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SUPPRESSION OF MULTIPHOTON EXCITATION IN RESONANCE IONIZATION MEASUREMENTS*

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ABSTRACT: We describe experimental confirmation of strong suppressions of laser driven nonlinear absorption processes by electromagnetic fields through other nonlinear processes within a given atomic or molecular medium.

1. INTRODUCTION

Multiphoton excitation of specific atomic and molecular energy levels is ubiquitous in many modern laser spectroscopic techniques. One or more forms of the process can be used in very sensitive and highly selective analytical methods, including resonance ionization spectroscopy, resonance fluorescence spectroscopy, resonance ionization mass spectroscopy, resonance Raman spectroscopy, and others. In several detailed studies of multiphoton excitation and associated nonlinear optical phenomena in gaseous media, we have found that laser driven excitation may, under some circumstances, become strongly influenced (even effectively eliminated) by new electromagnetic fields that are internally generated within the "sample." Additionally, in very recent studies we find that the forward directed component of stimulated hyper-Raman photon emission and the associated atomic excitation are both suppressed by a three-photon interference effect involving four-wave mixing in the sample. Moreover, the stimulated hyper-Raman emission itself (backward component) can lead to strong suppression of two-photon excitaton rates through an a.c. Stark effect.

Thus we have found dramatic suppression mechanisms for multiphoton excitation processes at elevated number densities arising from two different mechanisms.

a. Suppression due to an interference effect between multiphoton pumping by a laser beam and simultaneous pumping by an internally generated nonlinear wave-mixing field.
b. Suppression due to a.c. Stark shifting of resonant transitions by internally generated Raman and hyper-Raman fields.

We discuss examples of these effects and their implications in the context of certain analytical techniques.

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2. SUPPRESSION BY NONLINEAR WAVE-MIXING INTERFERENCES

Several years ago at the Oak Ridge National Laboratory (ORNL) it was discovered that RIS measurements involving three-photon resonant excitations of Xe yielded different results when conducted in atomic beam and static cell apparatuses (Miller *et al* 1980). Certain lines which were "missing" in cell experiments appeared normal under atomic beam conditions. These, and later experiments along the same lines, were quantitatively explained and/or predicted by Payne and Garrett (1981,1982,1983), who showed that when a one-photon allowed transition is excited, alternatively, through multiphoton excitation with an odd number of photons a greatly decreased multiphoton excitation rate will occur at number densities above fractions of a millitorr. The suppression arises from the internally generated four-wave mixing field which interferes with direct n-photon excitation. The effect is now well documented and has been demonstrated in a number of systems under various circumstances (Garrett *et al* 1986a,b). The effect behaves according to predictions in all cases including five-photon excitation (Garrett *et al* 1987).

In very recent studies we have predicted and experimentally demonstrated a new and somewhat more exotic consequence of the interference phenomenon involving three-photon excitation and an internally generated four-wave mixing field. The effect is associated with stimulated hyper-Raman scattering, wherein the nonlinear laser-atom interaction leads to absorption of two photons to produce a third photon and an excited atom. The angular frequency, ω_{HR}, of the hyper-Raman photon satisfies $\omega_{HR} = 2\omega_L - E_1/\hbar$ where ω_L is the laser frequency and E_1 is the energy of the excited atom. (See Fig. 1). On the basis of our earlier theoretical work one can

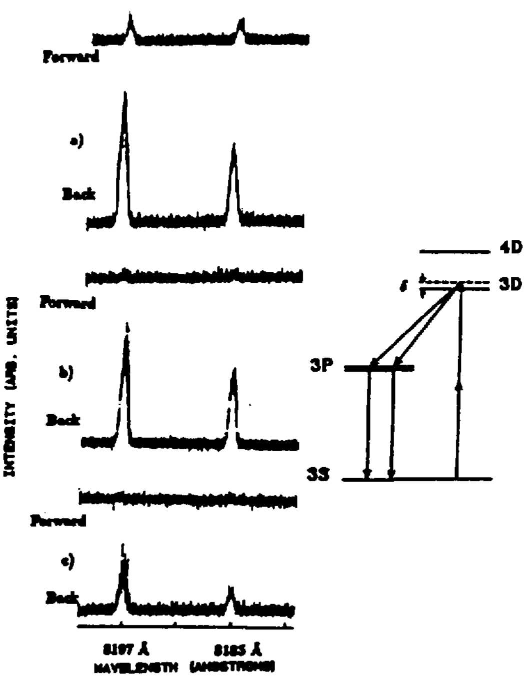

Fig. 1. Forward and backward hyper-Raman intensities at detunings, δ, of: a) 0.0Å, b) 0.1Å, c) 0.2Å, $P_{Na} = 1.5$ Torr

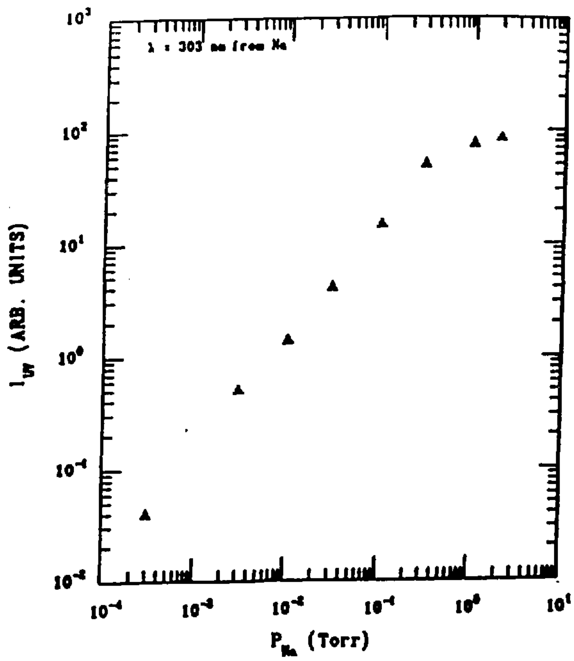

Fig. 2. Parametric four-wave mixing intensity (near 303 nm) versus P_{Na} for two-photon pumping at 14 mW/cm^2 near Na 4d state.

predict that at very modest number densities, *forward* hyper-Raman emission should become suppressed, due to an interference between the excitation of the atomic state through the HR process and that arising through generated four-wave mixing field at the resonant frequency $\omega_M = 2\omega_L - \omega_{HR}$. But the *backward* HR emission will not produce an associated interferring field and thus should behave normally. We conducted a set of experiments to demonstrate this suppression effect. Results for hyper-Raman emission associated with excitation of Na $3p_{1/2}$ and $3p_{3/2}$ states, when tuning near two-photon resonance with the $3d_{3/2}$ states are shown in Fig. 1. As the laser detuning, δ, from the 3d state is successively increased (such that the emission becomes pure HR) the forward component is found to disappear. (In this example the effect should be operative at all pressures above $\sim 8 \times 10^{-5}$ Torr.) The backward and forward HR emissions, and concomitant three-photon atomic excitation, behave according to prediction.

As already mentioned, two-photon pumping near Na 3d and 4d states produces on-resonant excitation of these states and excitation of lower lying p-states by hyper-Raman scattering. But additional nonlinear frequency generation takes place through parametric four-wave mixing (PFWM) to produce frequencies near the $d \rightarrow p$ and the $p \rightarrow s$ transition frequencies. This phenomenon also produces an interference effect, first described by Manykin and Afanas'ev (1965), which we show, in the present context, causes the generation of PFWM photons (near 303 nm for Na 4d excitation) to saturate with Na number density. This effect is responsible for the saturation behavior of PFWM intensity shown in Fig. 2. The saturation pressure of 0.5 Torr (at 14 mW/cm^2 pumping intensity) agrees exactly with our theoretical prediction. At this pressure, the two-photon Rabi rates, between 3s and 4d from two laser photons and from two PFWM photons become equal and opposite. Beyond this pressure regime (or at increased path length at the same pressure) no additional PFWM photons are produced.

3. SUPPRESSION OF TWO-PHOTON EXCITATION AND SATURATION OF EMISSION PROCESSES DUE TO A.C. STARK SHIFTING

In additional studies of processes associated with near resonant two-photon pumping of Na vapor, we have observed and quantified another type of Rabi-rate suppression mechanism. On the basis of theoretical estimates of three-photon ionization probabilities of Na when tuning to two-photon resonance with the Na 3d and 4d states, and of an independent RIS measurement of the 4d ionization rate in an atomic beam apparatus, we found greatly reduced resonant two-photon absorption in Na vapor concentrations available in a heat pipe oven (0.001 to 2.0 Torr). Several manifestations of reduced rates at elevated pressures and laser power densities for three nonlinear processes in the vapor were uncovered.

a. The total laser beam absorption at all pressures is much smaller than what would be predicted in the absence of some suppression mechanism (e.g., only 20% at 0.2 Torr as opposed to expected >60%).
b. Backward hyper-Raman emission increases as the square of I_L at low laser intensities, but grows only linearly with I_L at higher intensities. An example of this behavior is shown in Fig. 3. The slope and threshold energy agrees well with our predictions.
c. Two-photon resonant excitation and three-photon ionization yields are much smaller than corresponding values at very low (atomic beam) number densities.

d. Amplified spontaneous emission hyper-Raman emission profiles should show a dip at exact two-photon resonance. This theoretical prediction arises from a.c. Stark shifting/broadening of strongly coupled $d \rightarrow p$ states, where the coupling results from backward HR emission. Results for the SHR profiles at different P_{Na} are shown in Fig. 4. Experimental data confirm the theoretical prediction of HR gain profiles. The reduction, R, in hyper-Raman gain is predicted to have the form $R = (2\Gamma_L)^2)/\left[(2\Gamma_L)^2) + (|\Omega_R|^2/\delta)^2\right]$ where Γ_L is the laser bandwidth and Ω_R is the $d \rightarrow p$ Rabi rate due to the HR field.

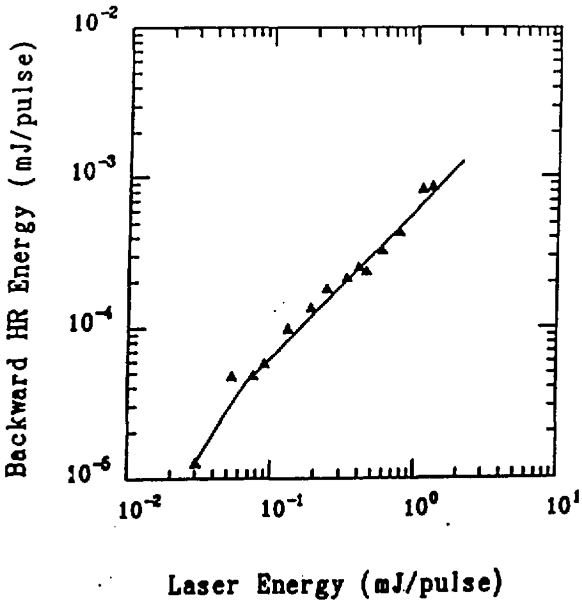

Fig. 3. Backward hyper-Raman output versus laser energy at 0.07 Torr Na.

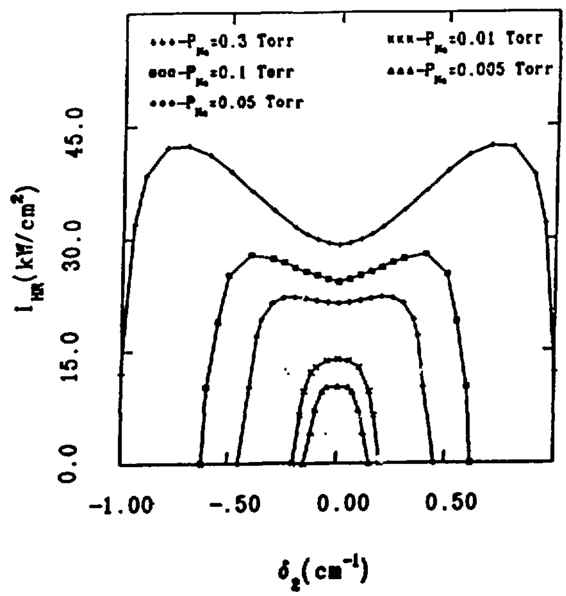

Fig. 4. Theoretical stimulated hyper-Raman output versus detuning from two-photon resonance Na with Na 4d pressures as labeled.

The theoretical predictions, based on a.c. Stark influence on two-photon excitation, three-photon ionization, backward hyper-Raman intensity versus laser intensity, and HR gain profiles all show quantitative agreement between theory and experiment.

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