CONF-870784--3 3

DE87 013545

# THIRD-HARMONIC GENERATION AND MULTIPHOTON IONIZATION SPECTROSCOPY

C.Fotakis*, J.A.D. Stockdale,** and M. J. Froctor

*Research Center of Crete, Institute of Electronic Structure and Laser*
*P.O. Box 1527, Iraklion, Crete, Greece*

## 1. Introduction

Nonlinear phenomena, such as multiphoton excitation (MPE) processes leading to ionization and third-harmonic generation (THG) in gases have become the issue of extensive studies over recent years. Studies in rare gases in particular have resulted in several interesting observations in this respect [1]. Thus, it has been established that three-photon resonantly enhanced multiphoton ionization (MPI) in the vicinity of states which are single photon optically coupled to the ground state may occur in efficient competition with THG. A characteristic example is the competition between the MPI and THG in xenon when tuning through the 6s[3/2]J=1 three-photon allowed intermediate state [1]. Several novel aspects related to these effects have been treated theoretically by Garrett et al. [2] and by Jackson and Wynne [3] in a series of papers. In these papers, the THG in the negatively dispersive side of three-photon resonances is treated quantitatively. Thus, the dependence of the wavelength range of the third-harmonic radiation profile on gas pressure, gas composition, and exciting beam intensity may be predicted with a high degree of accuracy.

Finally, in a recent study of four-photon nonresonant excitation in krypton in the autoionizing region above the first ionization threshold, it has been shown that the presence of third-harmonic radiation may result in a strong enhancement of the observed signal [4]. Recent calculations by Lambropoulos and his co-workers are consistent with these observations [5].

The present work demonstrates several new effects which may appear when third-harmonic radiation is present during MPI.

## 2. Experimental Setup

For the purposes of this work a six-way cross ionization cell, capable of background pressures smaller than $10^{-6}$ Torr, was used. The output of a KrF pumped dye laser was focused in the ionizing region by means of a 3.8 cm focal length lens placed in adjustable positions inside the cell. The dye laser beam could be focused to a spot of ~10 $\mu$m giving a power density of ~100 GW $cm^{-2}$. Along the laser beam axis, the cell was coupled via a LiF window either to a 0.2 m vacuum ultraviolet (VUV) monochromator equipped with a solar blind photomultiplier or to a second ionization cell for

---

*Also Department of Physics, University of Crete, Greece.

**Permanent address: Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6125, U.S.A. (Oak Ridge National Laboratory is operated by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400 with the U.S. Department of Energy.)

single photon excitation studies using the third-harmonic radiation generated in the first cell.

## 3. Linewidth and Lineshape Effects

The MPI spectra of high lying even parity Rydberg states in xenon and krypton have been reported by Blazewicz et al. [6] The p and f series and the p′ and f′ series leading to the $P_{3/2}$ and $P_{1/2}$ ionization limits have been identified and were attributed to a direct four-photon excitation. More recently, Proctor et al. by recording simultaneously MPI spectra and third-harmonic radiation have shown that in the case of high pressures of krypton, THG arising from the negatively dispersive region of the 5S state, i.e., at pump laser wavelengths shorter than 349.4 nm, may contribute significantly to the observed ionization signal [4]. In Fig. 1 the 9f′ line of krypton is shown in greater detail. This figure clearly demonstrates that:

a. The linewidth <u>decreases</u> with <u>increasing</u> pressure, and

b. The asymmetric line profile is <u>reversed</u> by <u>increasing</u> the pressure.

These observations may be interpreted on the basis of the participation of third-harmonic radiation in the excitation process. At low krypton pressures, the phasematching conditions do not favor THG and the observed MPI spectra are attributed to a direct four-photon excitation process which occurs with the highest probability in the region of strongest focusing. For the laser intensities used in our experiments, field strengths of ~10 V cm$^{-1}$ are expected at the focal point. These high field strengths should in turn give rise to intense Stark broadening of the observed lines. As the pressure increases, phasematching favors THG. In this work, THG was initially observed by means of the VUV monochromator and the solar blind photomultiplier. In later experiments THG was observed by using the second ionization cell (cf experimental setup) which could be filled with [illegible], CO, or another rare gas. In Fig. 2 are shown the single-photon ionization spectra of nitric oxide due to the THG produced in the krypton gas in the first cell. These spectra clearly demonstrate the increase of intensity of THG, together with a shift to shorter wavelengths of the THG profile with increasing pressure of krypton. These observations are consistent with the theoretical predictions of Garrett et al. [2]. It should be noted that the observed structure can be attributed to the existence of autoionizing states of nitric oxide, which have not been reported before in this wavelength region. Similar experiments with CO or Ne instead of NO resulted in characteristic structureless THG profiles.

The increasing intensity of THG with pressure leads to an increasing contribution to the observed ionization signal of a two-photon excitation process, involving one third-harmonic photon and one dye laser photon. The efficiency of this two-photon process is expected to be high even in regions outside the strong focusing region, where the Stark broadening effect is weaker. This is compatible with the observed line narrowing with increasing pressure shown in Fig. 1. Additional support for this qualitative interpretation is provided by recent theoretical work, where it is estimated that the cross sections for the two-photon process involving

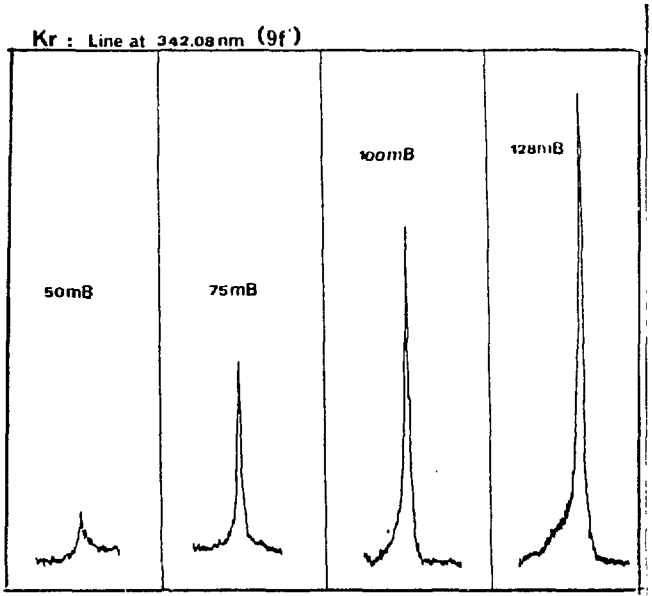

Fig. 1. Line asymmetry reversed.

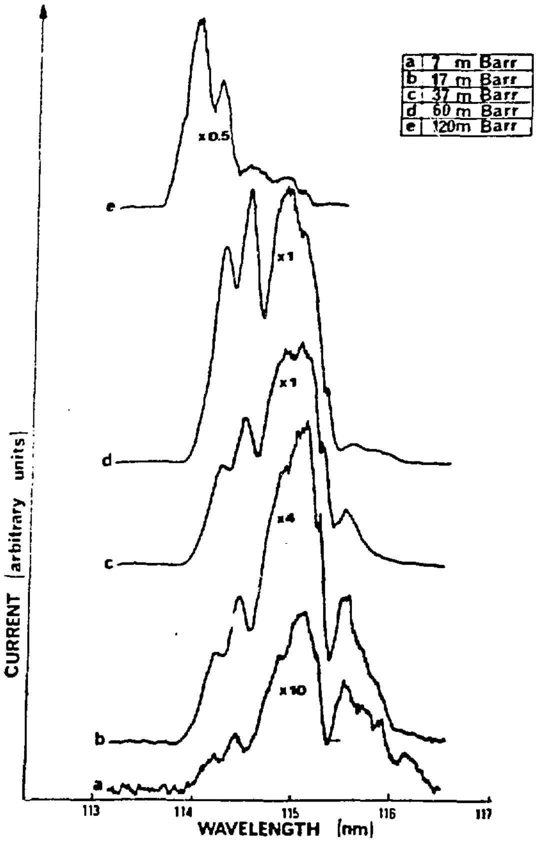

Fig. 2. Single-photon ionization spectrum of nitric oxide reflecting the shift in THG with Kr pressure.

one THG photon and one dye laser photon under our experimental conditions is four orders of magnitude higher than the direct four-photon excitation cross section [5].

The change in asymmetry of the lineshape could also be explained in terms of THG involvement in the ionization process, in the sense that the Fano "q" factors, which determine the asymmetric lineshapes of autoionizing states [7], will involve matrix elements dependent on the near-resonant intermediate states. These states will be different for four- and two-photon ionization, resulting in different "q" values. Recent preliminary calculations by Lambropoulos and his co-workers, however, do not reproduce the lineshape asymmetric reversal effect [8].

## 3. Observation of Rare-Gas Dimers and THG Profiles

In regions where the third-harmonic radiation produced in a rare gas is strongly absorbed by rare gas dimers, intense molecular MPI may occur. This has been demonstrated by Proctor et al for the III* band of $Kr_2$, which has been observed by one VUV photon resonant, two-photon ionization [4]. By altering the pressure or using another buffer gas, shift in the THG profile may be induced allowing the probing of different parts of the upper

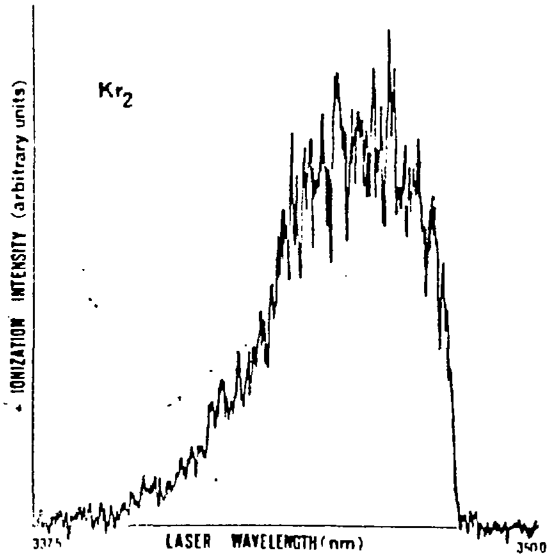

Fig. 3. $Kr_2$ two-color two-photon ionization spectrum.

potential surface. A typical two-photon excitation spectrum of the Kr2 III* band obtained in this way is shown in Fig. 3.

In other cases, however, the THG profiles do not overlap with absorption features of the dimer. Structureless broad features may then be observed in the MPI spectra, due to two-photon nonresonant excitation in the medium, reflecting the THG profiles, as shown in Fig. 4 for xenon. The broad features at 342 nm and 333 nm correspond to THG in the vicinity of the 7S[1 1/2]J=1 and 6d[1 1/2]J=1 states of xenon correspondingly.

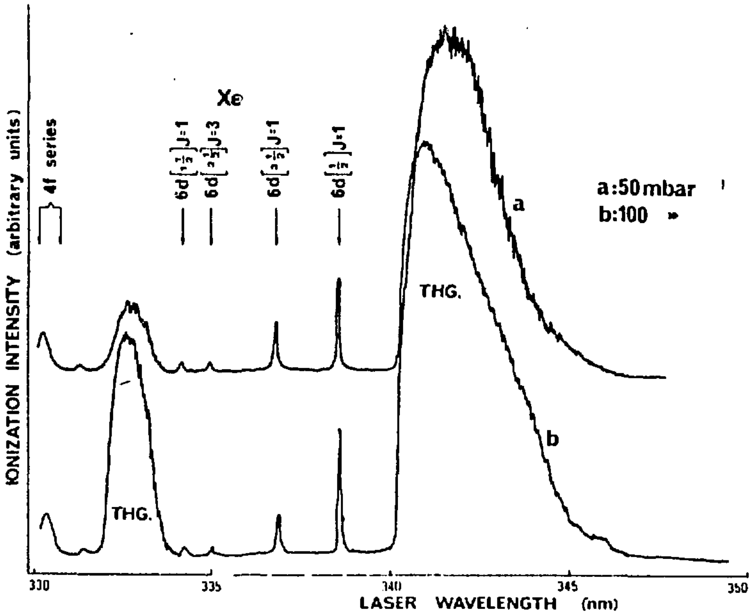

Fig. 4. THG profiles in pure xenon and MPI spectra.

## 4. Concluding Remarks

It has been demonstrated that THG in rare gases may influence drastically the expected intensity, linewidth, lineshape, and the observed spectral features in the MPI spectra. Such effects are expected to be important in a wider range of atomic and molecular systems and their potential contribution should be considered when deducing spectroscopic or lifetime information from MPI spectra.

## 5. Acknowledgments

The authors are indebted to Professor P. Lambropoulos for many stimulating discussions. Support under NATO Collaborative Research Grant No. 86/423 is acknowledged.

## References

1. J. C. Miller, R. N. Compton, M. G. Payne, and W. R. Garrett, Phys. Rev. Lett. 45 (1980) 114.

2. M. G. Payne, W. R. Garrett, and W. R. Ferrell, Phys. Rev. A 34 (1986) 1143; and references therein.

3. D. L. Jackson, J. J. Wynne, and P. H. Kes, Phys. Rev. A 28 (1983) 781.

4. M. J. Proctor, J.A.D. Stockdale, T. Efthimiopoulos, and C. Fotakis, Chem. Phys. Lett. (June 1987).

5. X. Tang and P. Lambropoulos (to be published).

6. P. R. Blazewicz, J.A.D. Stockdale, J. C. Miller, T. Efthimiopoulos, and C. Fotakis, Phys. Rev. A 35 (1987) 1093.

7. U. Fano, Phys. Rev. 124 (1961) 1866.

8. P. Lambropoulos (private communication).