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NEW NONLINEAR OPTICAL PROCESSES IN MOLECULES AT INFRARED FREQUE--ETC(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This final report details progress in the study of optical nonlinearities in molecules at infrared wavelengths. The objectives have been to investigate the nonlinear optical properties of triply resonant and two photon or Raman resonant molecules. The techniques of third harmonic generation, multiphoton absorption, and degenerate four wave mixing have been used, with a CO ₂ TEA		

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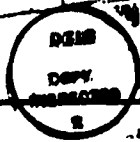
laser as the excitation source.

An outstanding accomplishment has been the successful application of third harmonic generation techniques to study collisionless multiphoton excitation in sulfur hexafluoride. Depending on the excitation frequency, one or two-photon processes have been identified which deplete the population of the discrete vibrational energy levels into the quasi-continuum. Similar third harmonic generation experiments have yielded lower conversion efficiency in ammonia than in sulfur hexafluoride. Only a single rotational level in ammonia is found to be resonant, so the susceptibility is only minimally enhanced.

A second area of work is the study of the two photon Raman resonant molecule CD_4 . Third harmonic generation results were obtained for CD_4 at room and cryogenic temperatures. Problems of fundamental wavelength absorption were eliminated and the nonlinearity was enhanced at 193K.

The final area of work was a study of degenerate four-wave mixing in SF_6 . A model was developed to fit the experimental data for conjugate reflectivity versus gas pressure. The main feature of the model is that it accounts for pump wave saturation and absorption in the resonant media.

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I. RESEARCH OBJECTIVES

The overall objective of this research program is to study vibrational and hybrid (vibrational and electronic) optical nonlinearities in molecules at infrared wavelengths. The experimental studies all employ optical third harmonic generation (THG), multiphoton absorption, and degenerate four-wave mixing (DFWM) to probe the nonlinear behavior of different classes of molecules. When used with a tunable laser, this experimental technique can be used to determine the non-linear susceptibility as well as possible limiting processes such as multiphoton absorption.

The first general class of optical nonlinearity that has been studied is the purely vibrational nonlinearity which is at least approximately triply resonant. The nearly regular spacing of molecular vibrational energy levels makes simultaneous one-, two-, and three-photon resonances possible. The nonlinear susceptibility in this case is determined by vibrational transition matrix elements exclusively.

The second class of nonlinearity utilizes only a single two-photon resonance with a molecular vibrational energy level. The susceptibility in this case will be determined by both vibrational and electronic transition matrix elements. Usually, the susceptibility is determined primarily by electronic transitions even though the two-photon resonance is vibrational energy level. These resonances are thus hybrid or Raman.

A specific objective in the study of triply resonant nonlinear interactions has been to investigate the limiting processes in mole-

cules such as SF_6 , where there is an exact resonance and strong absorption for the one-photon transition. An extensive study of this effect by THG and DWM has been conducted, in order to determine the exact nature of the multi-photon excitation processes which deplete molecular population from the discrete, resonant energy levels.

To avoid the debilitating absorption at the fundamental frequency, the general approach is to use molecules with larger rotational constants, and hence, widely spaced vibrational levels. The laser is now tuned to a gap in the one photon resonances while two and three photon resonances are made as close as possible. An example of a molecule of this type with a 10 micron resonance is NH_3 . Results for NH_3 were disappointing because only a small fraction of the molecules were in resonant rotational levels.

The objective of the Raman resonance work is to enhance the susceptibility of two-photon resonant molecules by choosing species with an unusually narrow and strong two-photon resonance. Cryogenic temperatures are used in conjunction with this selection process to further concentrate the molecular population in the resonant levels. A further aid to the select process is the relation between the non-linear susceptibility for this two-photon resonant case and the spontaneous Raman scattering cross-section. Absorptions are due to high J and hot band absorptions from other vibrational manifolds in the molecule. A solution for this problem should be to lower the temperature of the gas and depopulate the absorbing levels. Such a molecule is CD_4 , and it is studied by THG at room and cryogenic temperatures, where the effect of one photon absorption is minimized.

II. PROGRESS AND ACCOMPLISHMENTS

The outstanding accomplishment of the first year was the successful application of THG techniques to study collisionless multiphoton excitation in the low lying energy levels of SF_6 . The details of this work may be found in the two papers^{1,2}. The significant findings will be summarized here.

The experimental approach in this work was to observe the THG dependence on excitation wavelength and excitation intensity in 0.2 torr of SF_6 gas at both 193K and 294K. The laser radiation from the 10.6 micron band of a CO_2 TEA laser was directed into a dewar gas cell and the third harmonic radiation was detected. In this case, the incident radiation is within the fundamental absorption band of SF_6 . Near resonances also exist at two- and three-photon frequencies. At the experimental intensities of 10-200 MW/cm^2 , the linear absorption is strongly saturated. The THG versus intensity also showed saturation behavior above $\sim 100 \text{ MW}/\text{cm}^2$. In addition, the THG showed strong frequency dependent structure. This is the first time that any spectroscopic technique has ever showed a sharp structure associated with the multiphoton excitation spectrum of SF_6 .

The saturation behavior of the THG and the observed THG spectroscopic structures allowed the assignment of several excitation mechanisms in the discrete vibrational states of SF_6 . First, the order of the process depleting the discrete state population to the quasi-continuum was determined from the experimental data. For CO_2 laser lines P(16), P(20) and P(22) a 2 photon Fermi Golden Rule (FGR) deple-

tion process was observed and for P(24) and P(26) a one photon FGR depletion was observed. Based on the depletion mechanism, the THG spectrum, and the known spectroscopy of SF_6 , we have proposed the following excitation processes in SF_6 :

1.) P(16), P(20) and P(22)

There is a two photon Rabi precession involving the ground state population. Depletion follows from the two photon excited state via a two photon FGR transition to the quasi-continuum.

2.) P(24) and P(26)

There is a three photon Rabi precession from the ground state. Depletion follows from the three photon excited state via a one photon FGR transition to the quasi-continuum.

Although exact resonances have been proposed for some of the above cases, the effects of power broadening and the remaining uncertainties in the SF_6 spectroscopy make exact identifications difficult at this time.

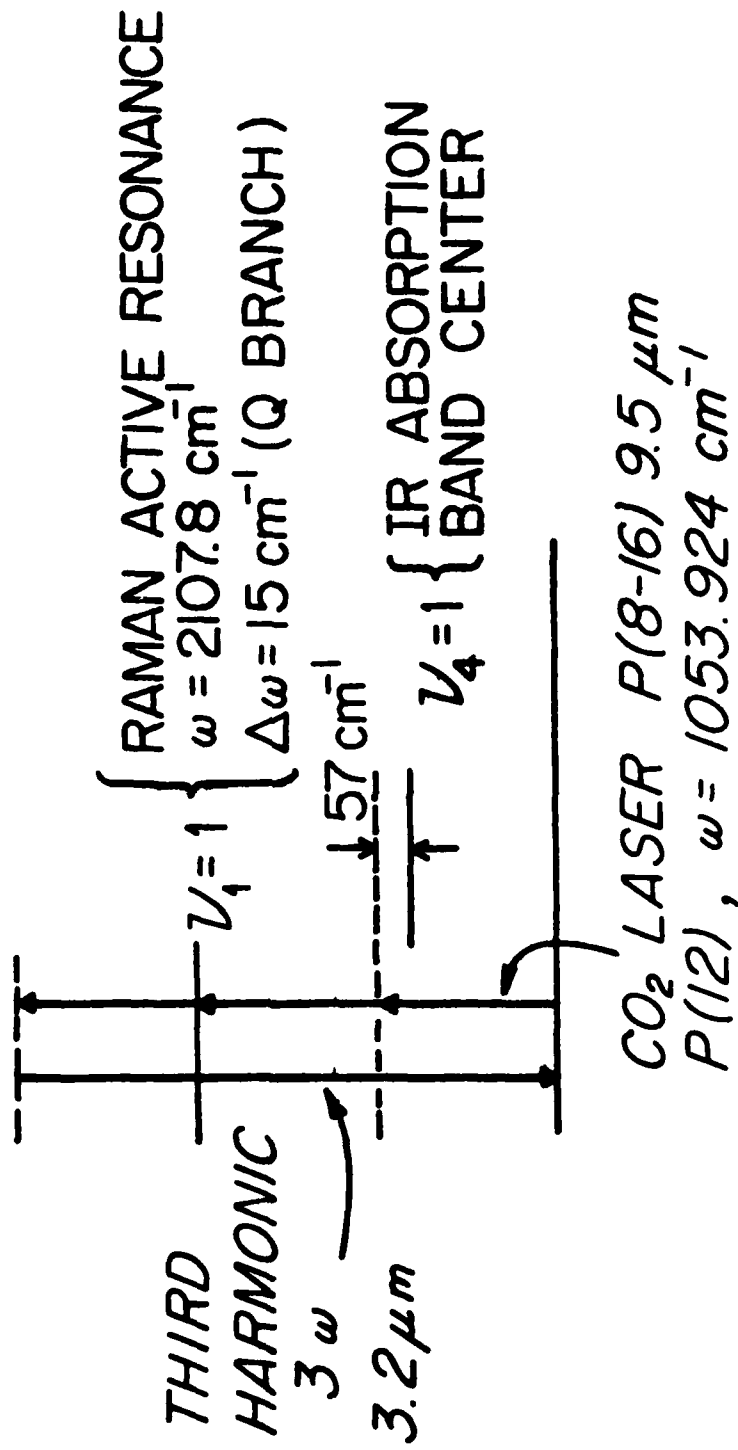
Third Harmonic Generation THG experiments were also performed with NH_3 . Ammonia, like SF_6 , has a fundamental vibrational resonance within the 10.6 micron band of the CO_2 laser. However, unlike SF_6 , it has a much larger rotational constant and the individual vibrational-rotational spectral lines are distinctly separated. In NH_3 , it is possible to have an exact two-photon resonance without fundamental absorption. In this specific case, two P(24) photons are

resonant with the $a_s Q(1,1) - 2 a_s Q(1,1)$ two-photon transition. The notation for the two-photon transition is given as two sequential one-photon transitions in order to indicate the nearest resonant one-photon state. The $a_s Q(1,1)$ is 8.9 cm^{-1} detuned from the P(24) laser and thus no fundamental absorption occurs. Unfortunately, this exact resonance at only one rotational line means that only a small fraction of the total molecular population contributes resonantly to the susceptibility. In this case, the $J=1$ population is only 1% of the total. At 294K the population peak is at $J=14$. The population at $J=1$, and hence the THG conversion, should increase with decreasing temperature.

Experimental THG data was taken for the P(22), P(24), and P(26) laser lines in 14 torr of NH_3 where P(24) and P(26) gave larger THG (THG for other lines was not observable). A maximum conversion efficiency of 4.5×10^{-10} was obtained at 230 MW/cm^2 . This value is about 1/10 of that calculated from an anharmonic oscillator quantum model for the susceptibility. These numbers can be improved by decreasing the gas temperature; however, the results should be predictable and not dramatic.

During the second and third years, our experimental effort has concentrated on the two-photon resonant molecule, CD_4 . An energy level diagram is shown in Fig. 1. It has a strong Raman active resonance at 2108.7 cm^{-1} , which is two-photon resonant with the CO_2 laser line P(12) in the 9 micron band at 1053.024 cm^{-1} . As a symmetric molecule, the two photon resonance of CD_4 has only a single narrow Q-branch. Raman scattering data shows this Q-branch to be

CD₄ ENERGY LEVELS

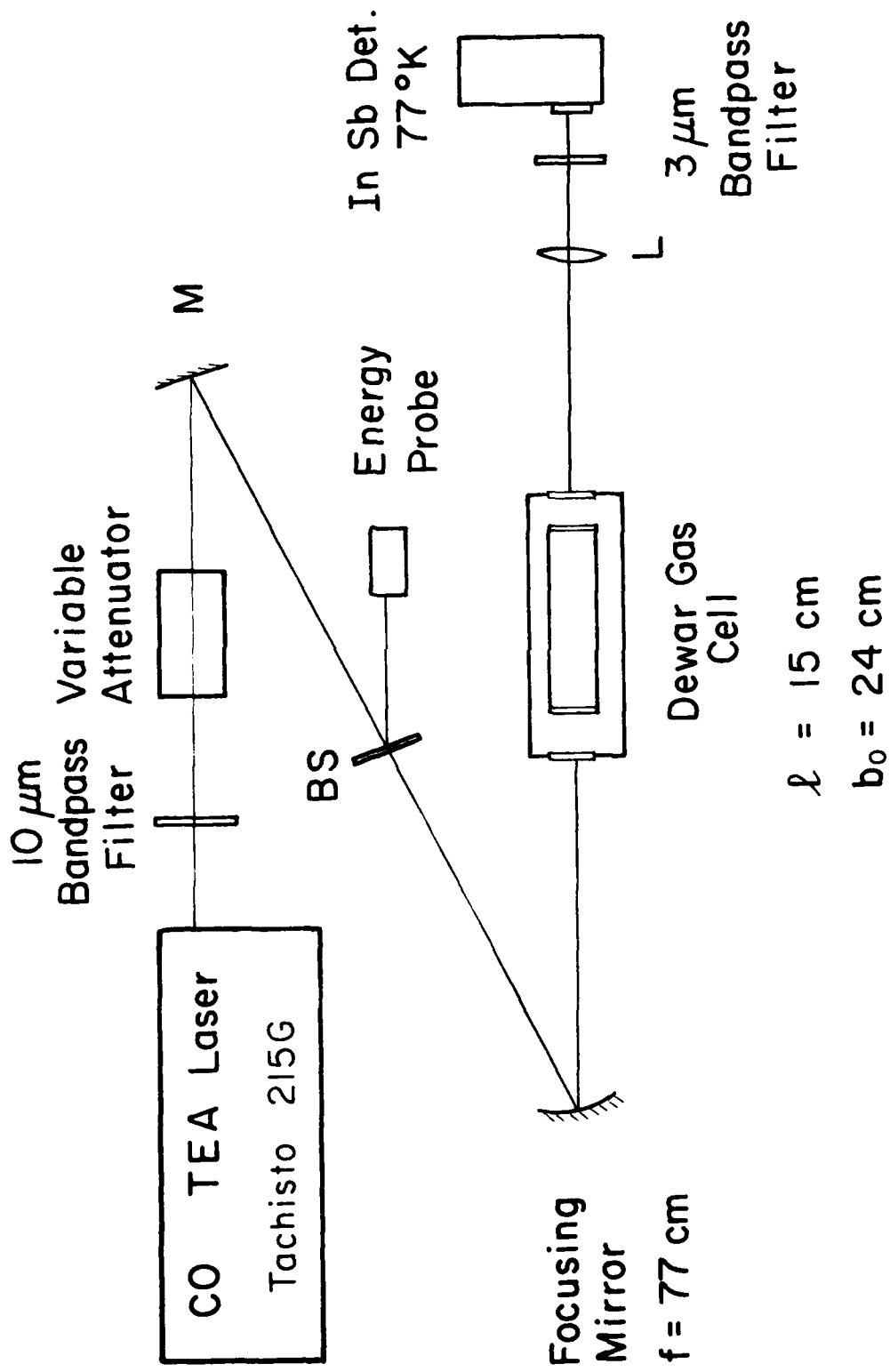


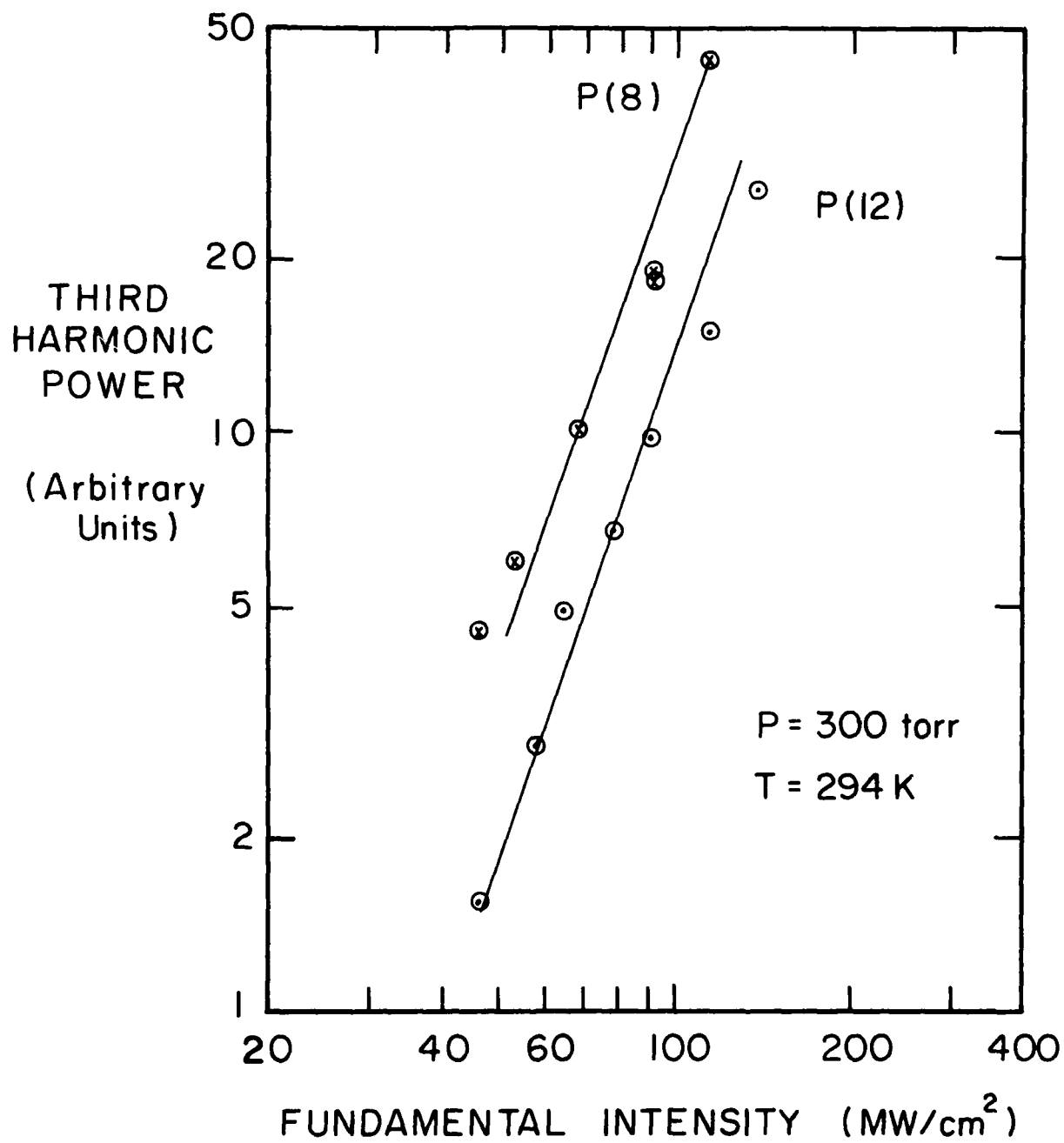
15 cm^{-1} in linewidth and to have nearly two times the Raman cross-section as CO, hence one would expect slightly less than four times the THG.

A series of THG experiments have been performed on CD_4 at room temperature and at 193K, exciting with the P(8) through P(16) lines in the 9 micron band of a CO_2 TEA laser. The room temperature results have been published³ while the complete publication is still in preparation. The experimental configuration is shown in Fig. 2. We measured the THG dependence on gas pressure and fundamental laser power for these lines. Due to fundamental absorption at about $J=20$ on the tail of the ν_4 absorption band, the maximum THG signal occurred at 300 torr pressure. The THG power did have a consistent cubic dependence on fundamental power, as shown for two typical laser lines in Fig. 3. At lower pressures, a factor of three enhancement in THG was observed compared to CO.

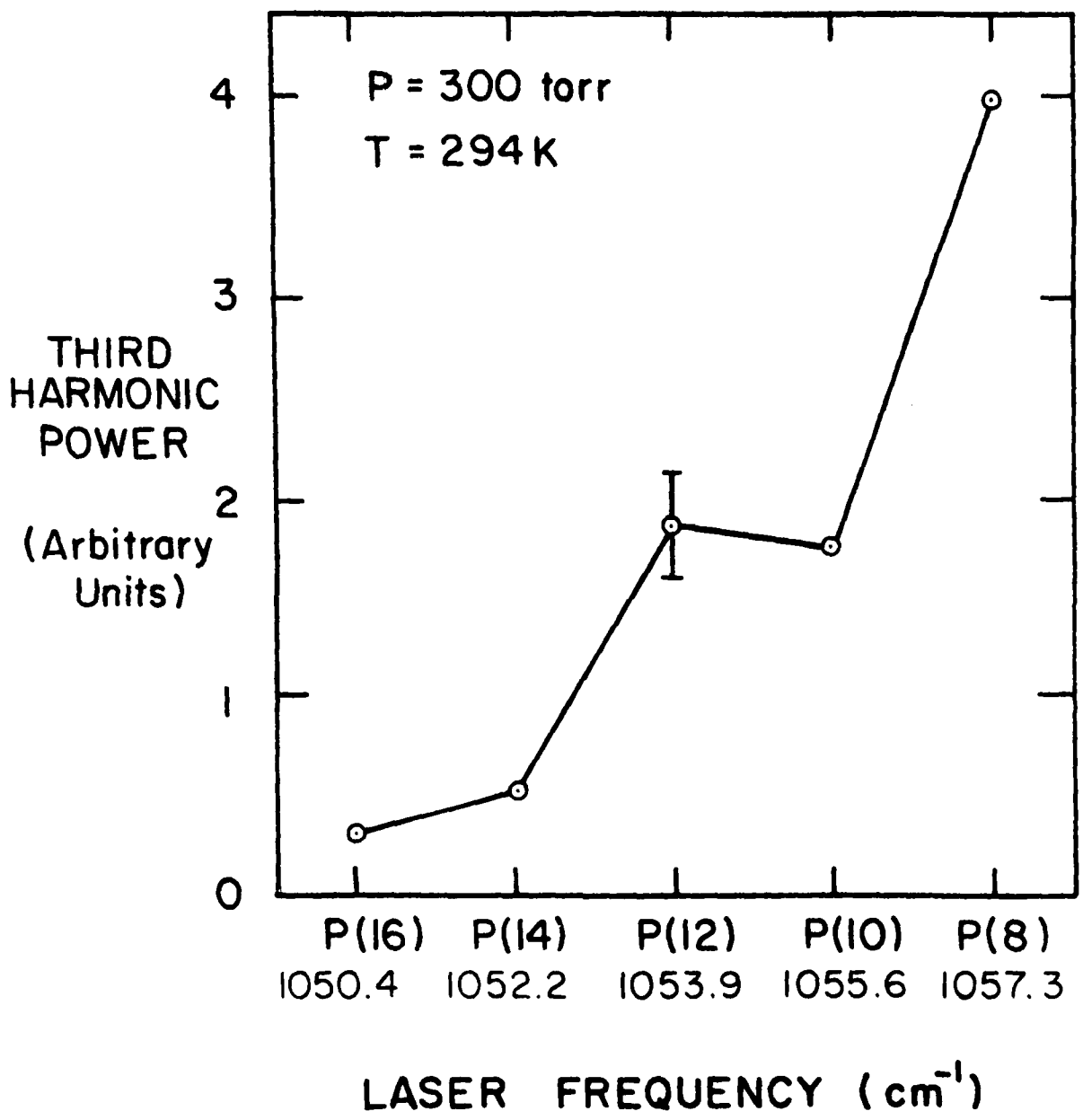
The spectral dependence of the THG, shown in Fig. 4, shows an unexpected feature. The 15 cm^{-1} wide ν_1 resonance is expected to be centered at the P(12) line. The increasing trend at the higher frequencies is not predicted by any strong spectral features in the Raman spectrum of CD_4 . Unfortunately P(8) is the high frequency limit for lasing in our laser on this band of lines and the behavior at higher frequencies could not be studied.

Recent high resolution Raman spectra of CD_4 have been taken by A. Owyong at Sandia Labs. The data includes part of this region near P(12) and not near P(8). Modeling based on this data is, as a result, incomplete.





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These results suggest double benefits to be gained by cooling the gas. First, the high J absorption of the fundamental should decrease dramatically; and second the Raman spectrum in the vicinity of the two-photon resonance should simplify. The result should be higher ultimate conversion efficiency in the first case, and a more easily interpreted THG spectrum, with possibly higher conversion, in the second case.

Experimental data confirms these predictions. The absorption did fall below the measurement limit, and the THG efficiency did increase by a factor of 3-4 depending on laser frequency. Modeling of this data is still underway and a publication is being prepared.

An experimental study of degenerate four-wave mixing (DFWM) in SF_6 gas was also undertaken. DFWM and the accompanying losses were studied for the P(8) through P(28) CO_2 laser lines in the 10 micron band. Parameters were gas pressure, buffer gas mix, and pump wave intensity.

The main objective of the work was to model and to verify experimentally the cause of the sudden drop in conjugate reflection efficiency for increasing gas pressures. Both increased absorption of the pump beams and the pressure broadening of the resonances were suspected.

Most of the experimental results were obtained with an experimental configuration with a retro-reflected pump wave. The backward travelling pump is attenuated by two passes through the gas cell. A symmetric configuration with identical pump waves was also used and showed qualitatively similar behavior to the retro-pump configuration. All modeling was done for the retro-pump case.

Experiments with N_2 as a buffer gas showed only a small, slow variation in conjugate reflectivity and absorption as a function of pressure. Thus, pressure changes in the resonance lines was eliminated from the model.

The final model which gave a good fit to the drop in conjugate reflectivity versus pressure, considered spatially dependent saturated absorption of the pump waves. The saturated absorption of the gas was first measured using conventional techniques. The intensity of the pump waves at any point in the saturable absorber can be determined. By an integration over the interaction length, the conjugate wave amplitude and reflectivity was then obtained. Pump wave depletion is included. Peak conjugate wave reflectivities of up to 27% were measured.

During the course of this work, a similar study was published by workers at Hughes Research Labs⁴ which duplicated much of our work, particularly the variation of the conjugate reflectivity with laser frequency. Our model for the effects saturated pump wave absorption and pump wave depletion remains as a unique result of this project.

References

1. M. F. Becker, K. M. Chung, and G. J. Stevens, "Investigation of Multiphoton Absorption in SF₆ by Third Harmonic Generation," Abstracts from the Europhysics Study Conference on Multiphoton Processes, 1979.
2. K. M. Chung, G. J. Stevens, and M. F. Becker, "Investigation of Multiphoton Absorption in SF₆ by Third Harmonic Generation," IEEE Journal of Quantum Electronics, QE-15, 874, September 1979.
3. M. F. Becker, G. J. Mauger, and Yihjye Twu, "Raman-Resonance Enhanced Third-Harmonic Generation in CD₄," Journal of the Optical Society of America, Vol. 70, 1582, December 1980.
4. D. G. Steel, R. C. Lind, and J. F. Lam, "Degenerate Four-wave Mixing in A Resonant Homogeneously Broadened System," Phys. Rev. A Vol. 23, P. 2513, May 1981.

III. List of Written Publications

- 1) M. F. Becker, K. M. Chung, and G. J. Stevens, "Investigation of Multiphoton Absorption in SF₆ by Third Harmonic Generation," Abstracts from the Europhysics Study Conference on Multiphoton Processes, 1979.
- 2) K. M. Chung, G. J. Stevens, and M. F. Becker, "Investigation of Multiphoton Absorption in SF₆ by Third Harmonic Generation," IEEE Journal of Quantum Electronics, QE-15, 874, September 1979.
- 3) M. F. Becker, G. J. Mauger, and Yihjye Twu, "Raman-Resonance Enhanced Third-Harmonic Generation in CD₄," Journal of the Optical Society of America, Vol. 70, 1582, December 1980.

IV. List of Professional Personnel

Dr. Michael F. Becker, Principal Investigator

Mr. Kang Min Chung*, Graduate Research Assistant

Mr. G. Joseph Mauger, Graduate Research Assistant

Mr. Yihjye Twu, Graduate Research Assitant

Degrees Awarded:

December 1979, Kang Min Chung, Ph.D., "Infrared Nonlinear
Optical Processes in Molecules."

December 1981, Yihjye Twu, M.S., "Phase Conjugation Via
Resonantly Enhanced Degenerate Four Wave Mixing."

To be awarded May 1982, G. Joseph Mauger, M.S., "Raman
Resonance Enhanced Third Harmonic Generation in CD₄."

V. Interactions

1. Conference Presentations

M. F. Becker, K. M. Chung, and G. J. Stevens, "Investigation of Multiphoton Absorption in SF₆ by Third Harmonic Generation," presented at the Europhysics Study Conference on Multiphoton Processes, Benodet, France, June 1979.

M. F. Becker, G. J. Mauger, and Y. Twu, "Raman-Resonance Enhanced Third Harmonic Generation in CD₄," presented at the Annual Meeting of the Optical Society of America, Chicago, Illinois, October 1980. This conference presentation was highlighted in Laser Focus, pp. 22-24, October 1980.

2. Consultations

December 1978. Visit by M. F. Becker to MIT Lincoln Laboratory to discuss experimental results with Dr. H. Kildal. Arranged for the loan of a nonlinear optical crystal for use in experiments at Texas.

June 1979. Discussions by M. F. Becker at the Europhysics Study Conference on Multiphoton Processes with Dr. P. Kelley, of MIT Lincoln Laboratory, about the results and implications of this research.

March 1980. Visit by M. F. Becker to Sandia Laboratories to meet with Drs. P. Esherick and A. Owyong and discuss nonlinear data from molecules and see their apparatus.

June 1980. Visit by M. F. Becker to MIT Lincoln Laboratory to discuss experimental results with Drs. H. Kildal and S. R. J. Brueck.

October 1980. While in Chicago at the Optical Society of America Annual Meeting, met with Drs. P. Esherick and A. Owyong of Sandia Laboratories to discuss spectroscopic data taken on CD_4 .