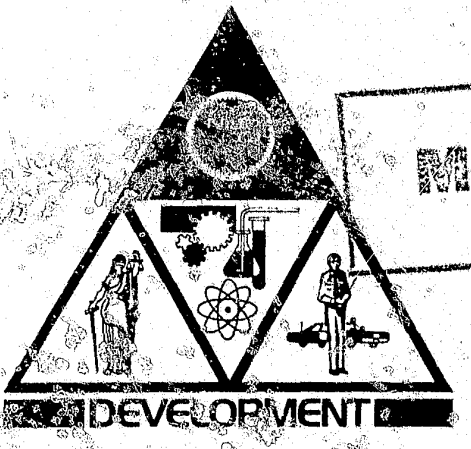
AEROSPACE REPORT NO.
ATR-76(7911)-1

EQUIPMENT SYSTEMS IMPROVEMENT PROGRAM

DOPPLER-FREE TWO-PHOTON CONCEPT FOR THE DETECTION OF EXPLOSIVE VAPORS

Law Enforcement Development Group

September 1975



Prepared for

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

The Aerospace Corporation

Aerospace Report No.
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Prepared for

National Institute of Law Enforcement
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Contract No. J-LEAA-025-73

This project was supported by Contract Number J-LEAA-025-73 awarded by the National Institute of Law Enforcement and Criminal Justice, Law Enforcement Assistance Administration, U.S. Department of Justice, under the Omnibus Crime Control and Safe Streets Act of 1968, as amended. Points of view or opinions stated in this document are those of the authors and do not necessarily represent the official position or policies of the U.S. Department of Justice.

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DOPPLER-FREE TWO-PHOTON CONCEPT FOR THE DETECTION OF EXPLOSIVE VAPORS

Approved

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ABSTRACT

A preliminary investigation of the Doppler-free method of counterpropagating beam two-photon spectroscopy for its applications to explosive vapor detection has been performed. This method holds great promise for providing direct excitation of single electronic states of molecules, thus permitting highly selective molecular excitation. Interference effects from other molecular species, which exhibit absorption bands in the same spectral region, would thereby be reduced. Absorption-line narrowing has been observed for nitric oxide, and resolvable spectral features have been recorded in the benzene absorption spectrum. The molecular structure of benzene resembles that of explosive vapors. The experimental results of this six-month effort confirm theoretical predictions and support the underlying hypothesis of this investigation.

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ILLUSTRATIONS

SUMMARY

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 this effect for isolated atoms in the vapor phase. 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 task was to verify that spectra of complex molecules could be resolved by this method as predicted by theory. Selective excitation of the species of interest would then allow detection in the presence of air and interfering species.

Thus far, two major results have been obtained in this program.

1. The first observations of Doppler-free absorption of electronic states in molecules have been achieved with nitric oxide and benzene. These results establish the feasibility of resolving individual rotational-vibrational-electronic states of large molecules such as explosive vapors. Thus, selective absorption by trace molecules should be possible.
2. Experimental methods to achieve narrow optical bandwidths that are critical for this work have been developed including a technique to verify overlap of the 50-μm-diameter counterpropagating beams.

CHAPTER I. INTRODUCTION AND BACKGROUND

The Aerospace Corporation has supported various research and development efforts for explosives detection or identification under contract to the National Institute of Law Enforcement and Criminal Justice of the Law Enforcement Assistance Administration (LEAA). 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. To date, there is no satisfactory method for the detection of untagged explosives. In a report prepared for the LEAA by Aerospace, 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).

It has long been recognized that the ultraviolet (uv) region of the electromagnetic spectrum is a highly desirable spectral region in which to detect trace gases. Most molecules exhibit many absorption lines in this region, and the strength of the absorption in this wavelength region is large compared to other spectral regions. However, in the uv region, absorption spectra appear as diffuse absorption bands instead of as sharp line spectra. The spectral width of an absorption band of a molecule of interest may be sufficiently large

to overlap the bands of other molecules that may be present in the environment. This would prevent selective excitation and impair the detection of the molecule of interest. In the absence of mechanisms that broaden absorption lines, the spectra of molecules would consist of many clearly resolvable absorption lines. The major requirement for detection of these molecules, namely, selective excitation of single states, could then readily be met. What is needed is a method to eliminate the spectral line broadening.

Electronic absorption spectra of atoms are caused by transitions of the outermost electrons and are clearly resolvable as spectral lines. However, when two or more atoms come together to form a molecule, additional structure is superimposed upon the electronic levels due to the vibrations and rotations of the molecule. If the width of the individual broadened absorption lines is greater than the line spacing, diffuse bands will appear. It is also noted that the line spacing depends inversely upon molecular weight, so that this effect is more severe for heavy molecules than for light ones.

For electronic transitions in the uv, the dominating factors that determine the widths of the individual absorption lines are pressure broadening and the Doppler effect; the latter is shown in Figure 1. Shifts in the frequency of radiation emitted by a molecule due to electromagnetic interaction between it and another molecule in proximity give rise to pressure broadening of the absorption lines. Pressure broadening can be reduced by a decrease in the total gas pressure. However, the Doppler broadening of spectral lines is more difficult to eliminate. It occurs because molecules in the gas phase are in continuous motion and travel in all directions. As a result,

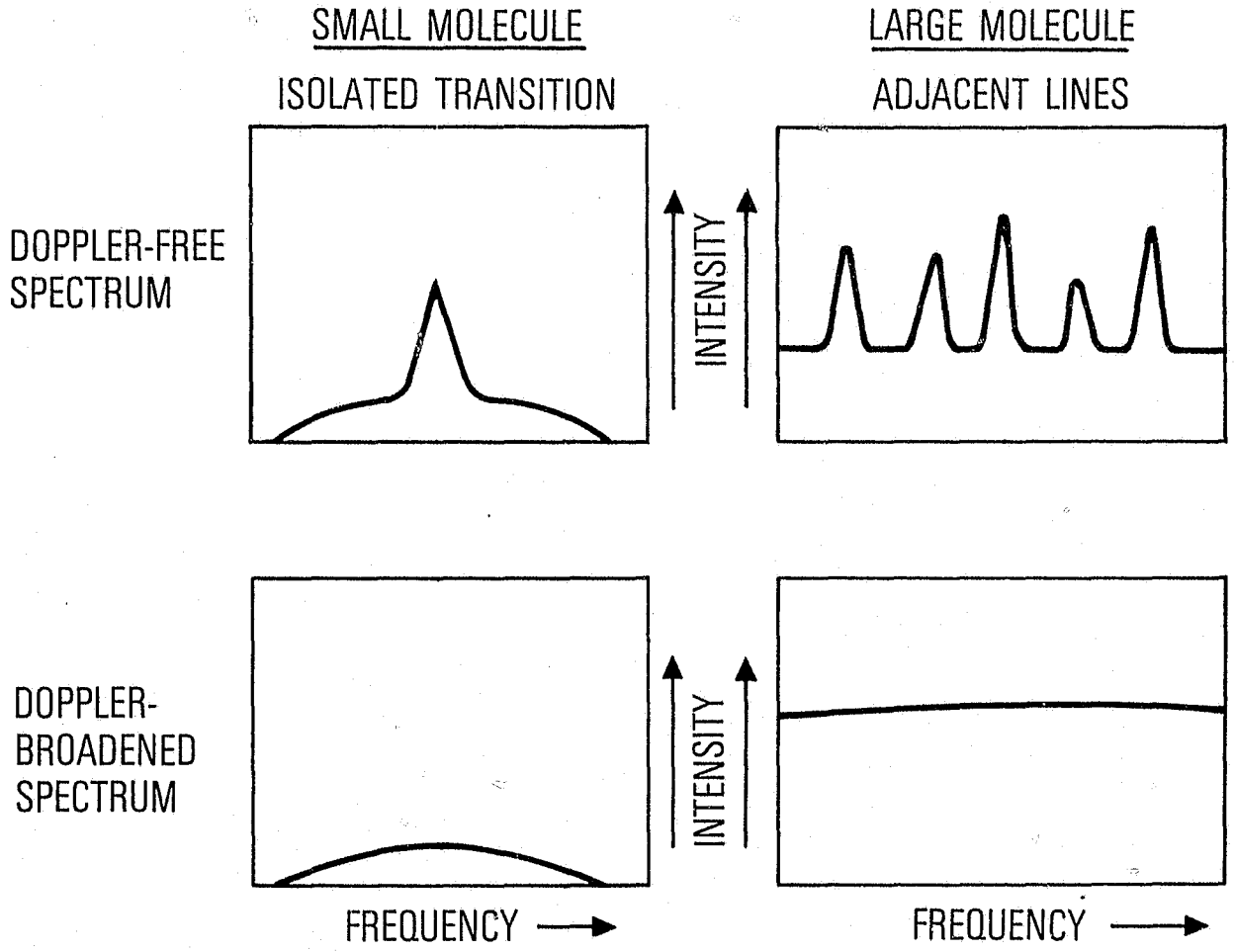


Figure 1. Effects of Doppler Broadening Upon Electronic Absorption Spectra of Small and Large Molecules

when light is incident upon the gas from one direction, the molecules that move toward the light intercept more wavelengths of the light per unit time than molecules that recede from the light. To molecules moving toward the light, the frequency of the light is upshifted, or blueshifted. Correspondingly, the frequency of the light appears downshifted, or redshifted, to those molecules moving away from the light source. The few molecules with thermal velocity components perpendicular to the light propagation direction experience no shift in optical frequency.

The acoustic counterpart of this optical Doppler effect is the familiar change in pitch of the whistle of a moving train. As the train approaches, an observer on the platform hears the whistle at a higher pitch than an observer on the train. After the train passes the platform, the whistle pitch sounds lower to the stationary observer than to the one on the train.

The optical Doppler effect is illustrated graphically in Figure 2. The intrinsic absorption peaks for two different molecules M_1 and M_2 with absorption peaks at λ_1 and λ_2 respectively are given by the upper and lower curves. The broadening of the lines by the Doppler effect causes the absorptions to overlap. Assume that excitation is provided at wavelength λ_1. It is seen that molecule M_2 is capable of absorbing a portion of this radiation, thereby preventing selective interaction with M_1. The absorption by M_2 constitutes a source of interference for the detection of M_1. If the Doppler width of the absorption could be eliminated, selective excitation of a single molecule would be possible and interference effects would be reduced. Alternatively stated, the elimination of the Doppler effect could yield highly selective, and hence specific, molecular excitation.

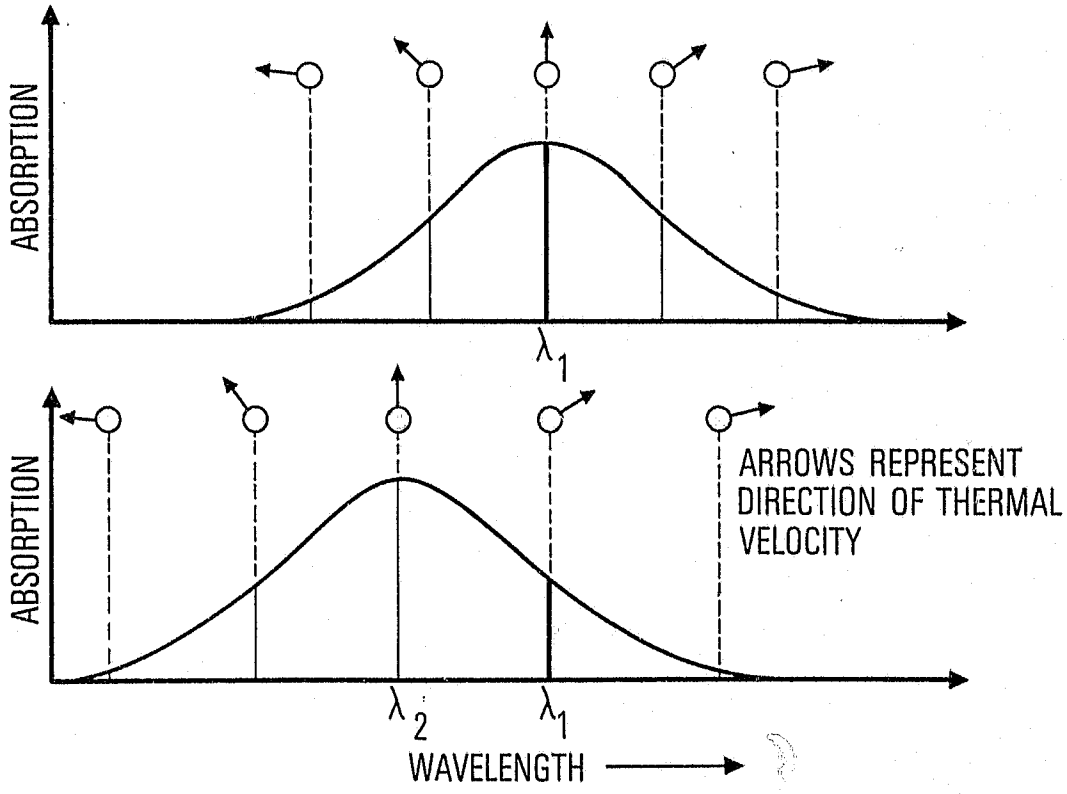


Figure 2. Doppler Broadening of an Absorption Line of Two Different Types of Molecules

The method that is proposed to eliminate the Doppler effect relies upon (1) simultaneous absorption of two-photons, and (2) a counterpropagating beam geometry. In the usual absorption process, a photon whose energy is exactly equal to the energy separation between the ground and excited levels of the molecule induces a molecular transition between the two levels. The number of excited molecules is directly proportional to the light intensity. In the presence of intense optical fields, it has been observed that molecular transition also occurs when the energy of the individual photons correspond to exactly one-half the transition energy. This type of transition has been shown to arise from the simultaneous absorption of two photons. In this so-called nonlinear process, the absorption varies as the square of the incident intensity. Whereas two-photon processes were once considered exotic and impractical, the advent of the laser, which provides high optical intensities, has made two-photon absorptions common enough to suggest practical applications.

Conventional two-photon absorption spectra, however, exhibit Doppler-broadened lines similar to the one-photon spectra. In order to eliminate the Doppler broadening, a counterpropagation beam geometry is coupled with a two-photon absorption process, as shown in Figure 3. When a two-photon absorption is induced whereby the molecule absorbs one photon from each of the oppositely directed beams, the Doppler frequency shift due to the relative velocity of the molecule with respect to the direction of one beam is exactly cancelled out by the Doppler shift relative to the second beam. Therefore, if the absorption requires an energy that is exactly double the

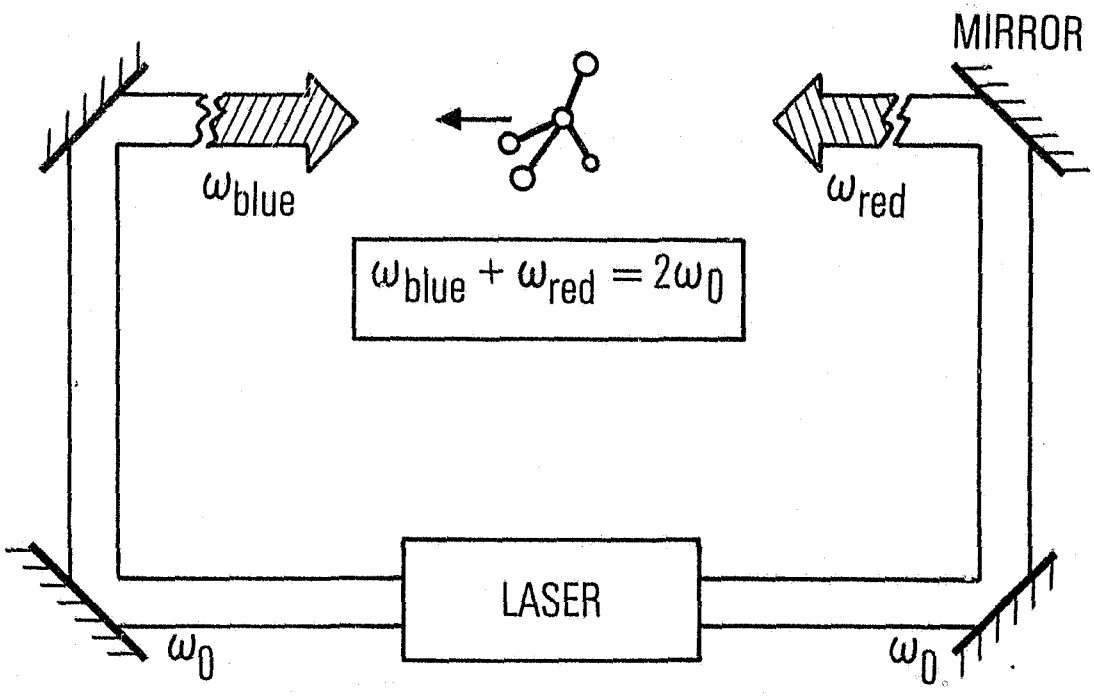


Figure 3. Counterpropagating Beam Two-Photon Concept. The molecular transition frequency is $2\omega_0$ and the laser frequency is ω_0. The molecule depicted moving to the left sees the frequency of the light beam from the left upshifted to ω_{blue} while the frequency of the beam incident from the right appears downshifted to ω_{red}.

energy of the incident photons, all the molecules can participate in the counterpropagating beam two-photon absorption process independent of their thermal velocities. Hence, the Doppler effect is eliminated. A slight shift of the photon energy off the two-photon resonance will drastically reduce the number of molecules capable of absorbing one photon from each of the oppositely directed light beams compared to those molecules that may absorb two photons from the same beam. As a result, the counterpropagating beam two-photon absorption peaks are much more intense and sharper than the Doppler-broadened, ordinary, two-photon absorption peaks, although both two-photon absorption processes may occur simultaneously in the gas.

The effect of counterpropagating beam two-photon absorption upon two closely spaced molecular transitions is illustrated in Figure 4. The dashed lines represent the Doppler broadening of the conventional two-photon absorption as discussed above. The two absorption lines overlap. Implementation of a counterpropagating beam geometry can produce the spectra shown by the solid curves in Figure 4. The absorption lines are clearly resolvable and their peak absorption strength is increased. In addition, the utilization of the two-photon process to induce a uv transition requires that the photon energies correspond to visible wavelengths. An important benefit from an operational system standpoint is gained since tunable, extremely narrow linewidth lasers are commercially available at visible wavelengths.

Early in 1974, Aerospace proposed that this method be explored to determine its potential for the detection of explosive vapors because of its suitability for detecting heavy molecules. The idea of eliminating the Doppler

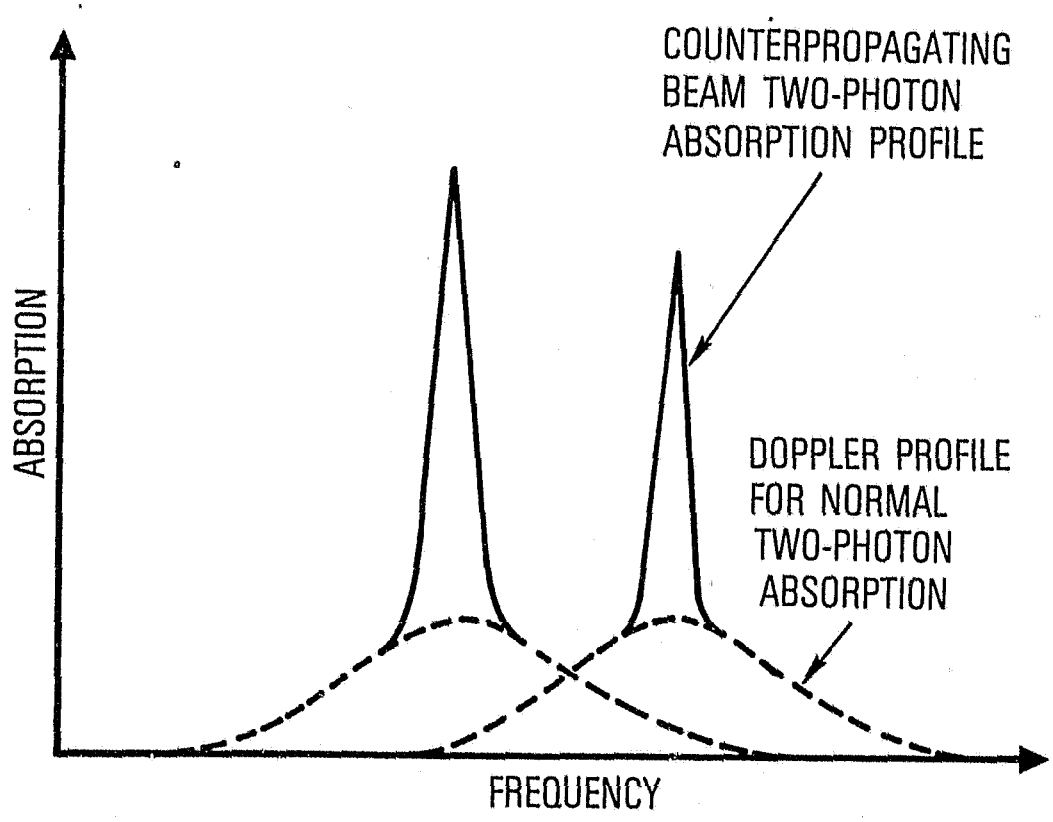


Figure 4. Two-Photon Absorption Spectra of Two Closely Spaced Transitions

effect by a counterpropagating beam two-photon method was originally suggested in 1970.[2] Nothing was done until mid-1974 when various groups applied the method to atomic[3-6] and infrared molecular spectroscopy.[7] Based upon these results, it is estimated that a hundredfold reduction in linewidths compared to the Doppler width is possible. A rough calculation of the sensitivity for trace vapor detection is presented in the Appendix for one particular apparatus configuration. This calculation indicates that the method has a reasonable chance of possessing sufficient sensitivity for explosives detection.

The major goal of the Aerospace preliminary investigation was to determine whether the spectra of complex molecules that appear diffuse when investigated by conventional spectroscopic methods could be resolved by the counterpropagating beam two-photon method of Doppler-free spectroscopy. This is a necessary first step towards achieving highly selective excitation of explosive molecules that could eventually be used for their detection.

The initial step was to examine a uv transition of a simple molecule to try to observe the anticipated reduction in spectral width. The simple molecule nitric oxide (NO), whose spectrum is well known, was selected. After successful verification of line narrowing, as will be discussed later, a more complex molecule was investigated to determine whether resolvable spectral lines could be uncovered through the elimination of the Doppler effect. Benzene, a molecule whose structure is akin to that of some explosives, was chosen.

CHAPTER II. EXPERIMENTAL PROCEDURE

The experimental apparatus employed in this program is shown in Figure 5. Tunable excitation was provided by a commercial pulsed dye laser (Molectron DL-300) pumped by a fixed wavelength nitrogen laser (Molectron UV-1000). By proper selection of dyes, wavelengths that span the entire visible spectral region (0.4-0.7 μm) could be generated. The energy was emitted in a series of 10^{-8}-sec pulses at a pulse rate that could vary in discrete steps from 10 to 100 pulses per second. The spectral width of the incident dye laser radiation was approximately 2.0 GHz. However, representative Doppler widths in the uv are of the order of 2.0 GHz, which corresponds to 1.0 GHz at the laser frequency. It was therefore necessary to reduce the optical bandwidth of the radiation further to attain excitation widths less than the molecular Doppler widths.

A scanning Fabry-Perot interferometer (Burleigh RC-40) was employed for this purpose. The output of the dye laser was passed through a telescope to reduce the divergence of the beam before it entered the interferometer. The interferometer acted as a spectral filter and was set to reduce the bandwidth of the beam to 0.2 GHz. In order to regain the power that was lost during the spectral filtration process, the beam was amplified by a cell containing the same dye as in the dye laser. Excitation was provided for the amplifier by splitting off a portion of the nitrogen laser radiation and directing it into the amplifier dye cell.

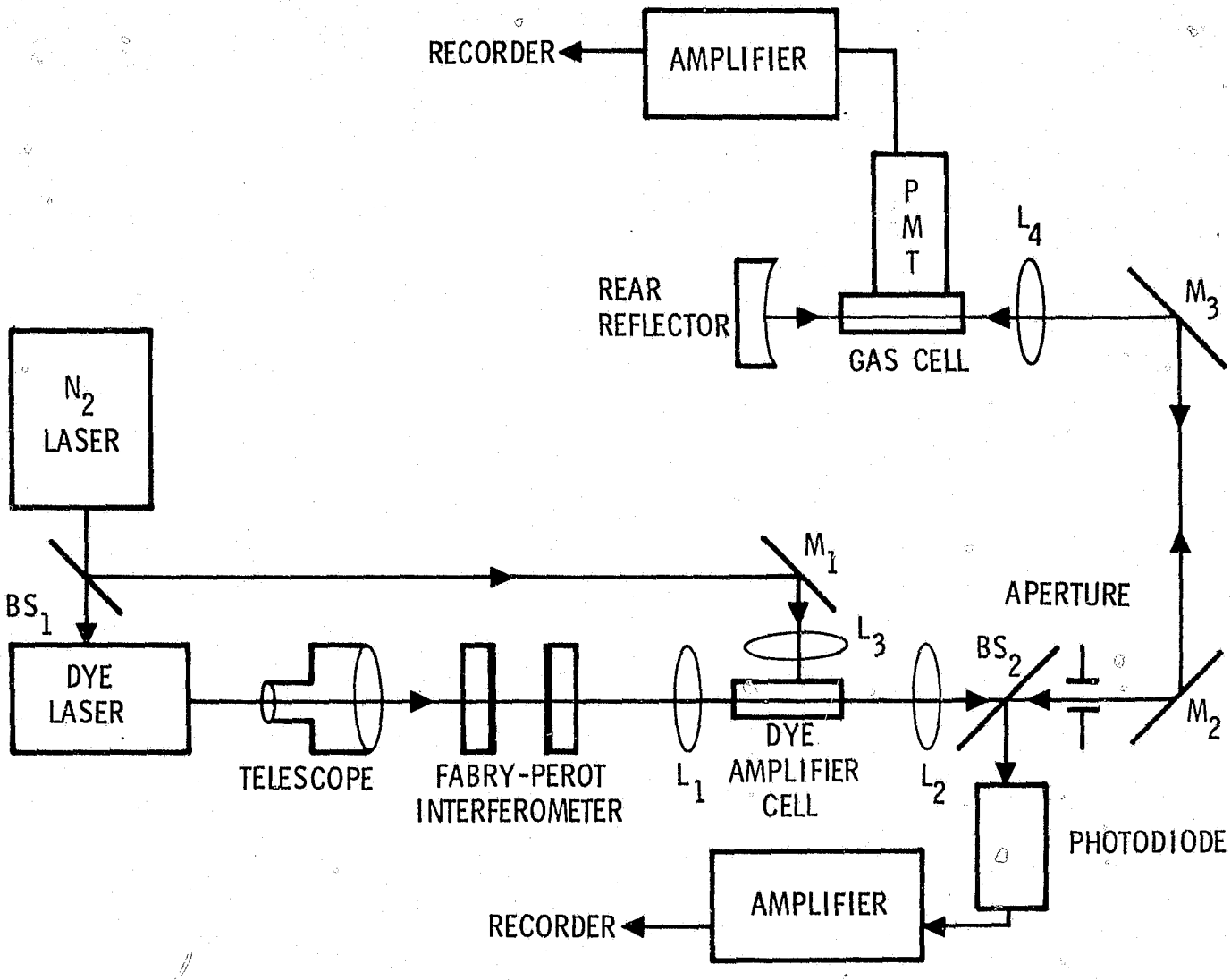
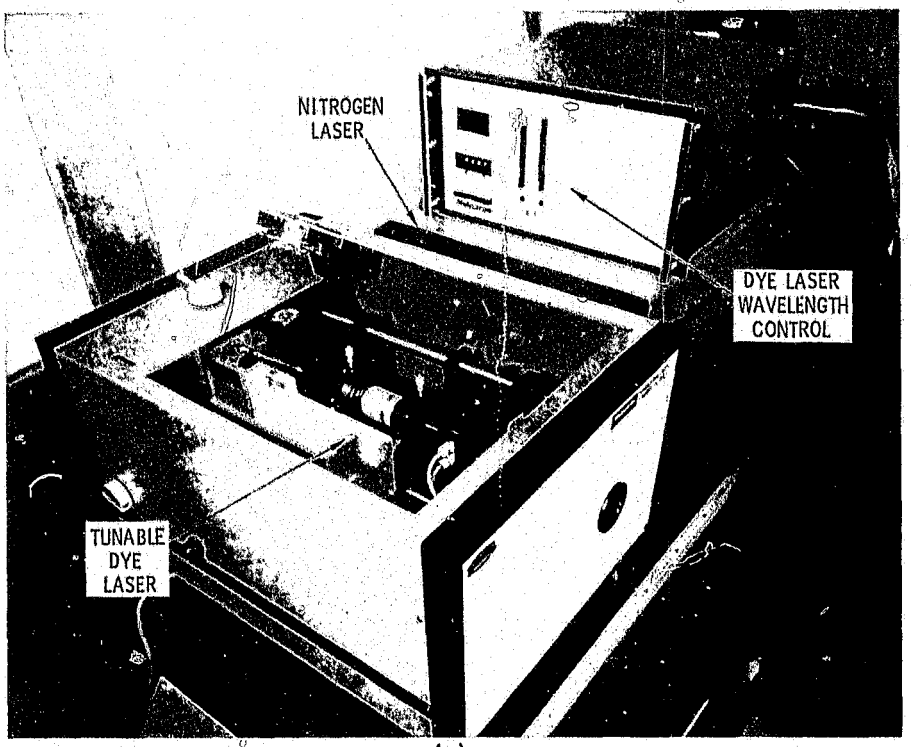


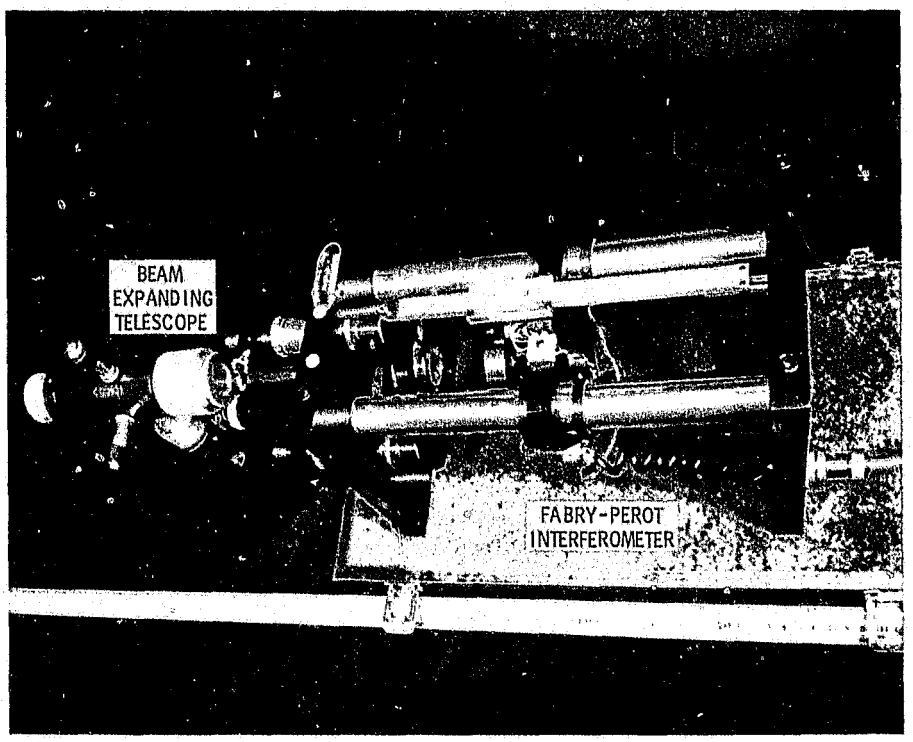
Figure 5. Counterpropagating Beam Two-Photon Doppler-Free Experimental Apparatus. BS is a beam splitter, L is a lens, M is a mirror, and PMT is a photomultiplier tube.

After amplification, the beam was directed by mirrors through the gas cell. In order to maximize the two-photon absorption processes, which are dependent upon the intensity of the incident radiation, a focusing lens reduced the beam to a small spot inside the gas cell. A mirror was placed at the exit of the gas cell to reflect the beam back upon itself to achieve the counter-propagating beam geometry necessary for Doppler-free absorption. A 100-μm aperture was placed in the beam path, and it was required that the return beam pass through the aperture to ensure overlap of both beams. After passage through the aperture, a beam splitter directed a portion of the return beam towards a photodiode that produced a signal proportional to the optical power incident upon the gas cell. Photographs of the test apparatus appear in Figures 6 and 7.

Absorption of the laser radiation by molecules in the gas cell was sensed by monitoring the fluorescence that was induced by the two-photon absorption. The fluorescence was monitored by a photomultiplier tube placed at right angles to the gas cell. Measurements were performed by electronically driving piezoelectric stacks on the plates of the Fabry-Perot interferometer, which causes the distance between the plates to change. The frequency of the spectrally narrowed radiation was scanned by this procedure. The outputs of the photomultiplier and the photodiode were recorded to obtain simultaneous measurements of the fluorescence induced by two-photon absorption and the incident power level.

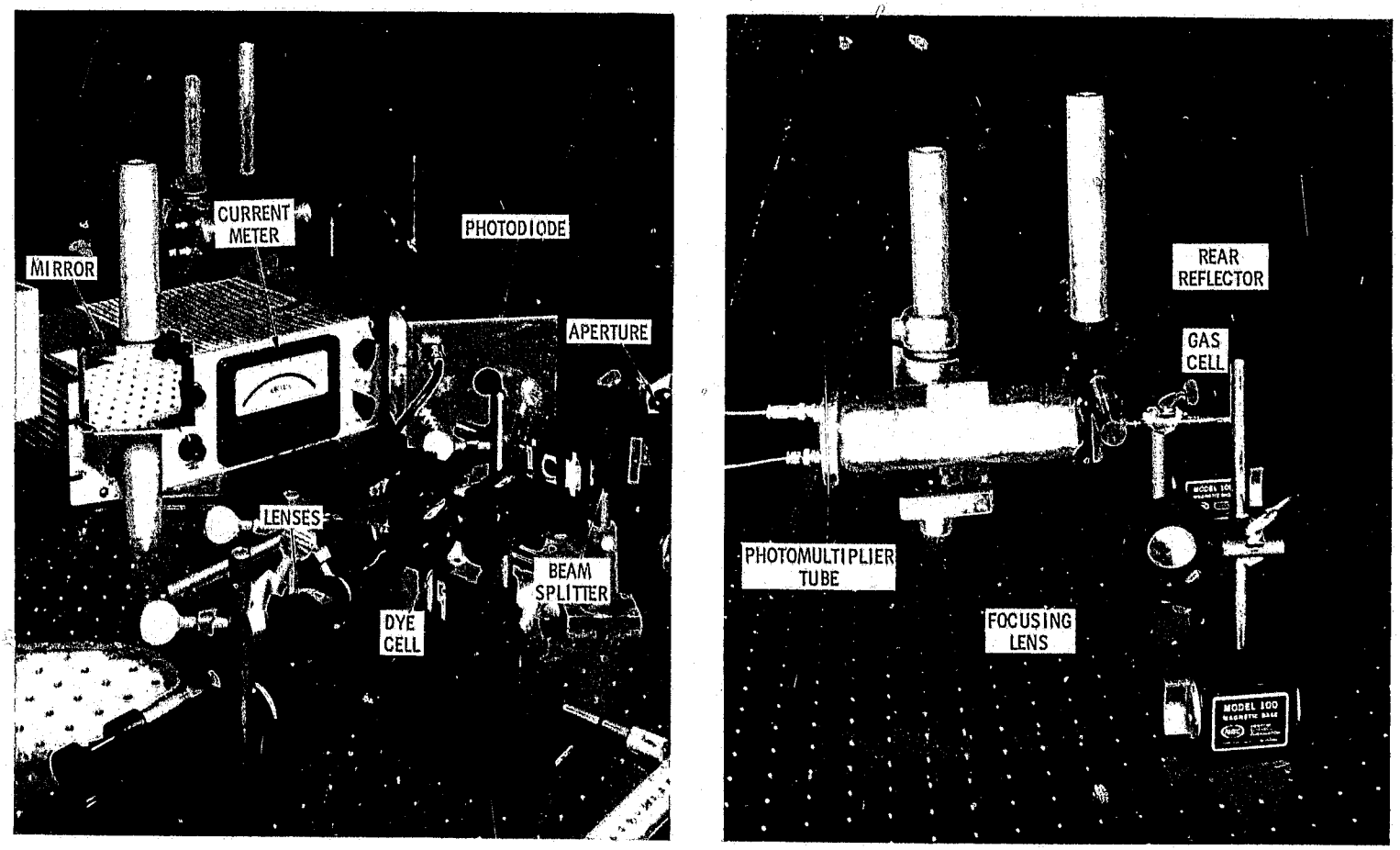


(a)



(b)

Figure 6. Experimental Apparatus: (a) Tunable dye laser and nitrogen laser; (b) Beam-expanding telescope and Fabry-Perot interferometer



(a) (b)

Figure 7. Experimental Apparatus: (a) Dye amplifier set-up consisting of the mirror M_1, lenses, and dye cell that appear in the foreground. The aperture, beam splitter BS_2, photodiode, and current meter comprise both the method of beam overlap verification and the technique for monitoring the radiation incident upon the gas cell. (b) Focusing lens L_4, gas cell, and rear reflector. The fluorescence decay of the excited state of the gas inside the cell was induced by the two-photon absorption process and monitored by the photomultiplier tube.

CHAPTER III. RESULTS

Doppler-free spectra have been obtained for NO and benzene. Figure 8 exhibits the measured spectra for NO using a 453-nm laser excitation. No correction has been made for varying laser excitation intensity. The upper curve represents the ordinary Doppler contour obtained by using nonoverlapping excitation beams. The lower curve was obtained when the counterpropagating beams are brought into coincidence.

The expected Doppler-free lineshape on a Doppler-broadened pedestal is evident in the NO spectrum of Figure 8. The sharp central peak arises from simultaneous absorption of separate photons from each of the oppositely directed beams. The 0.25-GHz resolution was instrument limited and represents a sixfold reduction in optical bandwidth compared to the Doppler width. The broad pedestal of the absorption is derived from absorption of two photons from a single beam and therefore should display the full Doppler width. The outer portions of the Doppler pedestal of the lower curve in Figure 8 appear distorted due to a decrease of laser intensity. Measurements were performed on NO at a pressure of 3 Torr.

This successful observation of the narrowing of the absorption confirms the expectations for the use of counterpropagating beam two-photon absorption to eliminate Doppler broadening. The remaining experiments were done using benzene, a gas whose molecular structure is more complex and representative of explosive vapors.

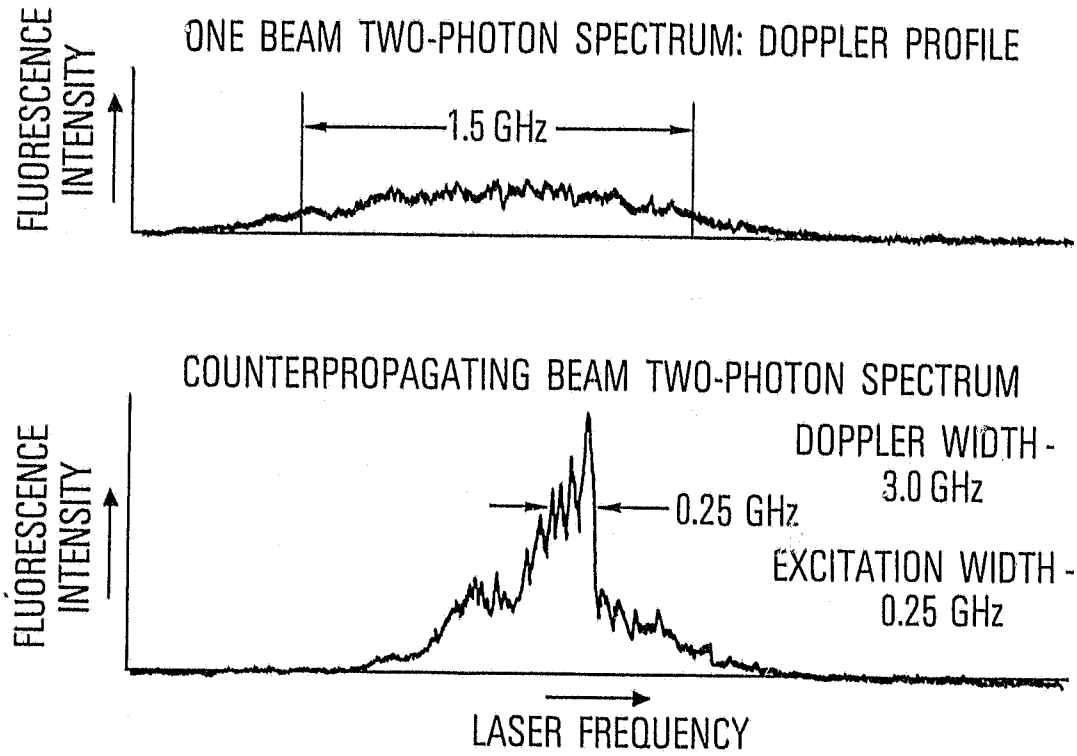


Figure 8. Two-Photon Excitation Spectrum of a Nitric Oxide Transition Excited at a Laser Wavelength of 453 nm

The measured counterpropagating beam excitation spectrum for benzene using a 504-nm laser excitation is shown in Figure 9. Again, no correction has been made for varying laser excitation intensity. The upper curve has been drawn through the data points obtained by averaging spectra obtained from three separate successive sweeps of the Fabry-Perot interferometer transmission frequency. The lower set of points represents the average excitation intensity for the three successive frequency sweeps.

The spectrum of benzene (for the region investigated) revealed at least three spectral features separated from each other by 0.7 GHz. The Doppler width of the benzene transition appropriate at the laser fundamental frequency is 0.9 GHz; thus, these features are unresolved by conventional high-resolution spectroscopic methods. Measurements were performed at a relatively high pressure of 10 Torr. A further reduction in linewidth would be anticipated at lower pressures. The primary limitation in linewidth, however, was the instrumental bandwidth of 0.4 GHz.

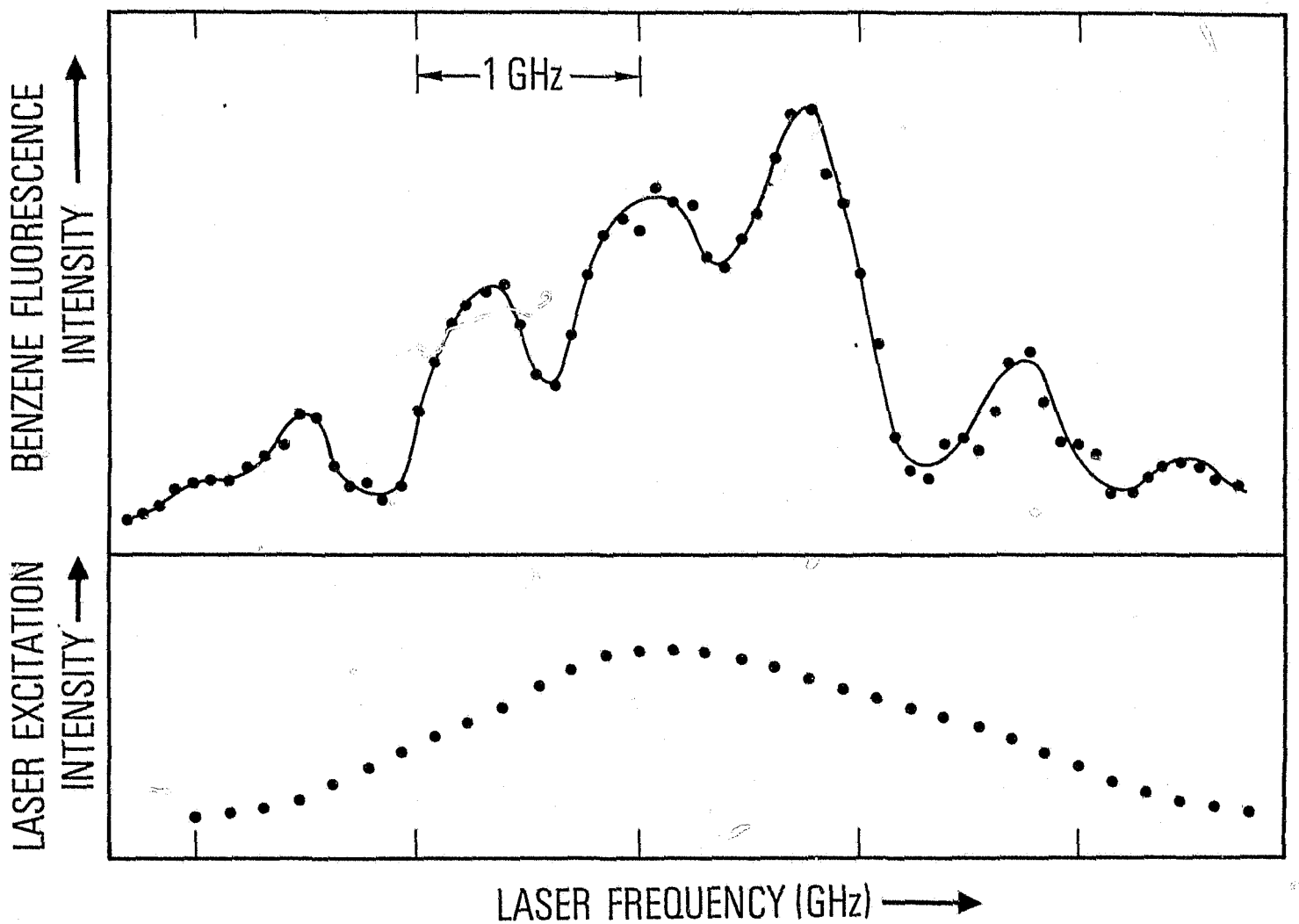
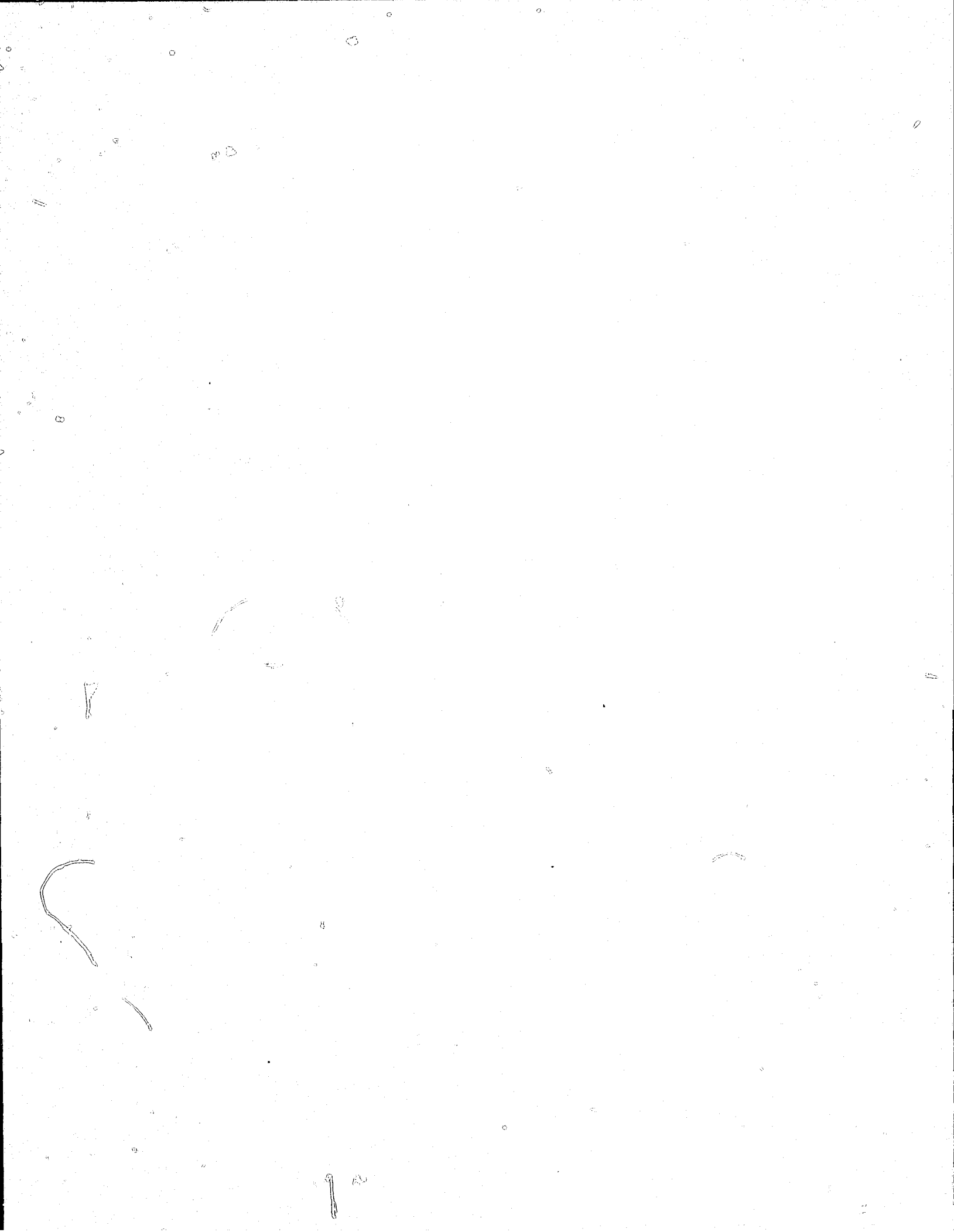


Figure 9. Two-Photon Excitation Spectrum of Benzene Excited at a Laser Wavelength of 504 nm



CHAPTER IV. CONCLUSIONS

Detection of explosive vapors by Doppler-free counterpropagating beam two-photon methods is attractive because it possesses a high potential for selectivity, operates at uv wavelengths where most molecules exhibit rich spectral features, and employs commercially available lasers. The heart of the detection method is the ability to achieve Doppler-free absorption so that heretofore diffuse uv electronic spectra of heavy molecules can be resolved into discrete lines. The direct excitation of single electronic states permits highly selective excitation and reduces interference effects from other molecular species that exhibit absorption bands in the same spectral region.

The experimental results obtained during this six-month effort confirm the theoretical predictions and support the underlying hypothesis of this investigation. Absorption line narrowing has been observed for nitric oxide, and resolvable spectral features have been recorded in the benzene absorption spectra. These features appear diffuse when observed by ordinary spectroscopic methods.[8] The molecular structure of benzene is related to that of trinitrotoluene and is comparable in complexity to that of other explosive vapors.

The goal of this preliminary investigation, namely, the determination of whether resolvable structure in the electronic absorption bands of complex molecules could be achieved by the counterpropagating beam two-photon method, has been achieved. The next several steps that need to be taken

towards the realization of a useful instrument for the detection of explosives based upon this method are itemized below.

The selectivity of this detection method improves in proportion to the ability to achieve narrow absorption linewidths. Therefore, (1) an effort should be devoted to obtaining even higher resolution spectra of complex molecules; (2) the spectra of actual explosives should be investigated; and (3) interference to detection of explosives by the presence of other molecules in the ambient air needs to be investigated. Molecules can emit energy either in the form of light or heat (or both) as they return to the ground state after excitation. These decay modes form the basis of a system for monitoring the counterpropagating beam two-photon Doppler-free absorption process. Additionally, (4) the method that possesses the greater sensitivity for monitoring the Doppler-free absorption of explosives should be determined; and finally, (5) the sensitivity for explosive detection should be quantitatively determined.

NOTES

1. G. W. Stupian and P. F. Jones, "A Review of Methods for the Detection and Identification of Explosives," Report No. ATR-74(7902)-1, El Segundo, Calif., The Aerospace Corp. (November 1973).
2. L. S. Vasilenko, V.P. Chetbotaev, and A. V. Shishaev, "Lineshape of two-photon absorption in a standing wave field in a gas," JETP Letters 12, 133 (1970).
3. M. D. Levenson and N. Bloembergen, "Observation of two-photon absorption without Doppler broadening on the 3s-5s transition in sodium vapor," Physical Review Letters 32, 645 (1974); N. Bloembergen, M. D. Levenson, and M. M. Salour, "Zeeman effect in the two-photon 3s-5s transition in sodium vapor," Physical Review Letters 32, 867 (1975).
4. F. Biraben, B. Cagnac, and G. Grynberg, "Experimental evidence of two-photon transition without Doppler broadening," Physical Review Letters 32, 643 (1974).
5. T. W. Hansch, K. Harvey, G. Meisel, and A. L. Schawlow, "Two-photon spectroscopy of Na 3s-4d without Doppler broadening using a CW dye laser," Optical Communication 11, 50 (1974); K. C. Harvey, R. T. Hawkins, G. Meisel, and A. L. Schawlow, "Measurement of Stark effect in sodium by two-photon spectroscopy," Physical Review Letters 34, 1073 (1975); T. W. Hansch, S. A. Lee, R. Wallenstern, and C. Wieman, "Doppler-free two-photon spectroscopy of hydrogen 1s-2s," Physical Review Letters 34, 307 (1975).

6. J. E. Bjorkholm and P. F. Liao, "Resonant enhancement of two-photon absorption in sodium vapor," Physical Review Letters 33, 128 (1974); "Lineshape and atomic efficiency of two-photon absorption using counter-propagating beams to reduce Doppler effects," Journal of Quantum Electronics 10, 906 (1974); P. F. Liao and J. E. Bjorkholm, "Direct observation of atomic energy level shifts in two-photon absorption," Physical Review Letters 34, 1 (1975).

7. W. K. Bischel, P. J. Kelly, and C. K. Rhodes, "Observation of Doppler-free two-photon absorption in the ν_3 bands of CH_3F," Physical Review Letters 34, 300 (1975).

8. J. H. Callomon, T. M. Dunn, and I. M. Mills, "Rotational analysis of the 2600 Å absorption system of benzene," Philosophical Transactions of the Royal Society of London 259A, 499 (1966).

APPENDIX. SENSITIVITY ESTIMATE

In this section, a calculation is performed to determine the ultimate sensitivity for the detection of trace vapors by counterpropagating beam two-photon Doppler-free spectroscopy. The geometry selected for detection appears in Figure A-1. The sample cell is placed inside the laser cavity to achieve maximum optical intensity. The fluorescence emitted by the molecule after the two-photon absorption is monitored by the photomultiplier tube (PMT). The photon-counting method of light detection is employed.

The two-photon absorption coefficient α_2 is expressed as

$$\alpha_2 = n\sigma_2 I \tag{1}$$

where n is the molecular concentration, σ_2 is the two-photon absorption cross section, and I is the photon flux. In terms of relative concentration c and total gas pressure p, α_2 can be written as

$$\alpha_2 = 3.5 \times 10^{16}\, cp\sigma_2 I \tag{2}$$

For transitions near 0.25 μm, the laser wavelength is tuned to near 0.5 μm, where there are 2.5×10^{18} photons/sec for each watt of laser power. Thus, the intensity of the laser radiation is given by

$$I = 2.5 \times 10^{18}\, P/A \tag{3}$$

where P is the laser power and A is the beam area.

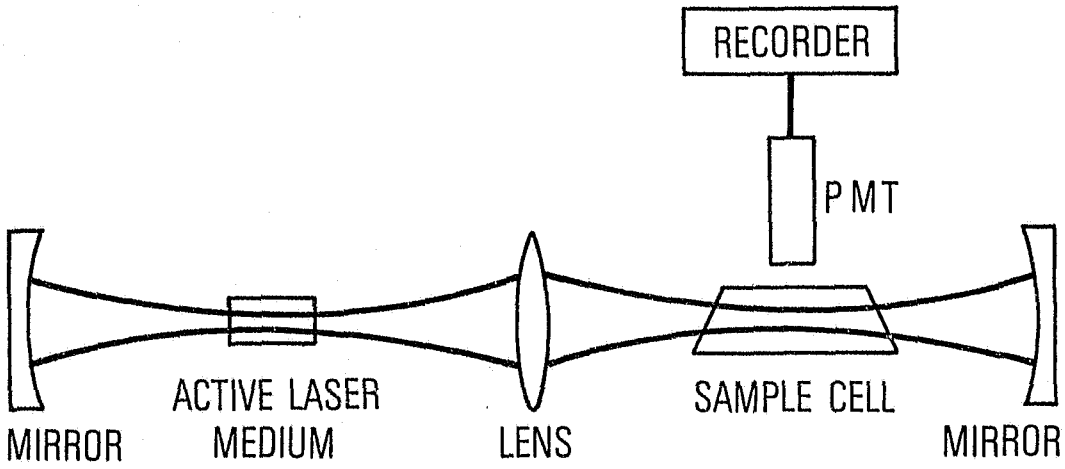


Figure A-1. Apparatus Configuration for the Detection of Explosive Vapors by Counterpropagating Beam Two-Photon Doppler-Free Spectroscopy

Substitution of Eq. (3) into Eq. (2) yields

$$\alpha_2 = 10^{35}\, cp\sigma_2\, P/A \tag{4}$$

The number of photoelectronic counts per second C recorded at the output of the photomultiplier tube is related to α_2 through

$$C = \alpha_a\, LP\, \eta_f\, \eta_c / 2h\nu_L \tag{5}$$

where L is the interaction length, η_f is the fluorescence quantum efficiency, η_c is the optical collection efficiency, h is Planck's constant, and ν_L is the laser frequency.

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

$$C = 10^{53}\, cp\sigma_2\, LP^2\, \eta_f\, \eta_c / A \tag{6}$$

Equation (6) is composed of two types of parameters: those that relate to operation of a system and those that are representative of the molecular species. Among the former are p, L, P^2, η_c, and A. The latter group includes σ_2 and η_f. Sufficient information is available to permit accurate estimates for the system parameters. They are as follows: p = 10 Torr, L = 1 cm, P = 10 W, η_c = 1%, A = 2.5×10^{-5} cm^2. Insertion of these values into Eq. (6) yields

$$C/c = 4 \times 10^{58}\, \sigma_2\, \eta_f \tag{7}$$

The state of knowledge of σ_2 and η_f for explosives is sparse. One can give rather broad ranges for the parameters. They are as follows:

$$\sigma_2 = 10^{-46} \text{ to } 10^{-50} \text{ cm}^2 \text{ (photon/sec} \cdot \text{cm}^2)^{-1}$$

and

$$\eta_f = 1 \text{ to } 10^{-3}$$

If these values are employed in a system in which the dark counts are 1 count/sec, it is readily shown that the sensitivity of detection in a 10-sec counting interval (i.e., the concentration of explosive vapor that produces a signal-to-noise ratio of unity) extends from less than one part in 10^{12} to one part in 10^5. Conservative estimates were used in the preceding calculation. Future improvements in the state of the art of laser technology could provide sensitivity for detection that is two orders of magnitude greater. Based upon currently available data on vapor pressures of explosive molecules, we estimate that a sensitivity of one part in 10^{10} is the minimum required to perform explosive vapor detection. This calculation indicates that the counterpropagating beam two-photon Doppler-free method of detection may possess the requisite sensitivity for explosive vapor detection.

GLOSSARY

Fabry-Perot Intermerometer	An optical instrument based upon the principle of interference of light waves. It consists of two highly reflective parallel mirrors and acts as a highly tuned circuit for optical frequencies, transmitting only very narrow-bandwidth optical radiation.
Fluorescence	Light emitted by an excited state molecule shortly after excitation as it decays to its ground state
GHz	One gigahertz, 10^9 cycles per second
nm	One nanometer, 10^{-9} meter
NO	Nitric oxide
Photodiode	A device used to convert medium-level light signals into electronic signals
Photomultiplier Tube (PMT)	A device primarily used to convert low-level light signals into electronic signals
Photon	A particle of light
Ultraviolet (uv)	Region of the electromagnetic spectrum directly on the short wavelength side of the visible region
μm	One micrometer, 10^{-6} meter

END