Fig. 2. The absorption pulse (lower trace) has the same lifetime as the laser pulse (except that it is broadened slightly due to the somewhat slower response of the type W plug-in). The temporal dependence of the absorption pulse on the laser pulse is indicative of a two-photon absorption process.

cilloscope tracings appear as is shown in Fig. 4 for α-chloronaphthalene. In this case the absorption matches the laser emission almost exactly. It is slightly broader because the type W plug-in has a slightly longer time constant. Actually the shape of both pulses is determined by the time constant of electronics since the length of the laser pulse is only about ten nanoseconds when a Pockels cell Q-switch is used.

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