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# Suppression and Shifting of Odd-Photon Resonant Excitations and Stimulated Hyper-Raman Emissions *

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## Abstract

When a principal atomic transition (dipole allowed from the ground state) is driven by odd-multi-photon excitation or by stimulated hyper-Raman scattering, a nonlinear multi-wave mixing field is generated at the transition frequency. A number of dramatic effects on such odd-photon mediated processes can ensue as a result of the internally generated wave-mixing fields. Excellent agreement between theory and experimental studies in Xe and in metal vapors is illustrated for a number of predicted effects including: suppression and strong shifting of resonance lines and hyper-Raman emissions under single and multi-laser excitation. We illustrate the dependence of the interference-related effects on pressure, oscillator strength, wavelength combination and relative propagation directions of pump laser beams. Contrary to most other nonlinear effects, we show that none of the features (in the semi-classical regime) depends on the intensity of the driving laser field.

## I. Introduction

Over the past several years a number of experimental and theoretical studies have established that, under well understood circumstances, resonant multiphoton excitation processes in gases and vapors can be very strongly influenced by optical fields that are generated by the nonlinear polarization of the medium which is undergoing resonant excitation. If a dipole allowed transition is driven by an odd-photon process which is resonant with a sum or difference frequency combination of the driving fields, the Rabi frequency term which mediates the transition also serves as a source term for generation of a nonlinear polarization at the sum or difference frequency. The field which is generated by this polarization has three characteristic features: it is strongly absorbed by the medium, since it is at the resonant frequency; it evolves 180° out of phase with the combined phase of the driving fields; it grows in magnitude until complete destructive interference is established between the laser and generated fields, at which point no additional excitations and no additional field strength are created. Early studies of this phenomenon demonstrated that three-photon-resonant excitation could be observed in Xe at molecular beam number densities[1], but not in a static cell at fractions of a Torr or greater pressures[2–5], unless a four-wave mixing (FWM) field was avoided by using both right and left circularly polarized pumping[6] or by counterpropagating the laser beam to produce overlapping beams propagating in opposite directions[7]. The predictions and observations at the time were that "normal" excitation occurs with counterpropagating geometry, because the wave-mixing field could be neglected in the pumping by photons from the combined directions. Results were extended to include demonstration of the predicted suppression effect in multicolor three-photon pumping[8] and in five-photon-resonant excitation[9] in Xe. Results were also extended to demonstrations of the effect in molecules[11–13], and it was shown by Garrett *et. al.*[14] that the same four-wave-mixing interference effect caused stimulated hyper-Raman emission to have zero gain for forward but normal gain for backward emission. Finally, Gilligan and Eyler[15] showed recently that with the use of very narrow bandwidth laser excitaiton, suppression of three-photon excitation in $H_2$ occurred even in a pulsed nozzle source at a number density $\simeq 10^{11}/cm^3$, in conformance with earlier theoretical bandwidth-related predictions by Payne and Garrett[4].

There was one exception to the observation that predictions and measurements of odd-photon mediated excitations with counterpropagating (cp) beams appeared normal. Ferrell, Payne and Garrett[16] used the cp arrangement to study pressure broadening of resonance lines in Xe and Kr. The study produced line widths which agreed with theory in the range of validity of the theory, but it also produced unexpected linearly pressure dependent violet shifts of the resonant profiles of all the transitions measured. Recently Friedberg et.al.[17] showed that the shift observed in Ref.16 could be explained on the basis of the cooperative response of atoms which are within approximately an absorption length for the field generated at the sum frequency of the pump fields. More recently, Payne and Garrett[18,19] extended the theoretical treatment of the problem to include several new features and to show the close connection between the suppression and shifting phenomena, both of which arise from the combined effect of pumping by laser and internally generated four-wave mixing fields. Indeed the shifts observed by Ferrell et.al. were produced by the FWM field which had been neglected in treating the problem in the c.p. configuration. Garrett et.al.[20] experimentally observed the large cooperative lineshifts in Xe and showed very good agreement between predicted and observed features of the phenomenon. Finally, in a very recent study Garrett et.al.[21] showed that the stimulated hyper-Raman process which is suppressed in the forward direction by the interference from FWM will, by the same token, also show a pressure dependent frequency shift in the backward emission. The prediction was verified in measurements of SHR emission from Xe at elevated pressures.

We now have aquired a fairly global view of the influence of FWM fields on principal atomic and molecular transitions mediated by three-photon resonant excitations. Contrary to the view held by all early investigators, including the present authors, the internally generated field cannot be neglected in any geometry (especially at high pressures). The interplay of the externally supplied laser fields and the internally generated wave-mixing fields produce lineshifts which have a simple linear dependence on pressure, but a fairly complicated dependence on pump wavelengths, crossing angle between pump beams and mode of excitation (whether resonance occurs at a sum or difference frequency of the pump fields). The total suppression that occurs under unidirectional pump geometry has the same basis as that of the shifts. Both of the processess are produced in a comprehensive treatment of the problem[19].

We present a sketch of the theoretical basis for the behavior of the resonant excitation and stimulated hyper-Raman emission problems, and present recent experimental results on these phenomena.

## II. Theoretical Considerations

The influence of internally generated fields on multiphoton excitation processes can be described by several alternative methods. For its generality and its capacity for including some interesting details, e.g., effects associated with laser bandwidths, etc., we describe the atomic response with a two-state model which we treat by a density matrix approach.

We consider two different modes for carrying out three-photon excitation by two laser beams. In the first mode two photons at frequency $\omega_{L1}$ are absorbed from laser 1 and one photon of frequency $\omega_{L2}$ is absorbed from laser 2. In the second mode two photons are absorbed from laser 1 and an emission is stimulated at $\omega_{L2}$ by laser 2. The unfocused laser beams have propagation vectors $\vec{k}_{L1}$ and $\vec{k}_{L2}$ which cross at an arbitrary angle $\theta$ ($\theta = 0$ corresponds to parallel and $\theta = 180°$ to anti-parallel propagation). For convenience we take the +z direction to lie along the wave vector $\vec{k}_m = 2\vec{k}_{L1} \pm \vec{k}_{L2}$ where the +

refers to the $2\omega_{L1}+\omega_{L2}$ mode and the $-$ refers to the $2\omega_{L1}-\omega_{L2}$ mode of excitation. We can represent $k_m$ in terms of $\theta$ as

$$k_m = (2k_{L1}+k_{L2})\left[1-\frac{8k_{L1}k_{L2}}{(2k_{L1}+k_{L2})^2}F(\theta,\pm)\right]^{1/2} \tag{1}$$

where $F(\theta,+) = sin^2(\theta/2)$ for the sum frequency mode and $F(\theta,-) = cos^2(\theta/2)$ for the difference frequency mode. Our system is described by two levels, $|0>$ as ground state, energy $E_0$, and $|1>$ as the excited state, with energy $E_1$. The effect of incoherent resonance energy transfer between excited state and ground state atoms is simulated by including a pressure-broadened width $\Gamma_P$ and small pressure-dependent shift terms $\Delta_P = \Delta_{bl} - \frac{4}{3}\Delta_0 = -1.11\Delta_0$ where $\Delta_0 = \pi N|D_{01}|^2/\hbar$. The collisional shift $\Delta_{bl}$ and Lorenz-Lorentz shift $-\frac{4}{3}\Delta_0$ are described elsewhere[18]. Spontaneous emission rates to other states can be ignored and the spontaneous rate between $|1>$ and $|0>$ can be neglected because this radiation is trapped.

The two-state model leads to the following equations for the elements $\rho_{ij}$ of the density matrix.

$$\frac{\partial\rho_{00}}{\partial t} = -\,2Im(V_{10}\rho_{01}/\hbar), \tag{2a}$$

$$\frac{\partial\rho_{01}}{\partial t} = -\,i\frac{V_{01}}{\hbar}[\rho_{11}-\rho_{00}] + i\left[(E_1-E_0)/\hbar + \Delta_{bl} + i(\Gamma_P+\Gamma_I/2)\right]\rho_{01}, \tag{2b}$$

$$\frac{\partial\rho_{11}}{\partial t} = 2Im(V_{10}\rho_{01}/\hbar) - \Gamma_I\rho_{11}, \tag{2c}$$

where $\Gamma_I$ is the ionization rate ( it is assumed that $\Gamma_P >> \Gamma_I$). The coupling, $V_{01}$ between the two levels is composed of two components. The first is direct three-photon pumping by two photons at $\omega_{L1}$ and one at $\omega_{L2}$, which is described in terms of a three-photon Rabi frequency $2\Omega_{01}^{(3)}$. (We have used reduced Rabi frequencies $\Omega_{ij}^{(n)}$ which are one-half the regularly defined n-photon Rabi frequencies.) The second part of $V_{01}$ is the coupling produced by the internally generated field at the sum or difference frequency $\omega_m = 2\omega_{L2}\pm\omega_{L2}$, with local value $E_{\omega_m}^{\mathcal{L}}$ (to be calculated as part of the problem). In the rotating wave approximation the total interaction term is

$$\begin{aligned} V_{01}/\hbar &= -\,\Omega_{01}^{(3)}e^{i\omega_m t}e^{-ik_m z} - \frac{D_{01}E_0^{\mathcal{L}}}{2\hbar}\exp(i\omega_m t)\,, \\ &= -\left(\Omega_{01}^{(3)} + \Omega_{10}^{(1)}e^{-\Delta k_r z}\right)e^{-ik_m z}e^{i\omega_m t}, \end{aligned} \tag{3}$$

where $D_{01}$ is the dipole matrix element between $|0>$ and $|1>$ and we have written

$$\begin{aligned} E_{\omega_m}^{\mathcal{L}} &= \frac{1}{2}E_0^{\mathcal{L}}\,e^{i\omega_m t} + c.c. \\ &= E_{\omega_m}^{\mathcal{L}+} + E_{\omega_m}^{\mathcal{L}-}. \end{aligned}$$

Also, $\Omega_{01}^{(1)} = \frac{1}{2\hbar}D_{01}E_0^{\mathcal{L}}e^{i(k_m+\Delta k_r)z}$ is the reduced one-photon Rabi frequency due to the sum or difference-frequency field and $\Delta k_r$ is the real part of the phase mismatch. At high concentration light generated at $\omega_m = 2\omega_{L1}\pm\omega_{L2} \cong (E_1-E_0)/\hbar$ is resonantly absorbed in a distance less than a wavelength. Thus, the Lorentz approximation can be used to relate the local field at the location of the atom, $E_{\omega_m}^{\mathcal{L}}$ to the locally space averaged field, $E_{\omega_m}$, which enters Maxwell's equations. The relation between the local and space averaged field is $E_{\omega_m}^{\mathcal{L}} = E_{\omega_m} + (4\pi/3)P_{\omega_m}$ where $P_{\omega_m}$ is the polarization of the medium at frequency $\omega_m$. The space averaged field $E_{\omega_m}$ must be derived through solutions to Maxwell's equation, with the polarization $P_{\omega_m}$ as source term. The resonant part of the polarization can be expressed in terms of the density matrix elements as $P_{\omega_m} = NTr(\hat{\rho}\hat{D})$, where N is the number density and $\hat{D}$ is the electric dipole operator. Maxwell's equation can be solved for plane wave fields involving no incoming waves in terms of an integral of the time retarded polarization source term over the length of the medium. The local field in Eq. 3 can then be replaced by this space averaged field plus the Lorentz polarization to yield an expression for $V_{01}$ in the form

$$V_{01}/\hbar = \frac{2i}{c}\omega_m \Delta_0 \int_0^L \rho_{01}(z', t - |z - z'|/c)dz' - \Omega_{01}^{(3)} e^{i\omega_m t} e^{-ik_m z} - \frac{4}{3}\Delta_0 \rho_{01}. \tag{4}$$

where $\Delta_0 = \pi N |D_{0,1}|^2/\hbar$ and the integral extends over the length L of the overlap region.

Eq. 4 can be substituted into Eq. 1b to yield an integro-differential equation for $\rho_{01}$.

$$\frac{\partial \rho_{01}}{\partial t} = -\kappa_{01} \int_0^l \rho_{01}(z', t - |z - z'|/c)dz' + i[(E_1 - E_0)/\hbar + \Delta_T]\rho_{01} - i\Omega_{01}^{(3)} e^{i\omega_m t} e^{-ik_m z} \tag{5}$$

where $\Delta_T = \Delta_P + i\Gamma_P$ and $\kappa_{01} = \frac{2\pi}{\hbar c}\omega_m N |D_{01}|^2$.

We arrive at a tractable equation which contains only slowly varying temporal and spatial dependencies by defining:

$$S_{01}(z,t) = e^{-i\omega_m t} e^{ik_m z} \rho_{01}(z,t). \tag{6}$$

If it is assumed that $\rho_{11}$ remains small ($\rho_{00} \sim 1$), then in presently applicable circumstances, where $\omega_m \Delta_0 L / c\Gamma_P >> 1$, the equation can be solved exactly in the adiabatic limit. With $\frac{\partial S_{01}}{\partial t} \equiv 0$, the equation for $S_{01}$ becomes

$$\begin{aligned} S_{01}(z,t) = &- \frac{\Omega_{01}^{(3)}}{(\delta_1 - \Delta_T)} \\ &+ \frac{i\kappa_{01}}{(\delta_1 - \Delta_T)} \int_0^L S_{01}\left(z', t - \frac{|z - z'|}{v_1}\right) \exp(ik_M(z - z')) \exp\left(-i\omega_M \frac{|z - z'|}{v_1}\right) dz' \end{aligned} \tag{7}$$

The solution to this equation is algebraically complicated but, over all but the margin of the beam overlap region, has the simple form

$$S_{01} = \frac{-\Omega_{01}^{(3)}}{[\delta_1 - \Delta_T] - \frac{\kappa_{01}}{4\pi}\frac{\lambda_{L1} \pm 2\lambda_{L2}}{1 - \cos(\theta)}}. \tag{8}$$

The solution can then be used in Eq.1c to give an equation for the diagonal element $\rho_{11}$.

$$\frac{\partial \rho_{11}}{\partial t} = 2\Gamma_P |S_{01}|^2 - \Gamma_I \rho_{11} \tag{9}$$

A principal result from ref.18 is obtained thereby, namely the excitation rate, R, for producing $|1>$ :

$$\begin{aligned} R =& 2\Gamma_P \frac{|\Omega_{01}^{(3)}|^2}{\left(\delta_1 - \Delta_0(-1.11 + \frac{\lambda_{L1} \pm 2\lambda_{L2}}{[1 - cos(\theta)]\lambda_{mix}})\right)^2 + \Gamma_P^2} \\ =& 2\Gamma_P \frac{|\Omega_{01}^{(3)}|^2}{\left(\delta_1 - \tilde{\Delta}_P\right)^2 + \Gamma_P^2}. \end{aligned} \tag{10}$$

We defined $\lambda_{mix} = 2\pi c/(2\omega_{L1} + \omega_{L2})$ and $\delta_1 = 2\omega_{L_1} + \omega_{L_2} - (E_1 - E_0)/\hbar$.

The excitation lineshape has the familiar form for a three-photon induced transition, but it now contains a total pressure dependent shift

$$\begin{aligned}\tilde{\Delta}_P &= \Delta_0 \left[ -1.11 + \frac{\lambda_{L1} \pm 2\lambda_{L2}}{[1 - cos(\theta)]\lambda_{mix}} \right] \\ &= \Delta_P + \Delta_c \end{aligned} \tag{11}$$

where $\Delta_P = \Delta_0(-1.11) = -\frac{4\pi}{3\hbar} N|D_{10}|^2 + \Delta_{bl}$ is the usual pressure induced shift and the last term is the cooperative shift

$$\Delta_c = \Delta_0 \frac{(\lambda_{L1} \pm 2\lambda_{L2})}{[1 - cos(\theta)]\lambda_{mix}}. \tag{12}$$

This cooperative shift is indeed very novel in character. It is positive (violet) for the + mode and negative (red) for the − mode of excitation, it is linear in pressure (since $\Delta_0$ is proportional to N) and is a function of the crossing angle $\theta$. Additionally, we see that use of various combinations of $\lambda_{L1}$ and $\lambda_{L2}$ produce different shifts. These can be very large (many nanometers) if $\lambda_{L1} >> \lambda_{L2}$ or if $\theta$ is small. Then there is an even more intriguing effect. If one of the beams, say $\lambda_2$, is retroreflected then a second coherent three-photon excitation path involving a new direction for $L_2$, and thus a different $\Delta_c$, is created. With this crossed and retroreflectd geometry a scan of $\omega_{L2}$ will produce two resonant peaks (see below). The width of the line (or lines) in terms of wave numbers and the shape remains the same and appears as a normal pressure broadened profile[18,19].

The total suppression of any excitation as $\theta \to 0$, which is the often-studied cancellation effect, can be obtained from a limit of Eq.7. The usual result, that R=0 when $\delta_1 = 0$, is obvious. That is, no excitation at the position of the unshifted resonance. When $\theta$ becomes small, and $\Delta_c$ large, the $z' > z$ contribution to the integral in (5b) can be neglected. In this limit the solution becomes

$$S_{01} \simeq -\frac{\Omega_{01}^{(3)}(1 - e^{-i\Delta kz})}{\delta_1 - \Delta_T - \kappa_{01}(\omega_m/c - k_m)}.$$

When $\Delta_c$ is large, $\Delta k$ is small, and the numerator in this expression is $\propto (\Delta kz)^2$ which remains small. Thus for $\theta \to 0$ we have the result that $S_{01}$, and thus $\rho_{01}$ and $\rho_{11}$, go to zero and excitation is strongly suppressed for all detunings.

It is fairly easy to show[21] that the same considerations which produce a shift in the peak of the three-photon excitation profile also produces an identical shift in the peak of the gain profile for stimulated hyper-Raman scattering. Indeed the equation for SHR gain contains the factor on the right side of Eq.10 with the minus sign (corresponding to the $2\omega_1 - \omega_2$ mode of excitation). This results in a pressure dependent shift in the SHR emission to shorter wavelengths. This prediction and an experimental confirmation in Xe is contained in a recent paper by Garrett et.al.[21]

### III. Experimental Results

Since there are a large number of published studies involving suppression of three-photon[2,5–16] (and five-photon[9,21]) resonant excitations in atomic and molecular systems (with unidirectional beams), we forego introduction of any additional data on this well characterized feature of the present topic.

Studies of the suppression of forward stimulated hyper-Raman emission associated with excitation of an optically allowed transition has so far only been reported for experiments in metal vapors[14,22], though the phenomenon should be universal. We report new results below in connection with confirmation of the predicted SHR shift in Xe. (See also Ref.21).

We now present abbreviated data from a series of experiments involving two-color three-photon-resonant excitation (and subsequent ionization by an additional photon) in Xe. The experiments were intended to explore all of the predicted features of the collective lineshifting phenomenon. Ten of these features are confirmed : 1) the cancellation of three-photon excitation under unidirectional pumping (already discussed at length) ; 2) production of cooperative line shifts linear in number density of target gas (for all geometries involving $\theta > \theta_{min}$); 3) production of two separate peaks when two-color pumping in crossed geometry if one beam is retroflected to produce two complementary crossing angles; 4) production of different shifts for a fixed geometry and pressure when different wavelength combinations are used for pumping a given state; 5) for different transitions, the slopes of shifts vs pressure are proportional to oscillator strength for coupling to the ground state; 6) dependence of the shift on crossing angle conforms to Eq.10; 7) forward Stimulated hyper-Raman emission is suppressed; 8) the collective shift for excitation in $2\omega_1 - \omega_2$ mode of excitation is opposite to that produced in the $2\omega_1 + \omega_2$ mode; 9) a collective shift, linear in pressure, is produced in stimulated hyper-Raman emission, and; 10) all of the effects are independent of the pump beam intensities.

With the exception of the last example below, all of the results described here were obtained with the use of a stainless steel ionization cell fitted with quartz windows. The cell contained a positively biased charge collection wire and it was traversed by beams from two dye lasers pumped by one Nd:YAG laser[19-22]. The results under item 9) were produced by a single dye laser pumped by an excimer pump.

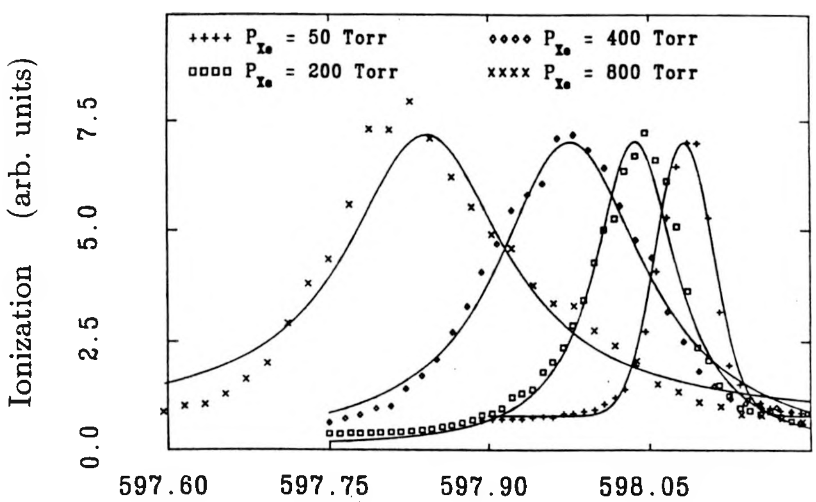
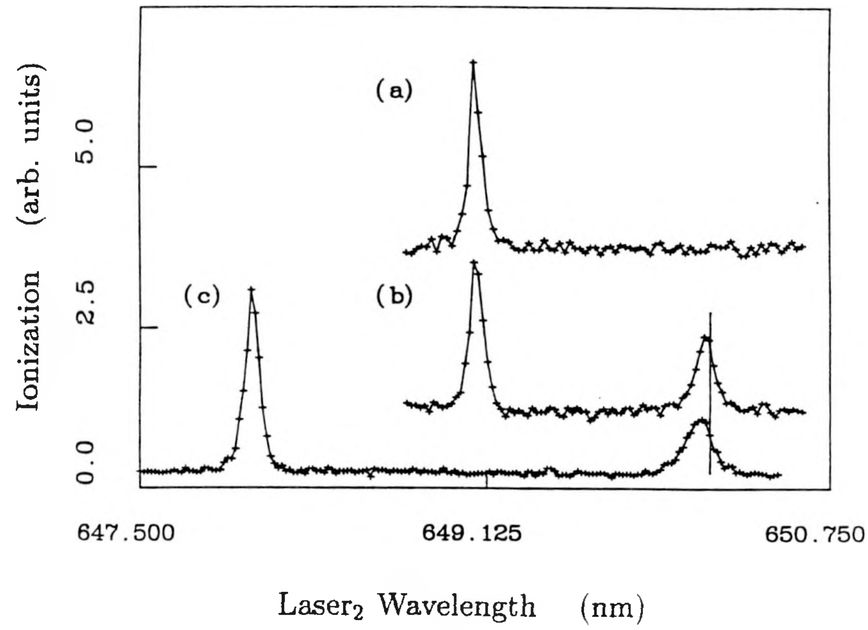



**Fig.1** Resonant ionization signals for three photon excitation of the $5d[3/2]^o_1$ level in Xe at pressures indicated. Laser$_1$ held fixed, laser$_2$ scanned. Crossing angle $\theta = \pi$.

Shown in Fig.1 are data for three-photon excitation of the $5d[3/2]^o_1$ level in Xe at pressures of 50, 200, 400, and 800 Torr. Laser 1 was held fixed and frequency doubled to 297.76 nm while laser 2 was scanned across three-photon resonance. The beams were overlapped at $\theta = \pi$ (i.e counterpropagated). Note the fairly large pressure dependent shift ( which is actually a minimum as a function of $\theta$ at $\theta = \pi$). Shown in Fig.2 are data for excitation of the same $5d[3/2]^o_1$ state but for laser beams of a different wavelength combination arranged in a different geometry. Here the first laser was set at $\lambda_{L1}$=291.9nm and the second was tuned across the 5d resonance, but at a crossing angle $\theta = 22.8°$. Xe pressure was 100 Torr in trace a) of the figure. In trace b) the pressure is unchanged, but laser 1 is retroflected with a dichroic mirror, thus providing an additional excitation pathway with $\theta = 157.2°$. This produces a second peak with only a small shift (position of the unshifted resonance is given by the vertical line).

Fig.2 Resonant ionization profiles for $2\omega_{L_1} + \omega_{L2}$ excitation of the $5d[3/2]_1$ level in Xe at $\theta = 22.8°$. a) 100 Torr Xe, both beams single pass. b) 100 Torr, but with retroreflection of $L_2$. c) 200 Torr Xe. Vertical line at unshifted resonance position.




In trace c) the xenon pressure is 200 Torr and both peaks shift farther to the blue. Note that the shifts in Fig.2 that are produced at 22.8° are much larger than those in Fig.1 at corresponding pressure, as

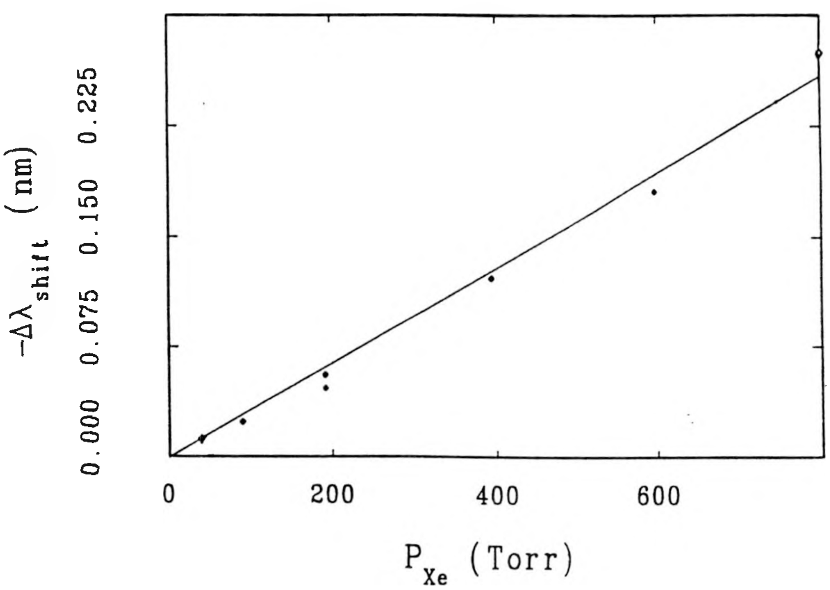



Fig.3 Pressure dependence of the collective shift of Xe $5d[3/2]_1^0$. Points are experimental data, solid line is the theoretical shift predicted from Eq.6.

expected from the functional dependence of $\Delta_c$ on $\theta$.

In Fig.3 the relationship of the experimental data of Fig.1, shown as diamonds, to $P_{Xe}$ is shown. The straight line is the theoretically predicted shift, using the experimental value of 0.346 for the 5d oscillator strength. The data show that the linear pressure dependence is valid and that the slope is quantitatively predicted on the basis of theory and a known oscillator strength.

In Fig.4 composite data are shown for measurements of the shift with pressure in the same 5d line but made at four different crossing angles. The straight lines are predicted results from Eq.7 (no adjustments). The departure of the results at the smallest angle (10.1°) from the theoretical prediction is due to contributions to the index from other states for these large values of $\Delta_c$. This is quantitatively treated in Ref. 20.

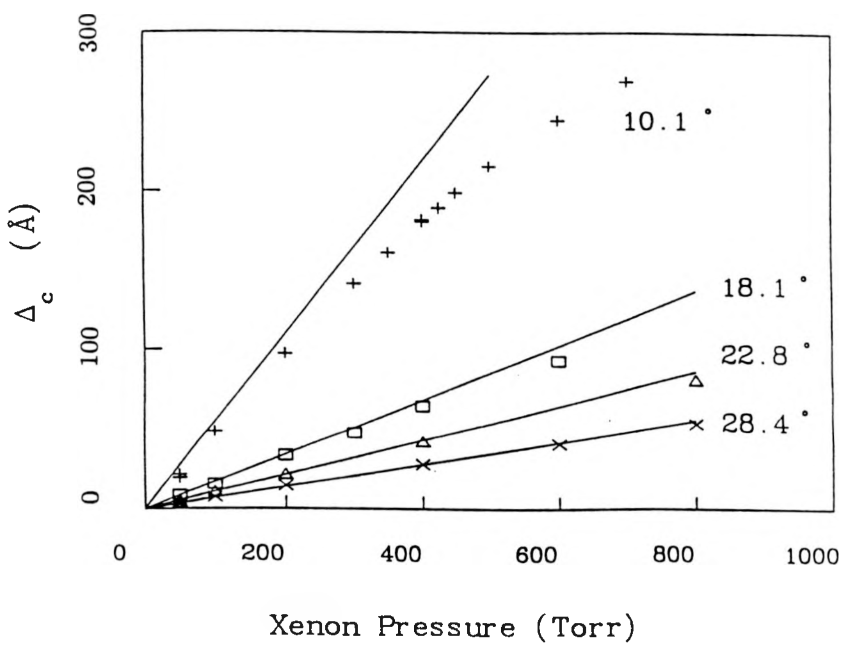



**Fig.4** Cooperative shift, $\Delta_c$, as a function of $P_{Xe}$ for four different crossing angles $\theta$, as indicated.

Now we turn to a consideration of measurements of stimulated hyper-Raman emission in Xe.

An excimer pumped dye laser was frequency doubled to produce $\simeq$ 224.3 nm photons which were focussed with a 10 cm f.l. lens. The focussed beam was in near two-photon resonance with the $6P'[3/2]_2$ level in Xe. Stimulated hyper-Raman scattering associated with excitation of the $6S'[1/2]_1^0$ and production of $\simeq$ 834 nm emission was measured. Backward and forward emissions were introduced into a 1.5 m monochromator and spectrally resolved. In Fig.5 we show example spectral traces of backward infrared emission in the region of $\simeq 834nm$ at a series of Xe pressures. The data are for Xe pressures of 200, 400, 800 and 1000 Torr, at a laser setting of 0.04nm from two-photon resonance with the $6P'$ level. We first note the dominant features of the spectra: for backward emission, two peaks are present; the separation between the peaks is pressure dependent; and that one peak occurs at a fixed wavelength while the other shifts with increasing Xe pressure; in the forward direction (not shown) only one peak appears, fixed in wavelength, at the position of the ASE peak on the right (though weaker and somewhat broader).

In the traces shown in Fig.5 the longer-wavelength peak, at fixed position, is ASE from the $6P'[3/2]_2$ level to the lower $6S'[1/2]_1^o$ state. The shorter-wavelength, shifting peak is SHR emission associated with excitation of the same $6S'[1/2]_1^o$ lower state through stimulated hyper-Raman scattering. With the uv pump intensities available in this study, SHR signals were observable only at very small detunings from two-photon resonance ($\delta_2 \leq .05nm$). At elevated number densities two-photon excitation on the wing of the $6P$ level produces some ASE output even at detunings exceeding the laser bandwidth.

Thus in backward emission we expect to see ASE at 834.6nm, and a second SHR peak displaced from the ASE by an amount determined by the laser detuning and the predicted pressure dependent shift. At low pressures the ASE emission should vanish at detunings greater than $\Gamma_L$, but at higher pressures the ASE peak should increase relative to SHR with increasing $P_{Xe}$ as in the figure. With our laser power we were able to see SHR emission only at pressure-detuning combinations where some remnant of ASE was still observable.

Finally for a fixed laser setting, we predict that the SHR emission profile will show a large shift which varies linearly with Xenon pressure. Moreover, since the dipole matrix element (oscillator strength) which enters the expression for the collective shift is known for the $6S'$ to ground state transition, the shift can be accurately predicted. Taking 0.179 for this oscillator strength[21] the hyper-Raman shift from Eq.6 is $\bar{\Delta}_P = -0.00039 P_{Xe}$ where $P_{Xe}$ is in Torr and $\bar{\Delta}_P$ is in $nm$.

The shift of the SHR-excited level is of opposite sign to that produced in three photon excitation of the $5d[3/2]_1$. That is, the excited level is shifted to lower energy, corresponding to a blue shift in the SHR emission with increasing $P_{Xe}$.

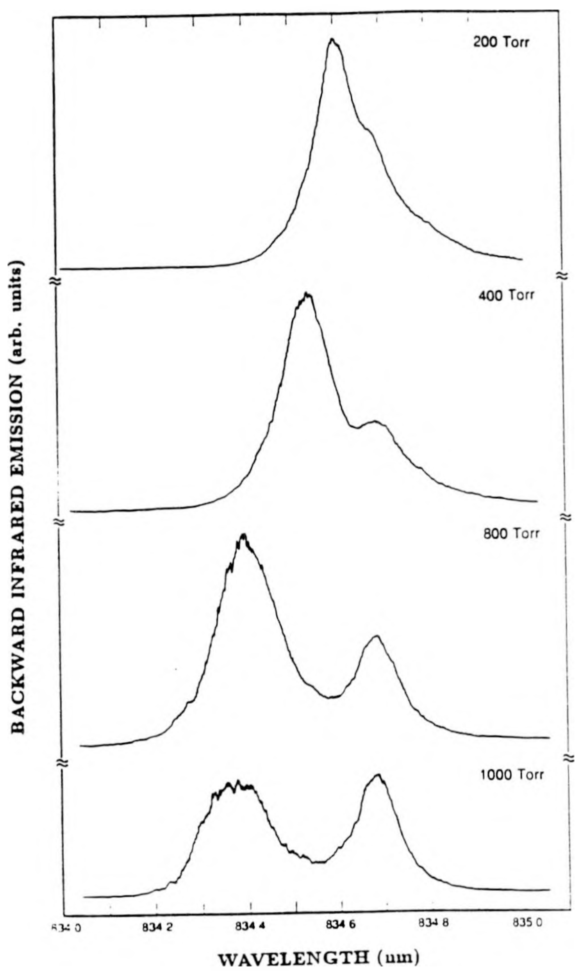



**Fig.5** Spectral scans of backward infrared emission associated with excitation of the $6s'[1/2]_1$ level while tuning near two-photon resonance with the $6p'[3/2]_2$ state. Laser tuned 0.04nm from two-photon resonance. Xe pressure changed successively to the values indicated. Righthand peaks, at fixed wavelength, are ASE. Lefthand peaks are SHR emission.

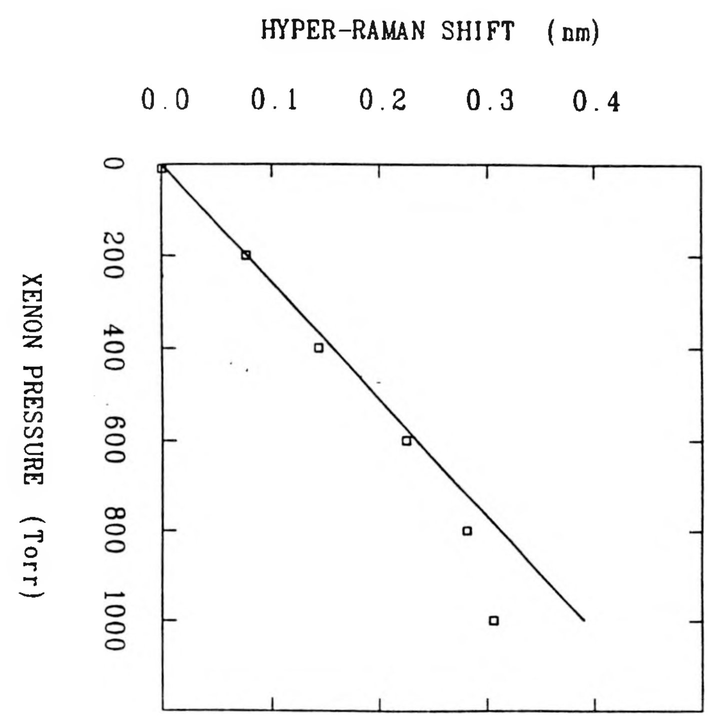



**Fig.6** Stimulated hyper-Raman shift as a function of $P_{Xe}$. Data points are shown as squares, straight line is the theoretically predicted shift.

Shown in Fig.6 is the magnitude of the shift, $\bar{\Delta}_P$, in the SHR profile as a function of $P_{Xe}$. The data are presented as squares. The predicted shift is given by the straight line. The data are in very good quantitative agreement with the predicted cooperative shift for $\Delta_P \leq .25nm$, i.e. at all but the highest pressures. Note that the lineshape at 1000 Torr also changes in appearence. This was typical of all the very high pressure results, including those described earlier. Presumably some other effect not included in the theory starts to become evident above a few hundred Torr. We conclude that in SHR excitation of a state which can also be excited from the ground-state by a single photon, the unavoidable generation of a FWM field at the resonant frequency $(E_1 - E_0)/\hbar$ not only suppresses SHR gain in the forward direction, but also produces a large pressure dependent shift in the SHR emission at nonzero angles.

## IV. Conclusions

The rather complicated suppression and shifting features associated with odd photon excitations of optically allowed transitions are rather counterintuitive in some instances and surprising in the efficacy of the observed effects over such wide ranges of experimental circumstances. The agreement between observations and experiments is uncommonly good. The independence of the effects on laser intensities, item (10) in the above list, is also seen to hold over the entire range of available laser intensities. The fact that this feature should be expected can be seen by inspection of Eqs. (7) and (8). The equation for $S_{01}$, and thus that for $\rho_{11}$, contains the direct three-photon pumping term $\Omega_{01}^{(3)}$ and a term which is an integral of the polarization (at the FWM frequency) over the source volumn for the FWM field. But this integral term (which ultimately interferes with the first term) also contains the same three-photon Rabi rate $\Omega_{01}^{(3)}$ as the only intensity-dependent factor. Thus the combined effect of the fields to produce suppression, shifting or whatever, is independent of the magnitude of the fields which make up $\Omega_{01}^{(3)}$. Thus, as observed experimentally, the shifts and the suppression effects are, unlike most other nonlinear phenomena, not dependent on pump intensities.

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