Nonlinear Optical Processes

Sub-Doppler Measurements of Predissociative Broadening

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Predissociation is a process where a bound molecular level a is coupled to an unbound level (or set of levels) *b*. This coupling is manifested by spectral broadening of transitions into and out of level *a* (in the frequency domain), and by shortening of the total lifetime of this level (in the time domain). In principle, both approaches should give the same physical information, but in practice, due to experimental limitations, the methods have been limited to non-overlapping ranges. Halogen and interhalogen diatomic molecules are a prime candidate for the study of this process, since their spectra are well known, and relatively simple to analyze. Clyne and Heaven performed many time domain experiments [1] on these molecules. The range of measurement has been limited by the laser pulse width – approx. 10 ns, or broadening of less than 30 MHz. In the frequency domain many works have been reported [2] – all of them limited to broadening larger than the Doppler width or about 1 GHz. Saturation spectroscopy is by now a well established means for obtaining sub-Doppler spectral information [3], and its application for the extension of the spectral measurement of predissociative broadening is discussed here.

A strong "pump" laser beam at frequency ν saturates the transition between a ground state level g and the level of interest a in a gaseous sample in a cell. Because of the Maxwellian distribution of velocities, only molecules with velocity $v_z = c(\nu - \nu_0)/\nu_0$ (here $h\nu_0 = E_a - E_g$) will be on resonance with the laser. A pump of intensity I_ν will decrease the population difference between levels g and a, and will burn a hole of spectral shape

$$(N_a - N_g)(\nu') = \Delta N_0 \frac{\left(\frac{\Delta\nu}{2}\right)^2 + (\nu - \nu')^2}{-\left(\frac{\Delta\nu}{2}\right)^2 + \frac{(\tau/t_{sp})\, C^2 \Delta\nu I_\nu}{8\pi^2 n^2 \hbar\nu^3} + (\nu - \nu')^2}, \quad (1)$$

where ΔN_0 is the population difference in the absence of a saturating field, $\Delta\nu$ is the homogeneous linewidth, t_{sp} is the lifetime for spontaneous emission, and τ is the total (not necessarily radiative) lifetime of level *a*. A weak probe now interacts with the same molecules and scans the hole described by (1). The physical information we are after is the rate of tunnelling across the predissociative barrier or the actual lifetime of level *a*. This parameter enters the formula in τ and in the homogeneous linewidth $\Delta\nu$. Thus it can be observed both from the width of the hole at low saturating power or from the saturation parameter I_s as given by Yariv [3]

$$I_s = \frac{2\pi^2 n^2 \hbar\nu^3 \Delta\nu}{(\tau/t_{sp}) C^2}.$$

The experimental system consists of two counter propagating beams from a ring dye laser (10–20 MHz) – a modulated pump and a weak probe – and phase sensitive detection. Several halogens and interhalogens were measured, and pressure broadening by a buffer gas [4] was used for calibration of the sensitivity. The question of what constitutes a homogeneous linewidth in molecular dissociation processes is briefly discussed.

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Weak-Wave Retardation and Phase-Conjugate Self-Defocusing in Si

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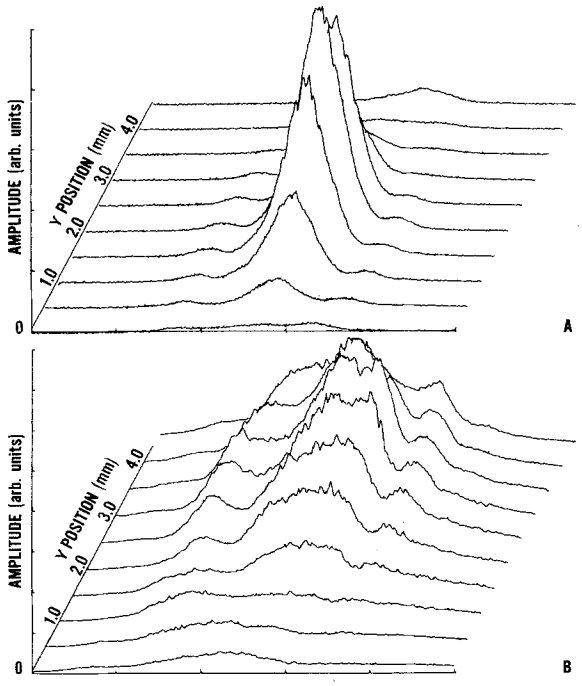
We describe and measure the effects of self-defocusing on the various coupling effects produced when two coherent, noncollinear, picosecond optical pulses (strong pump and weak probe) are both spatially and temporally coincident in a thin silicon wafer. We observe that the weak probe beam experiences considerably more defocusing than the pump beam. We believe this is the first direct confirmation of weak-wave retardation in light-by-light-scattering experiments. We also demonstrate the effects of this defocusing on the quality of the forward-traveling conjugate wave.

The observed defocusing is caused by the accumulation of free carriers created by linear absorption of 1.06 μm light. The additional increase in refractive index experienced by the weak probe was named weak-wave retardation by Chia and co-workers [1], who first predicted this effect. These workers later observed light-by-light scattering, but they did not verify weak-wave retardation [2].

We measure the degree of self-defocusing by observing the transmitted beam profiles with a vidicon detector. The self-defocusing of the transmitted probe and conjugate in Si has been studied recently by Hopf et al. [3] using nonlinear interferometers. They observed a substantial self-defocusing of the conjugate, but they were unable to detect weak wave retardation. For their work, the pulse width was comparable to the grating lifetime due to carrier diffusion.

Figure 1 illustrates the distortion of the pump and probe beam profiles during these selfdiffraction studies. The fluence of the pump pulse was 46 mJ/cm^2, and the fluence of the probe was a factor of 500 smaller. Figure 1A shows scans of the probe profile (in the far field) when the pump was blocked – the profile is reasonably Gaussian. Figure 1B and C show profiles of the transmitted probe and pump, respectively, when both were simultaneously present. The broadening of the pump caused by self-defocusing by the optically-created free carriers in the Si is evident, and the additional defocusing of the probe (weak-wave retardation) is clear.

Transmitted beam profiles and energies for all three beams (probe, pump, and conjugate) were measured for various excitation levels



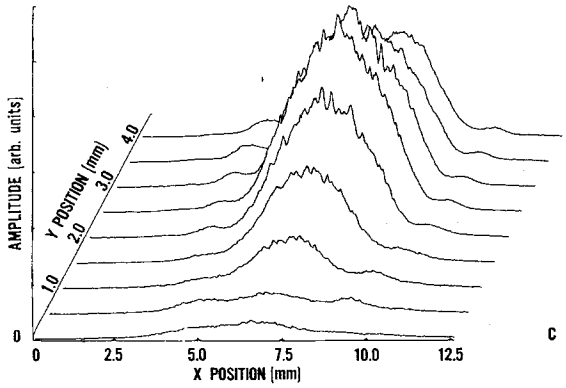


Fig. 1A–C. Vidicon scans of the spatial beam profiles of the (A) probe with pump blocked, (B) probe with pump, and (C) pump

and as a function of time delay. The observed distortion of the conjugate is different from either the probe or pump beam distortions contrary to the disparate conclusions of [1, 3].

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Nonlinear Laser Spectroscopy

Laser Excited Fluorescence from CO($A^1\Pi$)

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Vacuum *uv* fluorescence has been observed from CO($A^1\Pi$) following tunable uv laser excitation of high vibrational levels of the ground $X^1\Sigma^+$ state. The CO was formed in a flow system by process (1),

$$O + CS \rightarrow CO^{\neq} + S \quad (1)$$

known to be particularly efficient at converting the available energy of reaction (356 kJ mol^{-1}) into vibrational excitation [1], and this method of up-conversion of uv radiation to vacuum uv via the products of a chemical reaction has possible future applications in the operation of an efficient CO vacuum uv laser.

Oxygen atoms were formed by a microwave discharge in O_2/Ar, and mixed in the reaction vessel with CS_2 to form CS radicals by process (2)

$$O + CS_2 \rightarrow CS + SO \quad (2)$$

and subsequently vibrationally excited by CO reaction (1). Partial pressures of the flowing gases were in the ratio $Ar:O_2:CS_2 = 1000:10:1$, with a total pressure of 1 Torr. Strong vacuum uv fluorescence was detected with a solar blind photomultiplier following laser excitation at wavelengths between 213–230 nm, formed by generation of second and third antistokes stimulated Raman transitions in H_2 by means of frequency doubled dye laser radiation between 278 and 295 nm. Fluorescence was identified as originating from the CO($A^1\Pi$) $v' = 3,4,5$, and 6 levels produced by selective excitation of the 3–11, 4–12, 5–14, and 6–15 transitions. For the 6–15 band, the concentration of CO($v'' = 15$) was estimated as $< 5 \times 10^{-5}$ Torr, and this resulted in a S/N ratio of > 100 in the fluorescence spectrum, illustrating the sensitivity of this method in detecting low concentrations of vibrationally excited CO molecules.

Reaction (1) is known to produce CO with a vibrationally inverted population, peaking at $v'' - 13$, with essentially no direct formation of CO in levels < 7 [1]. Pumping these high vibrational levels before appreciable vibrational relaxation has taken place will thus lead to a population inversion between the $A^1\Pi$ state and low vibrational levels of the $X^1\Sigma^+$ state. For example, the largest Franck Condon factor for transitions from CO $A^1\Pi$ ($v' = 6$) is to the $v'' = 1$ level of CO $X^1\Sigma^+$ at 140.9 nm. Experiments are currently underway to test the feasibility of this novel method of up-conversion of laser radiation from uv to vacuum uv via the products of a chemical reaction. It is clear that problems such as vibrational relaxation of the initial CO distribution, and residual gas absorption at the vacuum uv wavelengths need to be overcome before gain on these transitions can be observed, and although the antistokes Raman shifting is a useful method of generating the appropriate pumping wavelengths, more powerful uv sources such as excimer lasers will probably be needed to create sufficient population inversion in this system.

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