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ATR-76(7911)-3

EQUIPMENT SYSTEMS IMPROVEMENT PROGRAM

FEASIBILITY OF DOPPLER-FREE TWO-PHOTON SPECTROSCOPY FOR EXPLOSIVE VAPOR DETECTION

Law Enforcement Development Group

August 1976

Prepared for

National Institute of Law Enforcement and Criminal Justice
LAW ENFORCEMENT ASSISTANCE ADMINISTRATION
U.S. DEPARTMENT OF JUSTICE

The Aerospace Corporation

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FEASIBILITY OF DOPPLER-FREE TWO-PHOTON SPECTROSCOPY FOR EXPLOSIVE VAPOR DETECTION

Approved

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ABSTRACT

The feasibility of applying Doppler-free two-photon spectroscopy for explosive vapor detection was investigated. This technique takes advantage of the sensitivity inherent in optical methods of detection while offering the potential to eliminate the major previous disadvantage of nonspecific detection caused by broadening of the absorption bands. Specifically, this technique eliminates the Doppler broadening caused by the random motion of molecules in the gas phase. A two-photon spectrometer was assembled and it was demonstrated for the first time that the method is applicable to the detection of commonly occurring molecules. The parameters required to determine the two-photon detection limits were measured using an appropriate laser system. It was shown that with the new method typical molecules such as benzene and nitric oxide should be detectable with high sensitivity even in the presence of other molecules. However, detection sensitivity for explosive vapors was found to be inadequate because the molecules do not fluoresce efficiently. It was shown that for representative explosive molecules the optical absorption bands remain broad even when the Doppler broadening is eliminated.

ILLUSTRATIONS

TABLE

SUMMARY

Today, there exist no completely satisfactory methods to detect a range of characteristic component vapors from explosives in the ambient air at the 1 part in 10^{10} concentration level which would be encountered in a typical operational environment. Ultraviolet spectroscopy would provide a solution to this problem if explosive molecules had unique characteristic ultraviolet absorption spectra that would enable specific identification. Unfortunately, these molecules have highly diffuse absorption bands that extend over large regions of the ultraviolet spectrum. As a result, those broad bands overlap absorption bands of typical atmospheric species, thereby producing interference to detection.

In January 1975, work was initiated by The Aerospace Corporation and supported by a contract with the Law Enforcement Assistance Administration to explore the concept of Doppler-free counterpropagating beam two-photon spectroscopy for the purpose of detecting explosive vapors. Prior to this effort, experiments had demonstrated that one of the major causes for broadening of absorption bands (Doppler broadening) could be eliminated for isolated atoms. However, it still remained to be shown whether the application of this Doppler-free method to complex molecules could also provide detailed spectral information that could not be obtained by conventional spectroscopic techniques.

The initial phase of the program demonstrated that typical electronic spectra of molecules can be resolved by the method as predicted by theory. Apparatus was developed to obtain the initial absorption spectra for nitric oxide and benzene which are common constituents of the urban atmosphere. Analytical calculations were performed to describe the detection limit in terms of laser system parameters. Another laser system was then designed and set up to measure the parameters required to evaluate the detection limit of the technique as applied to explosive vapors. A specialized system was required to achieve well-characterized excitation conditions. This was

accomplished with a tunable, continuous-wave dye laser uniquely modified to incorporate an intracavity absorption cell. The extremely high power achieved in this system was required to measure the detection limit parameters for explosive molecules.

The intracavity two-photon spectrometer was calibrated using compounds with known fluorescence efficiencies. The feasibility of the detection technique was established for molecules such as benzene. Then the explosive vapors of dinitrotoluene, trinitrotoluene, and ethylene glycol dinitrate were studied. It was concluded that these species cannot be detected at concentrations of less than 1 part in 10^7 with current laser technology and fluorescence monitoring equipment.

It had been anticipated that acoustic detection might be applicable if only a small fraction of the excited molecules emitted fluorescence light. However, if the fluorescence efficiency (i.e., the fraction of the excited molecules that give up their excitation as fluorescence) is less than about 0.1%, the uncertainty principle predicts that the molecular linewidths will exceed the Doppler width and no advantage will be obtained by Doppler-free methods. Therefore, measurement of fluorescence efficiency was undertaken. Exceedingly low fluorescence efficiency (less than 0.1%) was found for dinitrotoluene, trinitrotoluene, and ethylene glycol dinitrate. Thus, selective interference-free detection is not possible for these species. It was therefore concluded that the Doppler-free two-photon method is unsuitable for detecting explosive vapors.

CHAPTER I. INTRODUCTION

A. Background

It has been recognized that a device which could detect the presence of explosives before detonation would be of great benefit to law enforcement agencies in their quest to protect human life and property. At present, there is no satisfactory method for the detection of "untagged" explosives. In a report prepared for the Law Enforcement Assistance Administration by The Aerospace Corporation, a number of methods for detection of explosives were reviewed.[1] Optical detection techniques were considered to be among the most promising methods. Their advantages include high sensitivity and selectivity, ease of operation, nondestructive sample measurements, and real time readouts. Similar conclusions were reached independently by the Research Triangle Institute, North Carolina (contract report DAAK-02-83-C-0128, December 1973).

With these conclusions in mind, Aerospace began an intensive review of the current scientific literature to determine whether any existing optical method had sufficient potential for development as an explosive vapor detector to merit additional research. The Doppler-free two-photon method emerged from this review. This method has been shown for atomic species to achieve extremely narrow spectral linewidths and large absorption coefficients. If similar results could be obtained for explosive vapors, the method could provide for a selective and high sensitivity detector that would be free from interference effects.

The inherent problems of specific vapor detection by ultraviolet excitation and the manner in which the Doppler-free two-photon method may overcome these problems are now discussed. All molecules have strong transitions in the ultraviolet region that provide the potential for high sensitivity detection. Unfortunately, normal ultraviolet absorption spectra appear as diffuse bands due to physical mechanisms that broaden the individual spectral lines. When many species are present these absorption

bands overlap so that it is no longer possible to selectively excite the species of interest.

Ultraviolet-region molecular absorption spectra arise from electronic transitions of outer electrons. These transitions are highly complex for polyatomic molecules because of the simultaneous occurrence of vibrational and rotational motion, which combine with the electronic excitation to produce a multitude of closely spaced transitions.[2] In the upper figure of Figure 1, an idealized spectrum for a molecule the size of an explosive material is shown. This spectrum would describe a completely isolated, motionless molecule with stable excited states. Below it is shown the typical featureless spectrum which arises when each of the otherwise-sharp transitions is broadened (as described below) under ordinary observational conditions. It would be highly difficult to identify a substance at trace concentrations on the basis of the lower spectrum.

There are fundamental physical limits to molecular transition linewidths. These phenomena consist of (1) collisional broadening, in which interaction between colliding molecules shifts the energy levels; (2) Doppler broadening, in which molecular motion (all gaseous molecules are in motion at ambient temperatures) shifts transition energies; and (3) natural broadening, in which the finite lifetime of the excited state τ imposes a natural linewidth γ_n predicted by the uncertainty principle, i.e., $\tau\gamma_n = 1/\pi$.[3] A relative comparison of the lineshapes due to each of the above line broadening factors is shown in Figure 2 for strong electronic transitions in the ultraviolet at one atmosphere and room temperature. The observed broadening of a spectral line is a combination of the broadening due to each of the above effects.

Collisional broadening is easily suppressed by reducing the pressure inside the sample chamber. It becomes negligible at 1 to 10 Torr (about 10^{-2} to 10^{-3} atmosphere). Doppler broadening can be reduced by cooling to near absolute zero; however, at that temperature, all substances have zero vapor pressure and cannot be detected in the gas phase. The natural broadening is an inherent molecular property and cannot be reduced. Most molecules are

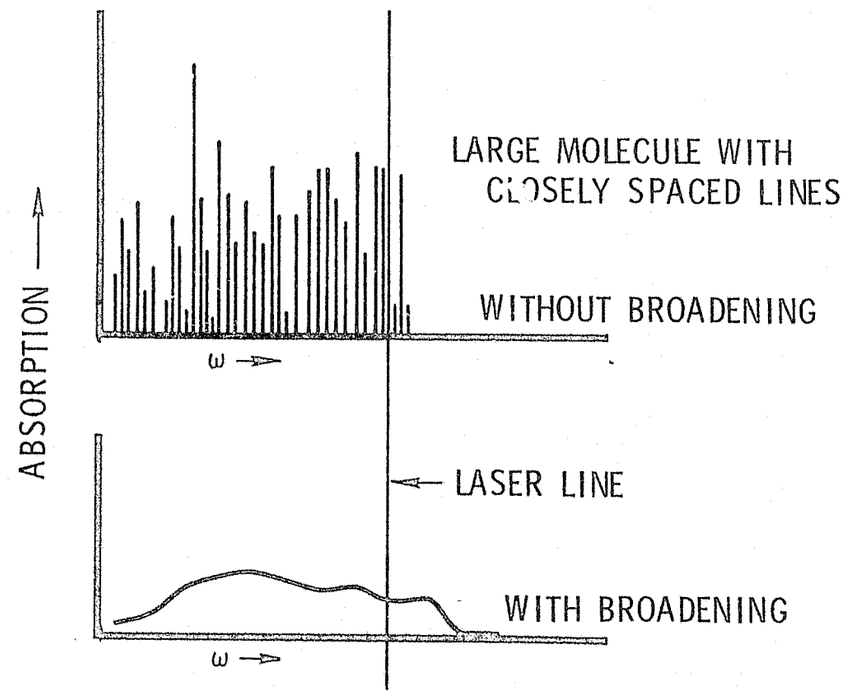

Figure 1. Effects of Spectral-Line Broadening Upon Electronic Absorption Spectra. The upper figure depicts the idealized spectrum for a molecule the size of an explosive. The lower figure shows the effects of line broadening under conventional observational conditions.

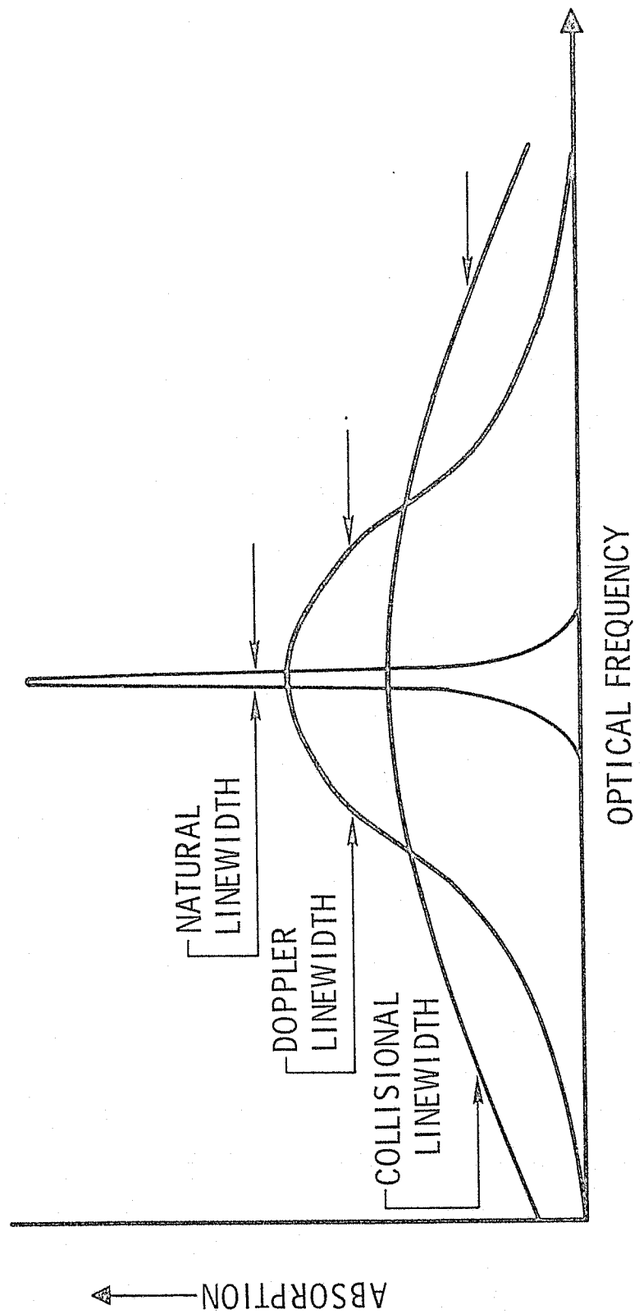

Figure 2. Relative Magnitudes of Different Line-Broadening Mechanisms Upon an Absorption Line of a Strong UV Molecular Transition. These are shown for a typical strong molecular transition at room temperature and 1 atmosphere.

known to fluoresce, which implies a substantial excited state lifetime; this, in turn, implies a small natural linewidth.[3] However, there are non-fluorescent substances. No literature information was available about gas phase fluorescence of explosive vapors at low pressures prior to this work. In the liquid phase, fluorescence has not been observed from nitro-compounds[4] with the exception of nitroazulene.[5] It was considered likely that interaction with the solvent could be responsible for the low fluorescence and that significant fluorescence would occur in the gas phase.

In the absence of collisional broadening, it can be seen from Figure 2 that elimination of the Doppler width $\Delta\nu_D$ of electronic transitions could yield extremely narrow spectral lines whenever γ_n is less than $\Delta\nu_D$. If γ_n is much less than $\Delta\nu_D$, then highly selective excitation and the potential for reduced interference from environmental species would be possible. In general, γ_n will be less than $\Delta\nu_D$ for species with high fluorescence yields. However, it is probable that γ_n will exceed $\Delta\nu_D$ for transitions of molecules that decay primarily by nonradiative processes (see Appendix A) and, thus, the potential for selective excitation by Doppler-free absorption will be lost for these species.

In conventional spectroscopy, a photon with energy exactly equal to the energy separation between the ground and excited states of a molecule induces a transition between the two levels. Normally, the molecule is initially in the lower state. Interaction with the photon excites the molecule to the higher energy state and the photon is removed (absorbed) from the light field. The number of molecules excited per unit time is then directly proportional to the light intensity. In the presence of highly intense laser optical fields, it has been observed that molecular transitions also occur when the energy of individual photons corresponds to exactly one-half the transition energy. This arises from simultaneous absorption of two photons. Because of the availability of tunable lasers, this form of nonlinear spectroscopy has become a routine scientific tool.[6]

A major reason for the practicality of this spectroscopic method is that weak absorption can be measured with extreme sensitivity. The excited

states generated by absorption may fluoresce; this fluorescence can be measured down to the level of a few photons per second. The fluorescence for the types of molecules of interest occurs in the ultraviolet region where detectors have maximum response and the ultraviolet is easily spectrally filtered from the laser excitation, which may be present at a flux of 10^{19} photons per second.

The conventional method of two-photon spectroscopy is limited by the same line-broadening mechanisms that apply to one-photon absorption. It is characterized by the same low degree of specificity applicable to conventional ultraviolet spectroscopy, the only major advantage being that existing tunable visible lasers could be used to excite ultraviolet transitions.

Reduction of the linewidth of molecular electronic transitions would increase the specificity of electronic absorption spectra so that trace gas identification might be possible. As mentioned previously, the collisional broadening component of linewidth can be reduced by going to subambient pressure. The natural linewidth can be quite small; therefore, the Doppler width has been the anticipated limitation.

A method involving two-photon absorption, which cancels the effect of Doppler broadening, has been developed and applied to atoms.[7] Most atoms or molecules in a gas move at high velocities in random directions because of their thermal kinetic energy. If a molecule absorbs simultaneously two photons coming from opposite directions, as shown in Figure 3, the blue Doppler shift applicable to the photon coming from the direction toward which the molecule moves $(+\frac{v}{c}\omega_0)$ is exactly canceled by the red Doppler shift applicable to the photon coming from the opposite direction $(-\frac{v}{c}\omega_0)$. Therefore, all molecules, regardless of velocity, are subject to an overall energy $2\omega_0$ and can participate in absorption independent of thermal velocity. Thus, Doppler broadening is eliminated.

The effect of counterpropagating beam two-photon absorption upon overlapping spectra of two closely spaced molecular transitions is represented in Figure 4. Because molecules absorb counterpropagating beams over an energy spread determined by the natural linewidth γ_n the spectra

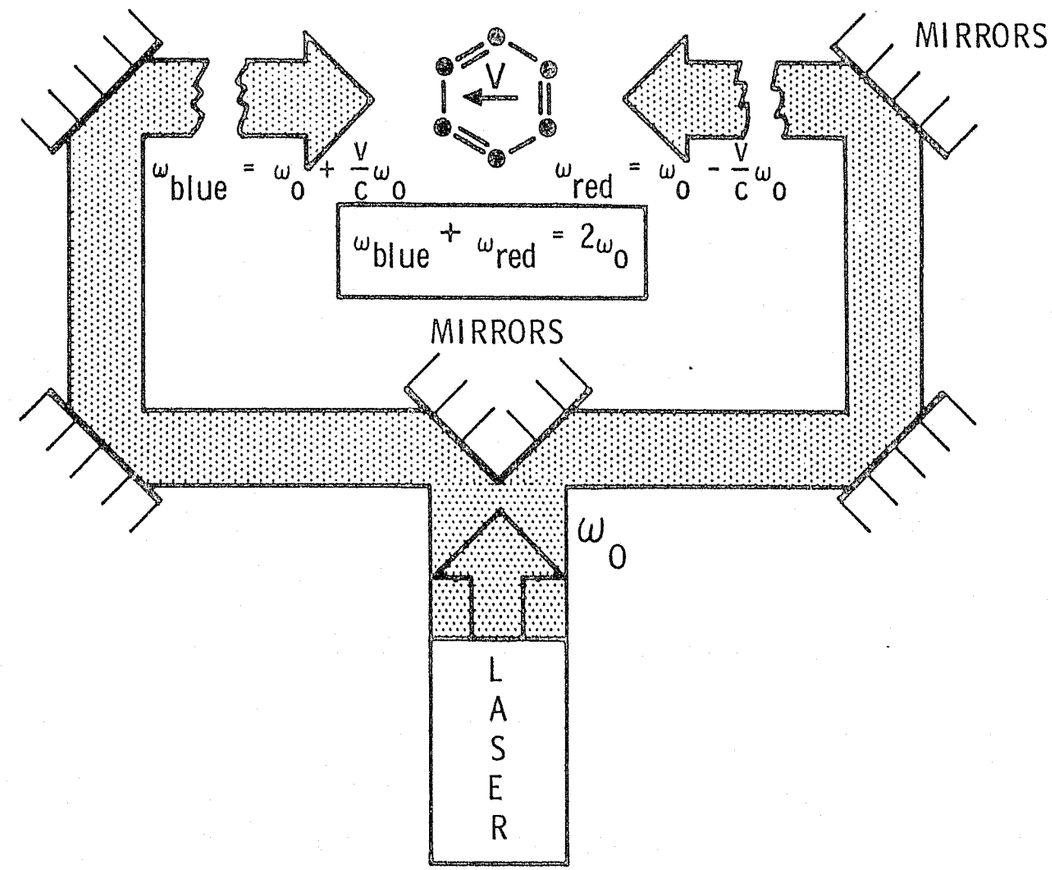

Figure 3. Counterpropagating Beam Two-Photon Concept. A molecule with resonance at $2\omega_0$ is shown moving with velocity v towards the left beam and experiences its optical field blue-shifted by $+(v/c)\omega_0$. The molecule is moving away from the right beam and experiences its radiation red-shifted by an equal and opposite amount $-(v/c)\omega_0$. The sum of the frequency of the blue-shifted light and red-shifted light is exactly $2\omega_0$ and is independent of molecular velocity.

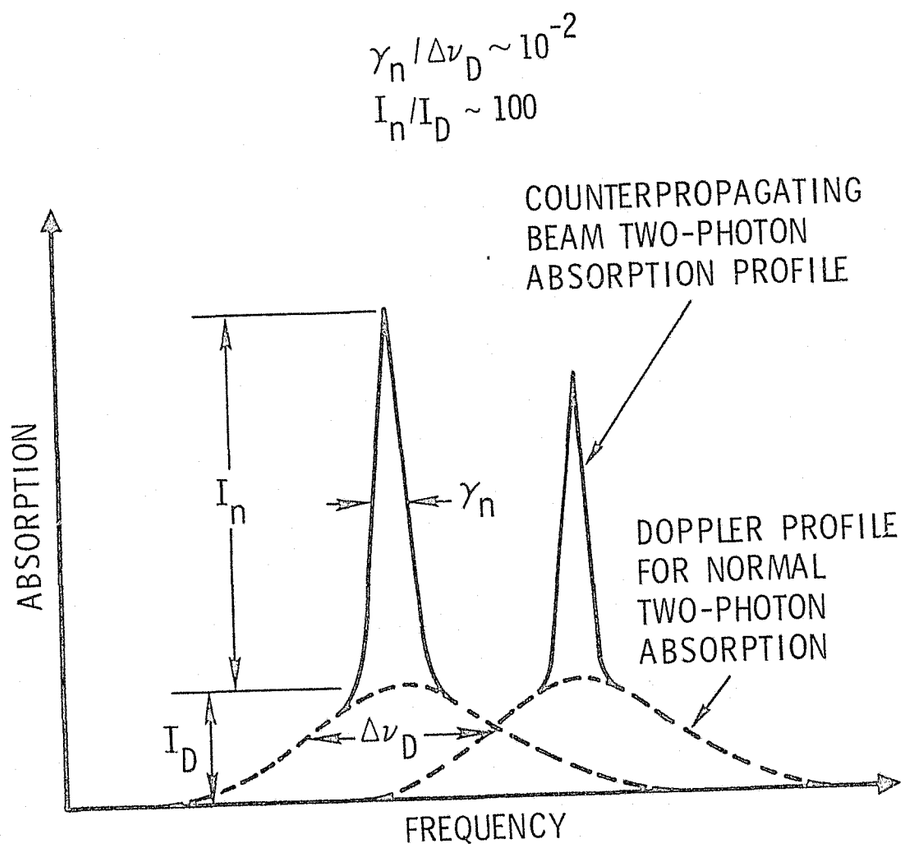

Figure 4. Two-Photon Absorption Spectra of Two Closely Spaced Transitions. The dashed curve is the conventional absorption spectrum whereas the solid lines represent Doppler-free absorption.

are expected to be much sharper, and, therefore, normally well resolved. Typically $\gamma_n/\Delta\nu_D \simeq 10^{-2}$ has been achieved for atoms. The peak absorption intensity is also much higher, by the ratio $\Delta\nu_D/\gamma_n \simeq 100$, because all molecules participate in this absorption, regardless of velocity. However, note that the molecules can also absorb two photons from a single beam simultaneously. This absorption has the conventional profile characterized by the Doppler width $\Delta\nu_D$. Therefore, the sharp Doppler-free absorption peaks rise above a smooth pedestal of overlapping Doppler contours. Two important advantages accrue from the fact that counterpropagating beam two-photon absorption profiles are much narrower and display more intense peaks than the ordinary Doppler-broadened two-photon absorption profiles. First, the extremely narrow absorption linewidths obtained in the absence of Doppler broadening minimize interference effects. Second, because the sensitivity of the method depends upon the strength of the two-photon interaction the increased intensity of the Doppler-free absorption peak provides for lower minimum detectable concentrations.

B. Program Goals

When the program was proposed, the concept of Doppler-free two-photon molecular spectroscopy was new. The method had been applied to sodium vapor by several research groups, and it was clear that it had great potential for trace gas detection. A program was initiated to evaluate its potential as an advanced concept for explosive vapor detection.[8] As none of the required physical parameters was available for explosive vapors, the program was largely exploratory in nature. The program proceeded in two phases with the first phase designed to test the theoretical basis and the second phase designed to test the feasibility for actual explosive component vapors.

The initial objective of the program was to verify that spectra of complex molecules could be resolved by the two-photon method as predicted by theory. This program goal was successfully achieved when the first observations of Doppler-free absorption of electronic states of molecules were recorded for nitric oxide and benzene. Following this phase, an

analysis of the critical parameters for a practical detection system was carried out. It revealed that the detection limit was dependent upon the product of the two-photon absorption cross section $\sigma_{2\phi}$ and the fluorescence quantum yield η_f. Although there were a limited amount of data available for $\sigma_{2\phi}$ from older condensed-phase experiments, there were no data applicable to gas-phase explosive molecules. It was known that nitro-aromatic compounds do not fluoresce strongly in condensed media, apparently because of photochemical reactions, but appropriate data were not available for the gas phase. Thus, the experimental effort in the second phase of this program was to determine the $\sigma_{2\phi} \times \eta_2$ for actual explosive vapors. If all early stages of the program supported applicability of the method to explosive vapor detection, measurements were to be made to assess the interference of environmental gases upon such detection.

CHAPTER II. DETECTION LIMIT AND OPTIMUM PRESSURE FOR DETECTION

Because pressure broadening is expected to be an important limitation in Doppler-free spectroscopy, analysis of the optimum pressure conditions is important. The fractional sensitivity is the parameter of concern. Therefore, if a detection system operates at subambient pressures, the same fractional concentration describes the mixture, even though the volumetric concentration may be greatly reduced.

A more detailed mathematical analysis of two-photon detection has been performed since the initial rough calculation given in the interim report.[8] It indicates that optimum fractional sensitivity is achieved at a specific pressure, which is determined by the fluorescence yield, natural linewidth, pressure broadening coefficient, quenching constant, and natural lifetime.[9]

The complete analytical treatment appears below. To summarize the results, for representative molecular parameters, a detection limit of 2 parts in 10^{11} is feasible. An order of magnitude improvement in detection sensitivity is likely to arise from technological advances in the next several years.

The ratio of the absorption coefficients per unit concentration for the counterpropagating beam two-photon process $\beta_{2\phi}$ to the one for the one-photon process β_ϕ is given by

$$\frac{\beta_{2\phi}}{\beta_\phi} = \frac{(\mu_{el}E)^2}{h\nu_{el}} \frac{\Delta\nu_D}{\gamma} = \frac{I}{I_o} \frac{\Delta\nu_D}{\gamma} \tag{1}$$

where

μ_{el} = transition dipole moment to an intermediate electronic state

h = Planck's constant

ν_{el} = electronic frequency

E = amplitude of optical electric field

$\Delta\nu_D$ = Doppler linewidth

γ = linewidth from other processes

I = optical field intensity

I_o = a normalized intensity defined in terms of μ_{el} and ν_{el}

One appropriate monitoring configuration is shown in Figure 5. A dye laser is tuned to exactly one-half the frequency of the molecular ultraviolet transition of interest. The sample cell is placed inside the laser cavity to (1) take advantage of the intense optical fields that exist there and (2) ensure the alignment of the counterpropagating beams. It is assumed for calculational purposes that some of the excited-state molecules decay through photon emission. The radiative emission near the two-photon frequency is collected and focused onto the cathode of a sensitive photomultiplier tube that is operating in the photon-counting mode and is placed perpendicular to the optical axis. An optical filter is inserted in front of the photocathode to reject radiation at the laser frequency and pass the shorter wavelength molecular emission. Dark-current-limited photodetection is thus effected.

The photoelectronic counts C recorded in this configuration are given by

$$C = \beta_{2_\phi} nL \frac{Pt}{2h\nu_L} \eta_f \eta_c \qquad (2)$$

where

n = molecular number density

L = interaction length

t = integration time

P = average intracavity laser power

ν_L = laser frequency

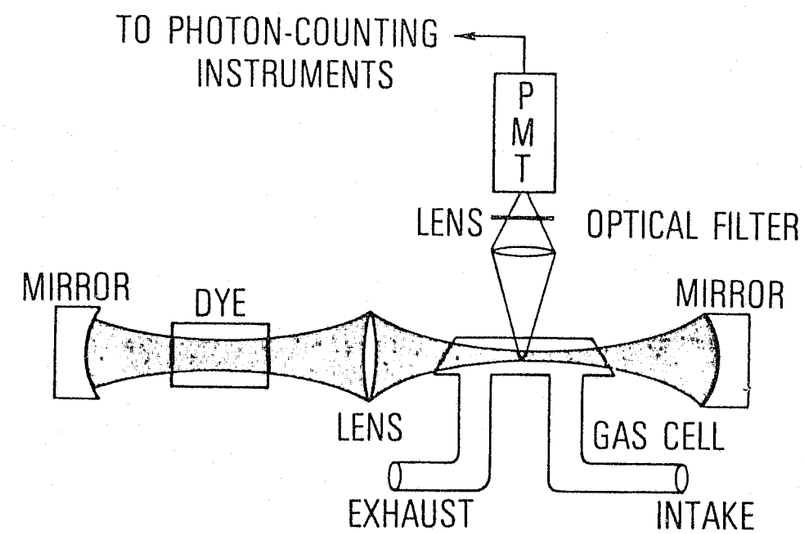

Figure 5. Schematic of Operational Two-Photon Explosive Vapor Detector

η_f = quantum efficiency for fluorescence

η_c = optical collection efficiency

For dark-current-limited photodetection, the minimum detectable counts C_m are approximately 1 count/sec·cm^2. For a nominal 1 cm^2 photocathode and integration time t (sec)

$$C_m = t^{1/2} \tag{3}$$

By the use of Eqs. (1) - (3), the minimum detectable molecular concentration n_m can be expressed as

$$n_m = \frac{2h\nu_L I_o}{(\Delta\nu_D/\gamma)\beta_\phi (L/A) P^2 t^{1/2} \eta_f \eta_c} \tag{4}$$

where A is the optical-beam area. For a laser operating in the TEM_{∞} mode,

$$\frac{L}{A} \sim \lambda^{-1} = \frac{\nu_L}{c} \tag{5}$$

where c is the speed of light and λ is wavelength.

Substitution of Eq. (5) into Eq. (4) yields

$$n_m = \frac{2hc\, I_o}{(\Delta\nu_D/\gamma)\beta_\phi \eta_f P^2 t^{1/2} \eta_c} \tag{6}$$

As expected, Eq. (6) indicates that molecules with transitions having large absorption coefficients, small natural linewidths, and large fluorescence quantum efficiencies are ideal candidates for detection by this method.

In the absence of Doppler broadening, the transition linewidth of atmospheric gases is determined by pressure broadening, radiative decay, and internal nonradiative processes. For this case

$$\gamma = k_1 p + \frac{1}{\pi\tau} \tag{7}$$

and

$$\eta_f = \frac{\tau/\tau_r}{1 + \tau k_2 p} \tag{8}$$

where k_1 is the pressure-broadening coefficient, p is the pressure (not to be confused with intracavity power P), τ is the natural lifetime, τ_r is the radiative lifetime, and k_2 is the collisional deactivation. Substitution of Eqs. (7) and (8) into Eq. (6) yields

$$n_m = \frac{2hc\, I_o}{\Delta\nu_D \beta_\phi P^2 t^{1/2} \eta_c} \frac{\tau_r}{\tau} \left(k_1 p + \frac{1}{\pi\tau}\right) (1 + \tau k_2 p) \tag{9}$$

The pressure dependence of the detection sensitivity is investigated to determine the ambient pressure that maximizes volumetric sensivitity S. It is related to n_m by

$$S = \frac{n_m}{3.5 \times 10^{16}\, p} \tag{10}$$

where p is expressed in Torr.

The maximization of S with respect to p allows the optimum pressure p_o for Doppler-free two-photon detection to be determined. This value is

$$p_o = \left(\frac{1}{\pi k_1 k_2 \tau^2}\right)^{1/2} \tag{11}$$

and depends solely upon parameters of the molecular transition.

The maximum volumetric sensitivity S_m is found by the substitution of p_o for p in Eq. (10), which yields

$$S_m = \frac{2hc\, I_o}{3.5 \times 10^{16}\, \pi \beta_\phi P^2 t^{1/2} \eta_c \Delta\nu_D} \frac{\tau_r}{\tau}\left[(\pi k_1)^{1/2} + k_2^{1/2}\right]^2 \tag{12}$$

Typical system parameters are P = 20 W, t = 100 sec, and η_c = 3%. Typical molecular parameters are β_ϕ = 100 cm^{-1}/atm, $I_o = 10^{15}$ W/cm^2, and $\Delta\nu_D$ = 3 GHz. The radiative lifetime of two molecular species is taken to be 100 and 1 nsec, respectively, and it is assumed that the excited state decays primarily by radiative relaxation in the absence of collisions, i.e., $\tau \approx \tau_r$. Note that transitions with radiative lifetimes that fall between 1 and 100 nsec have natural linewidths in the range of 300 to 3 MHz, respectively.[3] Commercial continuous wave dye lasers exhibit spectral bandwidths of ~1 MHz so that effective excitation of the two-photon transition can be readily accomplished with existing laser systems. For both gases, a representative value for the pressure-broadening coefficient of 10 MHz/Torr is selected, and the quenching of the excited state by collisions with other molecules is assumed to proceed with unit efficiency and to occur at the gas kinetic rate.

Substitution of the above parameter values in Eqs. (11) and (12) produces the result that the maximum volumetric sensitivity is achieved at a total sample pressure of 0.56 Torr for the long-lived species and 56 Torr for the short-lived one. For both species, $S_m = 2 \times 10^{-11}$, i.e., 0.02

CHAPTER III. RESULTS

A. Doppler-Free Spectra of Molecules with a Pulsed Dye Laser

The heart of the two-photon detection method is the ability to achieve Doppler-free absorption so that heretofore diffuse ultraviolet electronic spectra of heavy molecules might be resolved into discrete lines. The direct excitation of single electronic states could permit highly selective excitation and reduce interference effects from other molecular species that exhibit absorption bands in the same spectral region.

The experimental results obtained during the first phase of the program confirmed the theoretical predictions and supported the underlying hypothesis of this investigation.[8] Absorption line-narrowing was observed for nitric oxide, and resolvable spectral features were recorded in the benzene absorption spectra. These features appear diffuse when observed by ordinary spectroscopic methods. The molecular structure of benzene is related to that of trinitrotoluene and is comparable in complexity to that of other explosive vapors. These spectra are shown in Figures 6 and 7. In both cases, the resolution was limited by the bandwidth of the pulsed laser system, 0.25 GHz. The initial apparatus developed for these investigations consisted of a narrow-bandwidth pulsed-laser system. Excitation was provided by a nitrogen-pumped tunable dye laser. The output of the laser traversed an electronically scanned Fabry-Perot interferometer to reduce its spectral width. The beam then passed through an amplifier before it irradiated the sample cell. A concave mirror was placed on the exit side of the sample cell in order to focus the beam back on itself to obtain the counterpropagating beam geometry. Further details and photographs of the early experimental arrangement appear in the interim report.[8]

B. Detection Limit Estimate

The next phase of this effort involved the determination of the detection limit of the method. In the appendix of the interim report,[8] an expression was derived for the detection limit of the two-photon scheme. Parameters in this analysis included those of a laser system and those for the molecular

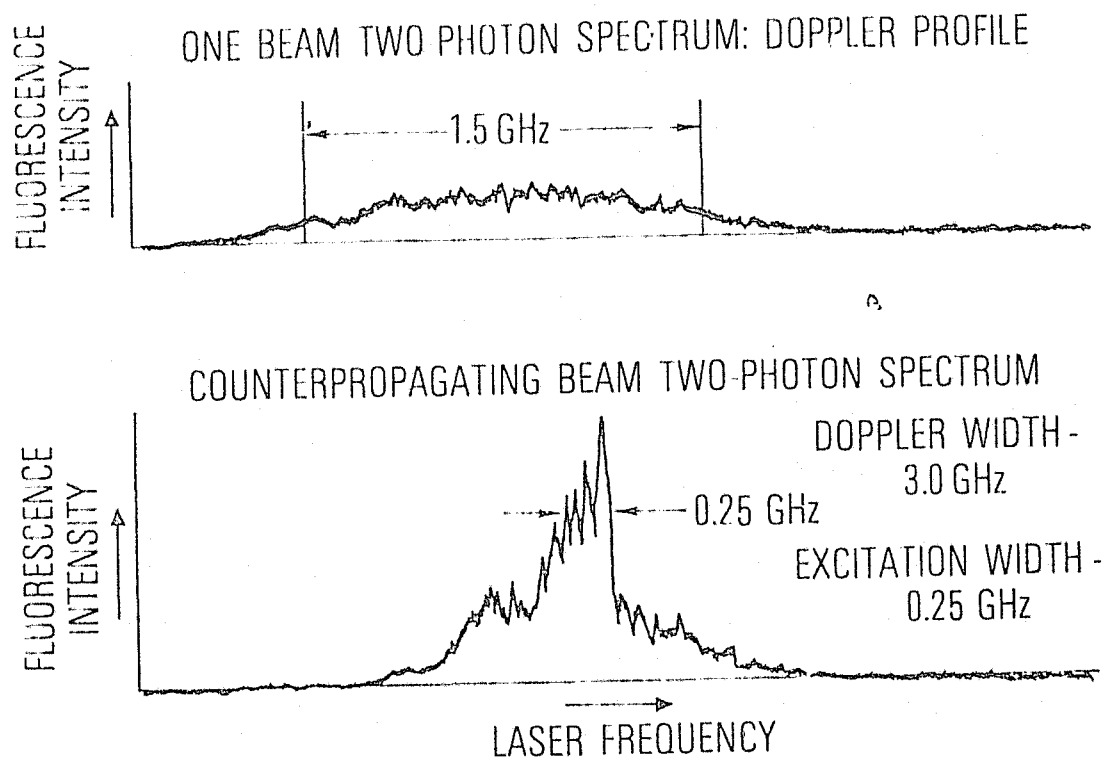

Figure 6. Two-Photon Excitation Spectrum of a Nitric Oxide Transition at a Laser Wavelength of 453 nm

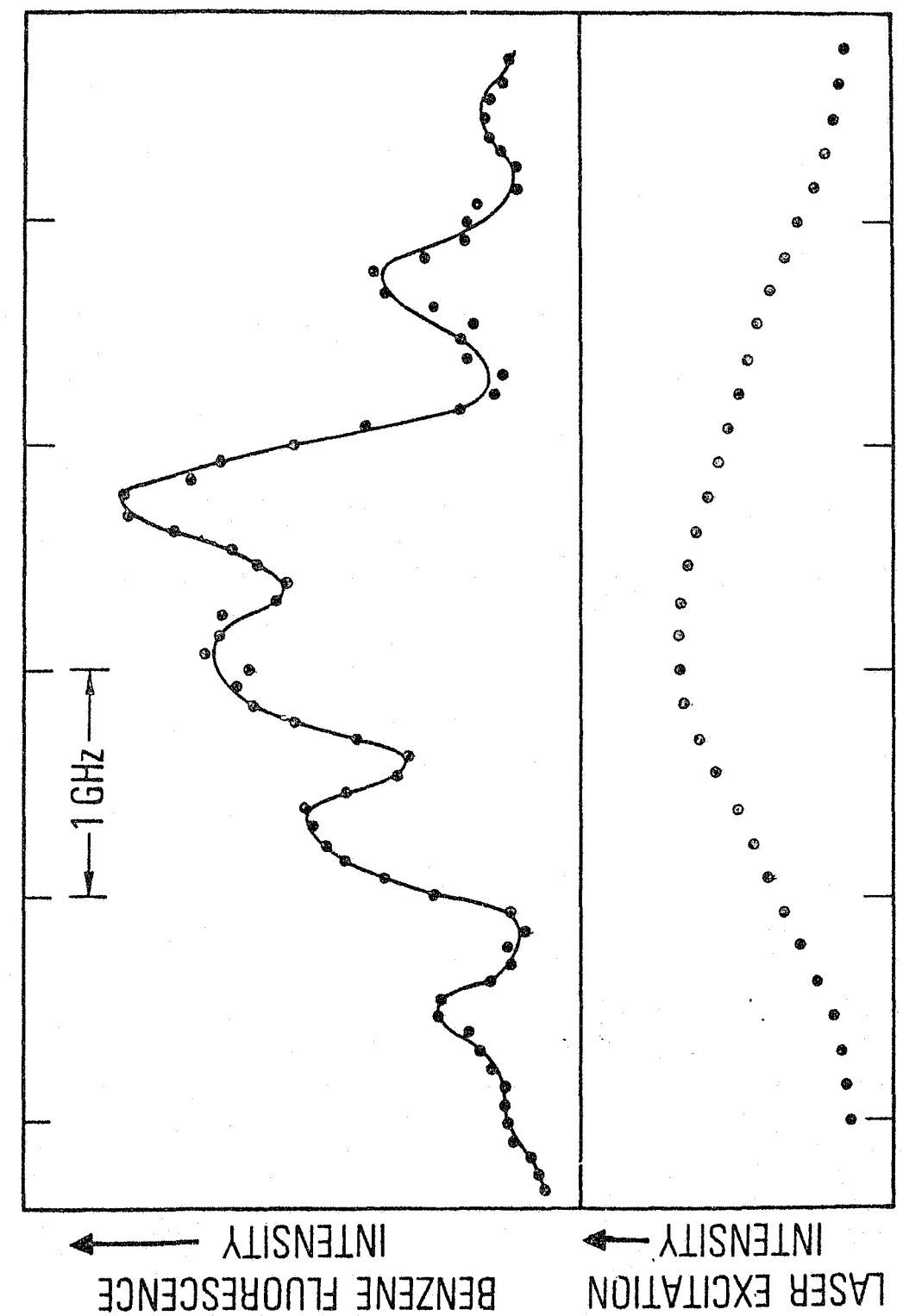

Figure 7. Two-Photon Excitation Spectrum of Benzene Excited with a Laser Wavelength of 504 nm. The upper curve is the counterpropagating-beam spectrum of benzene, without correction for the variation in laser intensity as a function of frequency. The lower curve shows the frequency dependence of the laser intensity.

species of interest. Substitution of typical values for a continuous wave laser system and representative molecular parameters predicted that the detection limit ranged from 1 part in 10^{12} to 1 part in 10^{5}. Further advances in the state of the art of laser technology or the use of a pulsed dye laser system could improve the detection limit by one to two orders of magnitude. The large spread in the detection limit arises from the lack of knowledge of the product of two parameters of explosive molecules. The product is $\sigma_{2\phi} \times \eta_f$, where $\sigma_{2\phi}$ is the two-photon absorption cross section and η_f is the fluorescence quantum yield. Based upon this calculation a $\sigma_{2\phi} \times \eta_f$ product of 10^{-49} cm^2/photon/sec·cm^2 would be required to attain a detection limit of 0.1 part per billion.

C. Two-Photon Measurements of Explosive Molecules with a Continuous Dye Laser

The major experimental thrust of the effort during the second phase of the program was directed toward the determination of the detection limit for the two-photon method by measuring the upper bound of the product of the two-photon absorption cross section and the fluorescence quantum yield for actual explosives. The explosives or explosive constituents studied were dinitrotoluene, trinitrotoluene, ethylene glycol dinitrate, and diphenylamine (a stabilizer in smokeless power). A special high-resolution tunable continuous wave dye laser two-photon spectrometer was assembled for this purpose. The bandwidth of a laser is ultimately limited to a value given approximately by the inverse of the pulse duration. Therefore, the continuous dye laser can provide much higher resolution two-photon spectra than can be obtained with a pulsed laser. The two-photon spectrometer is shown in Figure 8. Photographs of the apparatus appear in Figure 9.

At the heart of the spectrometer is a commercial jet stream dye laser (Spectra Physics #580A) pumped by the output of a commercial argon-ion laser (Coherent Radiation Model #CR-12). The argon-ion emission is composed of the following discrete wavelengths in the near ultraviolet, blue, and green spectral regions: 351 nm, 364 nm, 454 nm, 458 nm, 466 nm, 473 nm, 477 nm, 488 nm, 497 nm, 502 nm, 514 nm, and 529 nm. The dye laser

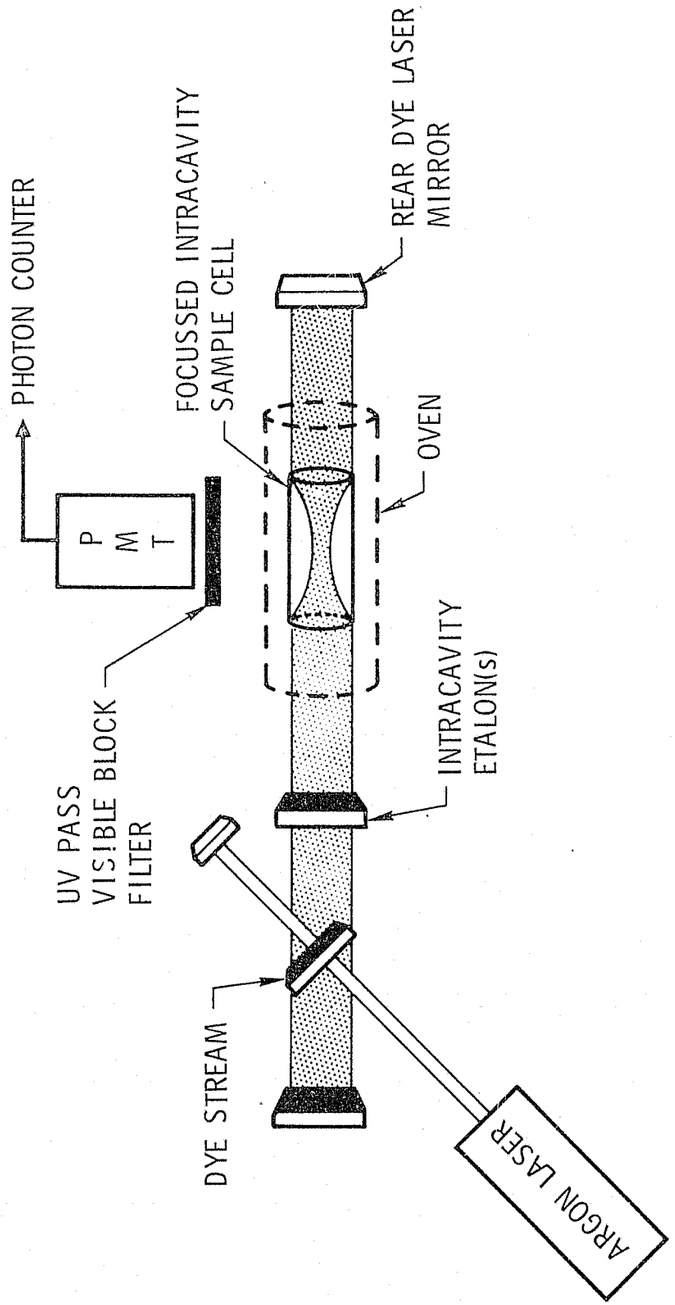

Figure 8. Schematic Representation of High-Resolution Doppler-Free Two-Photon Spectrometer Used for Obtaining Data for Explosive Vapors

detected from the evacuated cell when it was irradiated with maximum laser power at either the two-photon wavelength or wavelengths much longer than the excitation wavelength.

For work requiring sensitive detection and a chemically inert environment, a quartz cell was fabricated with end windows of antireflection lenses with small focal lengths (f = 2 cm). Inside the laser resonator the beam diameter is 0.5 mm. The diameter at the center of the quartz cell is 0.05 mm, thereby realizing a hundredfold improvement in two-photon absorption efficiency.

The lenses for this cell were glass rather than quartz because glass lenses of the proper diameter and focal length were in the laboratory and could be used immediately. However, upon laser irradiation of the cell, window luminescence was observed that severely limited the use of this cell for recording extremely small fluorescence signals. Therefore most of our two-photon measurements were performed with the stainless steel sample cell that had quartz windows. Intracavity focused cells with low luminescence quartz lenses should reduce this problem significantly.

Heating tape wrapped around metallic covers that fit over the sample cells provided a means for baking out the cells and permitted measurements at temperatures up to 80°C. No evidence of thermal decomposition of explosive vapors was observed for dinitrotoluene, trinitrotoluene, and diphenylamine. As discussed later, photodecomposition of ethylene glycol dinitrate was observed. High temperature operation was required to generate a sufficient concentration to perform two-photon measurements on several of the low vapor pressure explosive vapors. Parameters of the two-photon spectrometer appear below:

Wavelength Region (Intracavity Power) - 560-630 nm (1-3 W)
440-480 nm (0.1-1 W)

Spectral Width of Dye Laser - 30 MHz (Single Line)

Stainless Steel Cell:

Beam area - dye laser - 2.5×10^{-4} cm^2
- argon laser - 2×10^{-3} cm^2

Absorption path length - 1 cm

Quartz Cell:

Beam area/Absorption length - 6×10^{-5} cm

Light Collection Efficiency (Solid - Angle) - 7%

Photomultiplier Quantum Efficiency @ 330 nm - 0.2%
(EMR-542F)

The stainless steel sample cell was also used external to the laser cavity for $\sigma_{2\phi} \times \eta_f$ measurements with excitation from the argon-ion laser and for conventional one-photon induced fluorescence measurements. Before measurements were made, the cell was evacuated to a pressure less than 10^{-3} Torr and then baked out overnight. It was then placed into the experimental system to ensure that no signals were recorded from the empty cell. The explosive sample, in the condensed phase, was then placed inside the cell in a side arm, and the cell was once more evacuated to a pressure less than 10^{-3} Torr. The side arm of the cell was bathed in liquid nitrogen to prevent loss of high vapor pressure materials during pump down. The cell was then removed from the vacuum state station and measurements begun.

Each explosive vapor investigated was scanned throughout the wavelength ranges listed above. These wavelength regions include frequencies that correspond to one-half the frequency of the first strong one-photon absorptions. Photon counts at room temperature were recorded. While the system parameters were held fixed, the temperature of the cell was increased to near 80°C and photon counts were recorded again. For all the explosive samples investigated, the high temperature counts were indistinguishable from the low temperature counts. Thus, the maximum count rate attributable to the explosive sample was 5 counts/sec. Measurements of $\sigma_{2\phi} \times \eta_f$ were performed on benzene and naphthalene to verify the operational integrity of the two-photon spectrometer. Signals were recorded that were in excess of 100 times the variation in the background count rate, i.e., the noise, for both substances. These measurements established the minimum detectable $\sigma_{2\phi} \times \eta_f$ product at 2×10^{-51} cm^2/photon/sec·cm^2 at 10 mTorr and P = 1 W for this system, which represents a detection limit of two parts

per trillion. The results of the $\sigma_{2\phi} \times \eta_f$ measurements appear in Table 1. Vapor pressure data were taken from Note 10. The values for $\sigma_{2\phi} \times \eta_f$ are calculated from the following expression that relates $\sigma_{2\phi} \times \eta_f$ to the observable count rate C/t

$$\sigma_{2\phi} \times \eta_f = 2A\,(h\nu_L)^2 C/tLn\eta_c P^2 \qquad (13)$$

This expression is easily derived from Eq. (2) noting that

$$\beta_{2\phi} = \sigma_{2\phi} \times P/h\nu_L A \qquad (14)$$

A curious effect was observed for ethylene glycol dinitrate. Immediately upon excitation no signals were recorded. However, within ten minutes thereafter, the signal level built up to nearly 1000 counts/sec. Upon lateral translation of the sample cell in the beam, the signal level returned to zero and then built up again, which suggests that the effect occurs at the windows of the stainless steel cell. The effect was observed both with radiation from the dye laser at orange wavelengths and from the argon-ion laser lines in the blue-green spectral region. The result suggests that a method of ethylene glycol dinitrate detection based upon this effect might be possible (Comment 1). Attempts were made to observe the effect with the quartz cell, but the large luminescence from its glass windows overshadowed any signals from the ethylene glycol dinitrate sample.

D. <u>One-Photon Measurements</u>

To understand the surprising low value for the $\sigma_{2\phi} \times \eta_f$ product, and to investigate the possibility of photoacoustic detection, the independent measurement of η_f was undertaken. A standard one-photon fluorescence measurement system was configured (see Figure 10).

The question arises whether the fluorescence yield from levels excited by one-photon absorption will be the same as the yield under two-photon excitation. The well-defined parity of atomic electronic states prohibits

Table 1. $\sigma_{2\phi} \times \eta_f$ Measurements

Explosive	Sample Pressure (Torr)	Excitation Source	$(\sigma_{2\phi} \times \eta_f)_{max}$ (cm^2/photon/cm^2·sec)	η_f	Minimum Detectable Concentration[b] (ppm)
TNT	10^{-2} (80°C)	Strong Ar^+ lines	4×10^{-53}	—	> 1
		Weak Ar^+ lines	6×10^{-52}		> 0.1
DNT	0.2 (65°C)	Blue dye	10^{-53}	$\leq 3 \times 10^{-5}$	> 1
Diphenylamine	0.1 (70°C)	Orange dye	10^{-51}, 2×10^{-53}[a]	4×10^{-4}	> 1
		Ar^+ lines	2×10^{-52}		> 0.1
EGDN	0.15 (25°C)	Orange dye	6×10^{-54}	—	10
		514 nm Ar^+ line	5×10^{-52}		> 1

TNT trinitrotoluene
DNT dinitrotoluene
EGDN ethylene glycol dinitrate

[a] Focused intracavity cell

[b] Based upon $\dfrac{10^{-49}\ cm^2}{photon/cm^2 \cdot sec} \Leftrightarrow 0.1$ ppb

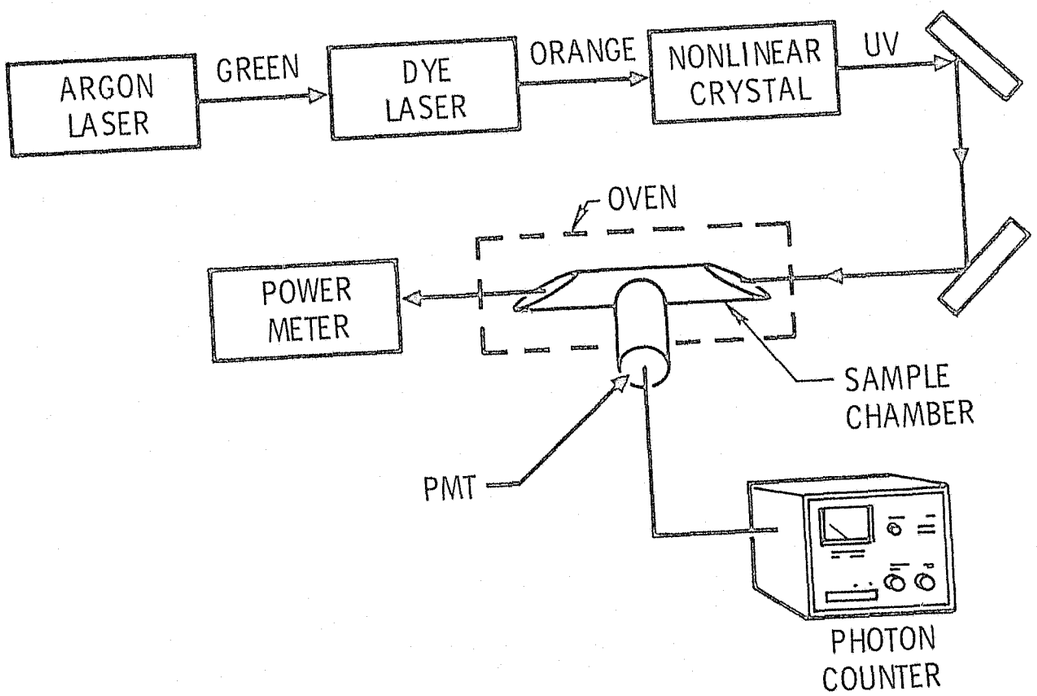

Figure 10. Schematic Representation of the Apparatus Employed to Measure the Fluorescence Quantum Yields of the Vapors from the Selected Explosives

one-photon transitions and two-photon transitions between the same pair of states through electronic dipole coupling so that η_f will not be the same for atomic levels. However, most molecules and especially large ones such as explosives lack an inversion center so that both types of processes are permitted between any pair of electronic levels. As a consequence of the lack of well-defined parity of states, η_f from levels excited both by one-photon and two-photon processes will be the same for explosive molecules.

In order to locate the region of maximum ultraviolet absorption, standard absorption spectra were acquired because gas-phase absorption spectra do not appear in the literature. A quartz cell containing the explosive was placed in a Cary 14 Spectrophotometer. Spectra were run at various temperatures. The absorption spectra of dinitrotoluene, trinitrotoluene, and diphenylamine obtained in this manner appear in Figures 11 and 12. Maximum cross sections are 7×10^{-16} cm^2 for dinitrotoluene, 3×10^{-16} cm^2 for trinitrotoluene, both occurring near 220 nm, and 2×10^{-17} cm^2 for diphenylamine near 270 nm.[10] A fluorescence spectrum was obtained for diphenylamine that revealed a fluorescence band centered about 330 nm (see Figure 12).

The experimental arrangement for measuring η_f directly by one-photon induced fluorescence is shown in Figure 10. Emission from the dye laser pumped by the argon ion laser was incident upon a second harmonic-generating crystal. For diphenylamine, Rhodamine 6G was the dye. Radiation near 580 nm was doubled and provided ~ 0.3 μW near 290 nm in the ultraviolet. The second harmonic beam was then directed into the heated stainless steel sample cell. The solar blind photomultiplier tube placed at the side viewing port monitored the one-photon induced fluorescence near 320 nm (the region of maximum fluorescence from diphenylamine; see Figure 12). A net signal of 5000 counts/sec was observed. The absorbed power was calculated based upon the difference in power at the exit port of the sample at low temperature and at high temperature. A calibration curve of the photomultiplier tube spectral response appears in Figure 13. The procedure followed to measure the photomultiplier quantum efficiency is outlined in Appendix B. The calculated value of η_f was 0.04%. In the same manner an upper limit of 3×10^{-5}

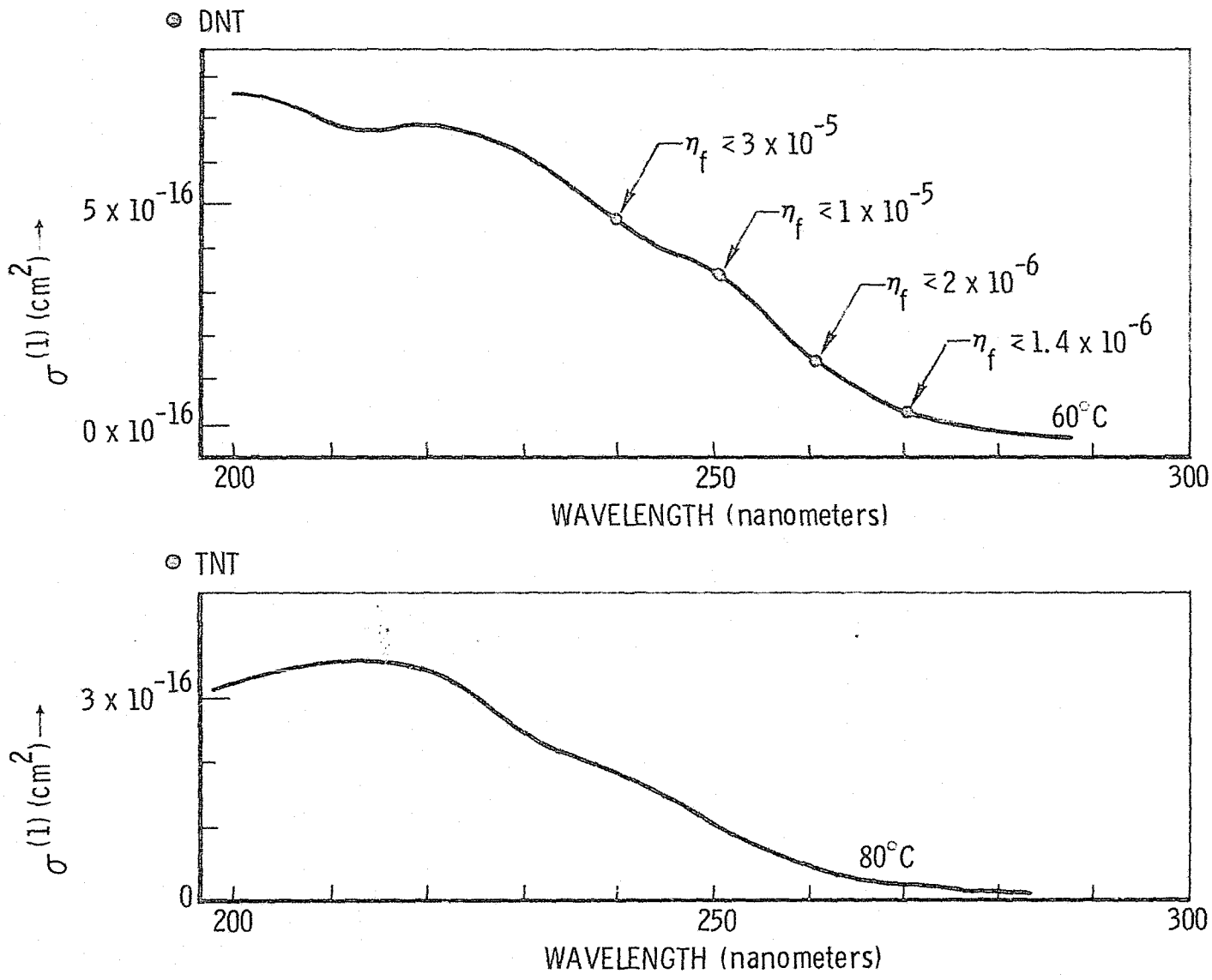

Figure 11. Absorption Spectra of Dinitrotoluene and Trinitrotoluene. Fluorescence yields (η_f) are shown for dinitrotoluene for selected excitation wavelengths

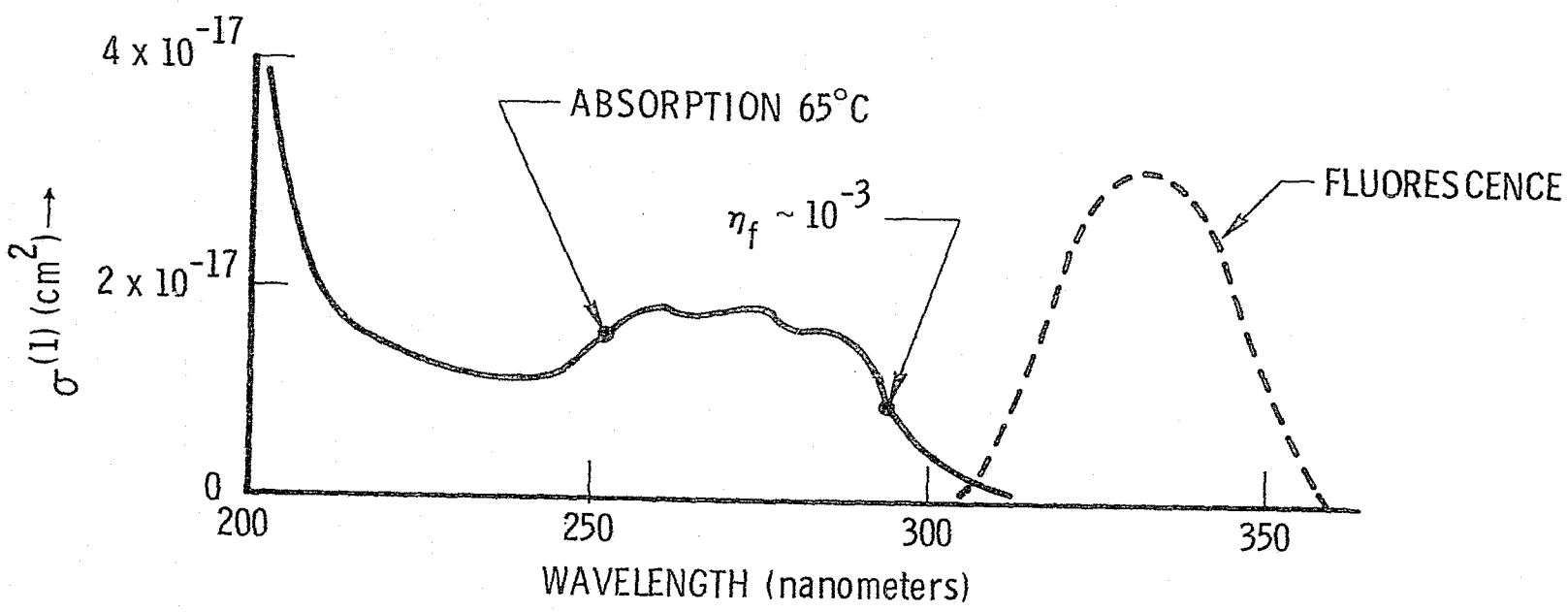

Figure 12. Absorption and Fluorescence Spectra of Diphenylamine

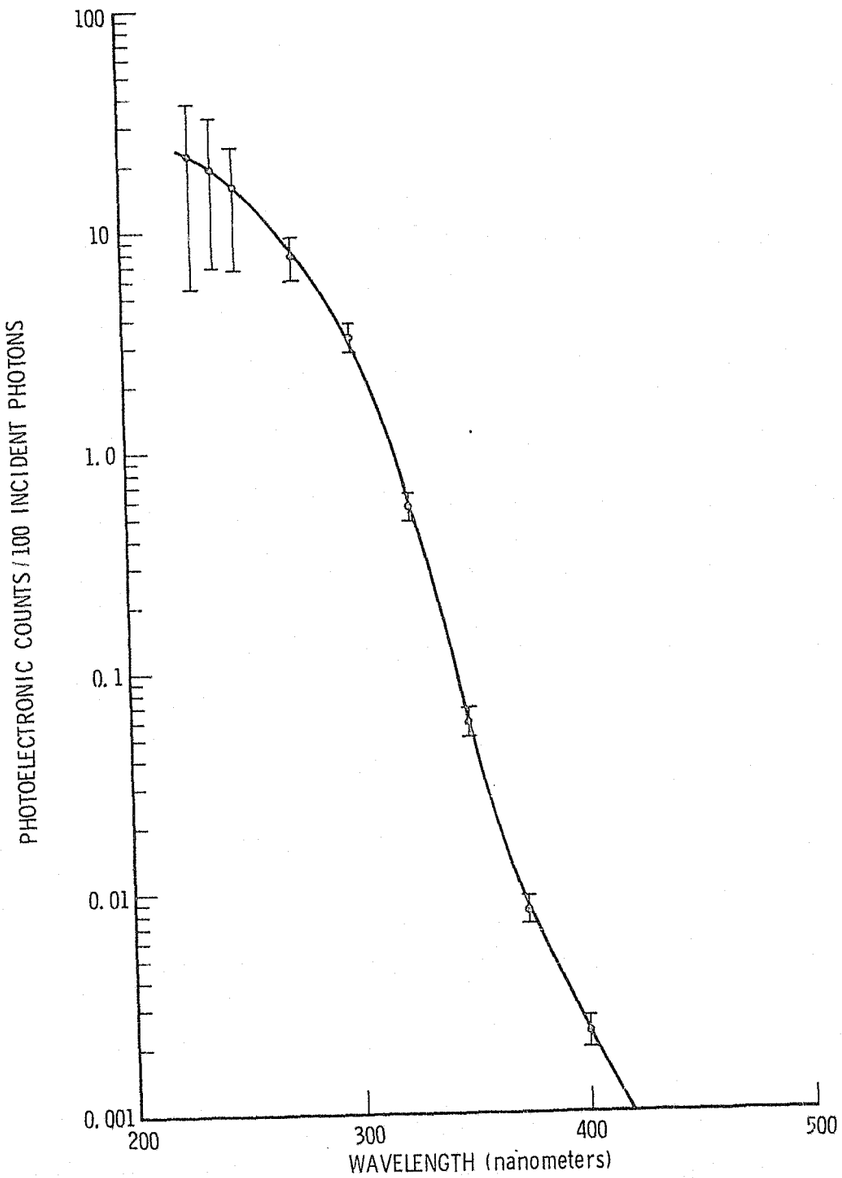

Figure 13. Measured Spectral Response Curve of the EMR-542F Photomultiplier Tube Used During the Course of Experimentation

was found for η_f for dinitrotoluene. The upper limit of η_f at various ultraviolet wavelengths for dinitrotoluene is indicated in Figure 11. No one-photon excited fluorescence was detected for trinitrotoluene and ethylene glycol dinitrate.

The values of peak one-photon absorption cross section σ_P and fluorescence yield η_f may be employed to estimate the natural linewidth γ_n of the transition (see Appendix A). For diphenylamine these values are $\sigma_p = 2 \times 10^{-17}$ cm^2 and $\eta_f \approx 10^{-3}$, while for dinitrotoluene they are $\sigma_p = 7 \times 10^{-16}$ cm^2 and $\eta_f \leq 3 \times 10^{-5}$. The corresponding natural linewidths are $\gamma_n = 20$ GHz for diphenylamine and $\gamma_n \geq 2 \times 10^4$ GHz for dinitrotoluene. Both of these values are greatly in excess of the Doppler width $\Delta\nu_D$ of ~ 1 GHz so that spectral-line narrowing upon Doppler-free absorption will not occur. Thus, the major feature of Doppler-free absorption, namely, highly selective excitation to gain specificity and the minimizing of interference effects will not be realized for these species. Consequently, by virtue of the small fluorescence yields for these species acoustic detection may be more sensitive for them than fluorescence monitoring; however, acoustic detection will not solve the problem of reduced selectivity and vulnerability to interference from environmental species.

CHAPTER IV. CONCLUSIONS AND OUTLOOK

The measured values for $\sigma_{2\phi} \times \eta_f$ imply that detection of the explosive vapors studied at concentrations less than 1 part in 10^7 is not feasible by fluorescence monitoring. This work further shows that even in the gas phase in the absence of collisions, the fluorescence quantum yields of the electronic transitions of explosive molecules are exceedingly low. The low fluorescence yield implies that all of the absorbed energy is dissipated by nonradiative processes, which may suggest to some that the photoacoustic detection method[11] may be appropriate for monitoring the two-photon absorption. However, as shown in Appendix A, a natural linewidth in excess of the Doppler width is associated with an electronic level that possesses such an exceptionally small fluorescence yield. Narrowing of spectral lines upon counter-propagating beam, two-photon excitation could not occur, and detection of this species would be highly susceptible to interference by other gases in the atmosphere; thus, the major advantage of the two-photon excitation scheme, namely, the reduction in linewidth, is negated. Based upon the measurements reported upon herein, it is concluded that Doppler-free two-photon spectroscopy can provide neither sensitive nor interference-free detection of explosive molecules.

While work on the two-photon program was in progress, an alternative approach to explosives detection was conceived. This approach utilizes the resonant enhancement of the two-photon absorption cross section $\sigma_{2\phi}$ in the presence of an intermediate state.[12] The technique involves a two-photon absorption process for which the energies of the two photons differ; one photon's energy is tuned to the energy difference between the lower level of the two-photon transition and the intermediate state while the energy of the second photon spans the energy gap between the intermediate state and the upper level of the two-photon transition. A resonant enhancement factor (i.e., the ratio of $\sigma_{2\phi}$ when one photon energy is tuned to the intermediate level energy to $\sigma_{2\phi}$ when the photon energy is far away from any intermediate state) of 10^9 was recorded for a two-photon transition in sodium vapor.[13]

If even a small fraction of the 10^9 enhancement factor could be realized for two-photon transitions of heavy molecules, the two-photon method might have sufficient sensitivity to monitor explosives at 0.1 part per billion concentrations. In this method the excitation need not be Doppler-free nor would a large γ_n significantly impair interference-free detection. Selectivity is accomplished by the requirement that the species of interest have transitions at two well-defined wavelengths. No experimental results have been published to-date on resonant enhancement of two-photon transitions of molecules. A basic research program would be required to gather experimental data upon which a realistic assessment could be made of the potential of the method for explosive vapor detection.

COMMENT 1

The fact that signals were observed after laser irradiation of ethylene glycol dinitrate suggests that a photochemical process took place that yielded fluorescing products. Any process specific to explosives that yields fluorescing products can be exploited for detection purposes. The well-known fact that explosive vapors undergo thermal decomposition at relatively low temperatures whereupon multiple oxides of nitrogen are released could also form the basis of an explosive vapor detection system. A detector that takes advantage of the above properties of explosives would consist of an inlet tube in which a metallic grid is located. An exhaust pump pulls the air stream across the metallic grid on which most of the explosive vapors in the air stream are absorbed. The sample volume containing the grid is then sealed off and moderately evacuated. The grid is then heated whereupon the explosive vapors decompose and oxides of nitrogen are generated. The oxides of nitrogen are then monitored by laser-induced fluorescence. This method should be capable of detecting explosive concentrations at the part per trillion level.

APPENDIX A

A relationship exists between the lifetime of an excited state τ (sec) and the peak one-photon absorption cross section $\sigma_p(cm^2)$.[14] It is given by

$$\tau = 4 \times 10^{-25}\ \eta_f/\sigma_p \qquad \text{(A-1)}$$

Recalling that the natural linewidth of the transition $\gamma_n = (\pi\tau)^{-1}$, an expression for γ_n(Hz) in terms of η_f, is given by

$$\gamma_n \sim 10^{24}\ \sigma_p/\eta_f \qquad \text{(A-2)}$$

A representative value for a strong molecular absorption is $\sigma_p \sim 10^{-16}\ cm^2$. The values of σ_p for dinitrotoluene, trinitrotoluene, and diphenylamine obtained in this study are $7 \times 10^{-16} cm^2$, $3 \times 10^{-16} cm^2$, and $2 \times 10^{-17} cm^2$, respectively. Substitution of $\sigma_p = 10^{-17} cm^2$ into Eq. (2) yields

$$\gamma_n = 0.01\ \text{GHz}/\eta_f \qquad \text{(A-3)}$$

Typical Doppler widths $\Delta\nu_D$ for ultraviolet transitions of large molecules are $\sim$ 1 GHz; thus, an enhancement factor $\Delta\nu_D/\gamma_n$ of 100 is possible for molecular transitions with $\eta_f = 1$. However, when η_f falls below $\sim 10^{-2}$, γ_n exceeds $\Delta\nu_D$ for strong molecular transitions and no reduction in linewidth is observed for Doppler-free absorption.

APPENDIX B

The quantum efficiency of an EMR 542F photomultiplier tube was determined from 230 to 425 nm using the procedure outlined in this appendix.

The spectral output of a 450 W xenon lamp (Osram, X130 450/4) was first calibrated using an Eppley thermopile to measure the light that passes through a Jarrell Ash double monochromator. The monochromatic light was focused onto the thermopile detector with a Suprasil lens. The thermopile output vs wavelength (λ) is shown below:

λ (nm)	Thermopile Output
230	$(0.05 \pm 0.03) \times 10^{-6}$ V
240	(0.10 ± 0.02)
250	(0.15 ± 0.01)
275	(0.5 ± 0.01)
300	(1.2 ± 0.01)
325	(2.3 ± 0.01)
350	(2.8 ± 0.01)
375	(3.2 ± 0.01)
400	(3.5 ± 0.01)
425	(3.4 ± 0.01)
450	(4.1 ± 0.01)
475	$(3.2 \pm 0.01) \times 10^{-6}$ V

The same lamp and monochromator system was then used to measure the 542F photomultiplier response over the same wavelength region. It was discovered that the light getting to the photomultiplier was much too intense, and a neutral density filter of OD2 was used in front of the photomultiplier, and two sets of screens with a combined OD of 3.47 were placed between the lamp and monochromators. This resulted in a total attenuation of the light

getting to the photomultiplier by 99.99945%. The response of the photomultiplier versus wavelength is shown below:

λ (nm)	542 Photomultiplier Counts
230	1.32×10^5
240	2.20×10^5
250	3.10×10^5
275	5.60×10^5
300	6.10×10^5
325	2.20×10^5
350	3.20×10^4
375	5.00×10^3
400	2.20×10^3
425	8.6×10^2

The absolute response of the thermopile was determined using a laser with known output to be 3.0 ± 0.5 mW/mV.

The photomultiplier response varied less than 5% with movement of the screens that were used as neutral density filters. The optical density of the screens was determined on a Cary 17 spectrophotometer.

The absolute response of the thermopile, along with the data in the above tables, was used to determine the quantum efficiency in counts per 100 photons versus wavelength for the 542F photomultiplier (see Figure 13).

NOTES

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GLOSSARY

$\beta_{2\phi}$	-	two-photon absorption coefficient
β_{ϕ}	-	one-photon absorption coefficient
c	-	speed of light
$\Delta\nu_D$	-	Doppler linewidth
η_f	-	fluorescence quantum yield
γ	-	homogeneous linewidth
γ_n	-	natural linewidth
$\sigma_{2\phi}$	-	two-photon absorption cross section
τ	-	lifetime of excited state
TEM_{oo}	-	lowest order mode of the laser cavity
v	-	velocity
cm	-	centimeter
GHz	-	Gigahertz (unit of frequency = 10^9 Hertz)
MHz	-	Megahertz (unit of frequency = 10^6 Hertz)
μW	-	microwatt
mm	-	millimeter
mV	-	millivolt
mW	-	milliwatt
nm	-	nanometer (1 nm = 10^{-9} meter)
sec	-	second
Torr	-	unit of pressure (760 Torr = 1 atmosphere)
UV	-	ultraviolet
V	-	volt
W	-	watt

END