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Laser Excited Nonresonant Fluorescence Spectroscopy Second Annual Progress Report

Prepared by J. A. GELBWACHS and R. P. FRUEHOLZ
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30 June 1980

Prepared for
DEPARTMENT OF ENERGY
Washington, D.C. 20545

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Laboratory Operations

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LASER EXCITED NONRESONANT FLUORESCENCE SPECTROSCOPY SECOND ANNUAL PROGRESS REPORT

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30 June 1980

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Report No.
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LASER EXCITED NONRESONANT FLUORESCENCE SPECTROSCOPY
SECOND ANNUAL PROGRESS REPORT

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I. INTRODUCTION

The objective of this program is to apply the technique of laser-induced nonresonance fluorescence spectroscopy to energy transfer studies on excited atoms. In addition to yielding fundamental knowledge concerning energy transfer processes, these studies result in improved elemental analysis. Significant progress was made in two areas during the past year.

The first part of our effort produced a novel method for improved continuous wave (cw) laser-induced atomic fluorescence detection. The method, known as "harmonic saturated spectroscopy," takes advantage of the nonlinear response of an optically saturated atomic system to reject background sources of interferences. A reduction in background and an improved signal-to-noise (S/N) ratio was demonstrated for sodium detection in an air-acetylene flame. The dependence of the harmonic signal on intensity, excitation waveform, and depth of modulation was also investigated. A complete description of this method and experimental results appears in Section II.

The second phase of our work concerns the effects of molecular resonances on energy transfer in excited atoms. A resonant pathway is said to exist when the energy difference between electronic levels in one species closely matches the vibrational-rotational spacing in the other colliding species. We obtained the relative populations of numerous tin levels populated by collisional energy transfer from an initially laser-pumped level. Studies of these populations yielded information concerning the relative rates of energy transfer for the various buffer gases studied. The results indicated two distinct energy transfer behaviors. First, nearly equal populations of levels were induced by diatomic and rare gas buffers. Second, examples were found for which diatomics readily populate levels nearly two orders of magnitude more than the rare gases. This latter behavior is attributed to near resonant pathways for $E + V/R$ and $V/R + E$ processes found in the diatomic collision partners. The former behavior indicated a lack of resonance effects, and both

diatomics and rare gases are believed to transfer energy by similar curve crossing mechanisms. A detailed description of this work and the significance to analytical detection is presented in Section III.

II. HARMONIC SATURATED SPECTROSCOPY FOR IMPROVED ATOMIC DETECTION

Laser-induced atomic fluorescence spectroscopy has been shown to be a sensitive detection method.¹⁻³ By use of laser intensities that are sufficient to saturate atomic levels, maximum photon emission per atom can be obtained, which permits extremely small atomic concentrations to be monitored. Employing saturated excitation, Gelbwachs, Klein, and Wessel have demonstrated what is perhaps the ultimate in detection sensitivity, namely, single-atom detection.^{4,5} In one experiment,⁵ a single sodium atom was detected in the presence of 10^{17} argon atoms.

While it is true that under saturated excitation the photon yield, i.e., fluorescence photons per incident photon, is less than it would be in the unsaturated case, there are numerous applications in which saturated excitation is clearly desirable or necessary. For example, saturated excitation is particularly valuable for concentration studies in environments where quenching of fluorescence occurs rapidly. In the fully saturated regime, fluorescence is relatively independent of quenching rates so determination of atomic populations requires only evaluation of detection geometry and efficiency and known molecular constants.⁶ This is useful in determining atomic populations in flames,^{6,7} internal combustion engines,⁸ and plasmas.^{9,10} Saturated excitation becomes likely when very small areas are probed with a laser beam. For sharp spatial resolution studies of any of the above environments, saturation will be encountered. Also, in areas such as microfluorescence very small regions are probed.^{11,12}

In the above mentioned single-atom detection experiment,⁵ excitation was provided by a cw dye laser rather than a pulsed laser because of its much longer duty cycle, namely, 100% vs 10^{-5} - $10^{-3}\%$. The longer duty cycle enables each atom to emit a correspondingly larger number of photons, which provides for greater detection sensitivity. However, cw dye lasers are currently available only in the visible-near IR spectral region at power levels of approximately 100 mW. Strong transitions of many atoms of analytical interest

fall in the UV spectral region. As a result, cw dye lasers have been used in trace detection for only a limited number of atoms. Recent developments in ring dye laser technology indicate that cw UV lasers with sufficient power to saturate atomic transitions will shortly become commercially available.^{13,14} When this occurs, methods to overcome practical problems associated with laser-induced fluorescence detection will be required in order to realize the full potential of saturated cw laser excitation for trace detection.

In many situations, scattering of the incident laser radiation by elements in the optical path may limit the practical detection limit that can be achieved. For example, Rayleigh scattering from gaseous components has been shown to limit atomic detection. Further, Mie scattering of the incident radiation by incompletely volatilized refractory forming elements can be a particularly severe interference. This interference has been found to be significant whether flame or graphite furnace atomization is employed.¹⁵ For analysis at low pressures, scattering from the atomization cell has been shown to limit detection.¹⁶

Various techniques have been used to minimize the effects of incident light scattering. A very effective method is to detect the atomic species of interest using nonresonant emission.^{17,3,4} However, this requires appropriate atomic energy levels. Both Rayleigh and Mie scattering display an angular dependence on the polarization of the incident light and the observation orientation.¹⁸ Omenetto et al.,¹⁹ making use of these dependences, improved fluorescence-to-scattering background ratios by factors ranging from 3 to 16. Another approach is to attempt to correct for light scattering by using two light sources, one at the resonance wavelength and a second at a nearby but nonresonant wavelength.²⁰⁻²² However, in the case of extremely intense scattering and weak emission, this method results in the subtraction of two large numbers and thus incurs a significant uncertainty. Finally, Goff and Yeung²³ employed wavelength modulation of a cw dye laser and phase sensitive detection at the modulation frequency to minimize the scattering interference. With a 1-kHz electro-optical wavelength modulator, barium was analyzed in a flame with an order of magnitude improvement in the detection limit compared with that from amplitude modulation.

A. DESCRIPTION OF METHOD

At incident intensities below that required to saturate an atomic transition, both laser-induced fluorescence and scattering will respond linearly to variations in incident laser intensity. When the intensity of the laser radiation is sufficient to saturate the transition, the fluorescence will begin to respond in a nonlinear fashion to incident light intensity variations. However, the scattered light will still exhibit a linear response. For a laser beam sinusoidally amplitude modulated at audio frequency f_0 , the nonlinear response of saturated fluorescence will enrich the harmonic content of the fluorescence signal, thereby introducing frequency components at higher harmonics of f_0 . The linearly responding scattering interference will only appear at f_0 . Using phase-sensitive detection at one of these harmonics (harmonic saturated spectroscopy) will allow observation of the fluorescence without the presence of the scattering background.

Consider a two level atomic system. The fluorescence power P_{fl} when irradiated by a laser at the resonance frequency ν is given by

$$P_{fl} = h\nu AL \frac{n_2}{\tau_2} \quad (1)$$

where $h\nu$ is the photon energy, A is the beam area, L is the interaction length, n_2 is the atomic density in the excited state, and τ_2 is the upper state lifetime. For a homogeneously broadened system²⁴

$$\frac{n_2}{n_0} = \frac{I}{I + I_0} \quad (2)$$

where n_0 is the atomic density, I is the laser intensity, and I_0 is the saturation intensity.

Substitution of Eq. (2) into Eq. (1) yields

$$P_{f1} = \frac{h\nu}{\tau_2} n_0 L A \frac{I}{I + I_0} \quad (3)$$

For the case in which the laser intensity is sinusoidally amplitude modulated at frequency f_0 ,

$$I(t) = I' \frac{1 + \cos 2\pi f_0 t}{2} \quad (4)$$

where I' is the maximum intensity.

The response of the two level system can be found by the insertion of Eq. (4) into Eq. (3). The response for fixed geometry, i.e., constant beam area, at the various harmonics is found by taking the Fourier transform of the resultant expression. Fourier analysis²⁵ yields a_n , the relative amplitude of the n th harmonic

$$a_n = \frac{(1 - \alpha)}{(1 - \alpha^2)^{1/2}} \left[\frac{(1 - \alpha^2)^{1/2} - 1}{\alpha} \right]^n \quad (n > 1) \quad (5)$$

where $\alpha \equiv I'/(2 I_0 + I')$.

The relative amplitudes of the dc component, the fundamental, second harmonic, and third harmonic have been plotted vs. I'/I_0 for constant beam area and appear in Fig. 1. From Fig. 1 it is readily seen that at low intensities the energy in each harmonic increases with increasing I' . It then reaches a peak and falls off toward zero at very large intensities. As the harmonic progression ascends, the intensity that maximizes the response increases. The peaks for the first three harmonics occur at $I' = 5I_0$, $18I_0$, and $38I_0$, respectively. At higher intensities the response falls toward zero as $(I'/I_0)^{-1/2}$. At first glance, the decline of harmonic amplitudes as the

Fig. 1. Relative Harmonic Response of Saturated Two-Level Atomic System to Sinusoidal Varying Intensity Given by $(I'/2) \cos 2\pi f_0 t$ for Fixed-Beam Area. The amplitudes of the dc signal, the fundamental, the second harmonic, and the third harmonic are denoted by a_0 , a_1 , a_2 , and a_3 , respectively.

system is pushed further into saturation is somewhat surprising. On a physical basis, it can be explained by noting that harmonics are produced during the portion of the modulation cycle during which the intensity falls within the nonlinear portion of the response, namely, the intensity region centered about I_0 . As I' increases, the fraction of the cycle spent near I_0 decreases; hence, the harmonic content is reduced.

Because the power available from cw lasers is constant, it is also of interest to determine the dependence of the harmonic signals on beam area, or inversely, on intensity for a fixed laser power P_L in order to optimize the response. This can be accomplished by the Fourier decomposition of Eq. (4) inserted into Eq. (3) with the substitution $A = P_L/I'$. The results are presented in Fig. 2. It can be seen from Fig. 2 that the response at f_0 is relatively constant at low intensities and then falls off as $(I'/I_0)^{-3/2}$ as the intensity increases. This behavior is easily understood. Low intensity corresponds to the unsaturated region in which the fluorescence photons emitted per atom vary linearly with intensity. On the other hand, the number of photons in the beam varies in an inverse fashion with area so that the product remains constant. At higher intensities, the transition begins to saturate; hence, the number of emitted photons per atom per unit laser intensity decreases. Thus, a decline in fundamental response occurs.

At $2f_0$, as the beam begins to be focused, the second harmonic response increases linearly with intensity (smaller beam diameter). The response then reaches a maximum. Further focusing causes the response to fall as $(I'/I_0)^{-3/2}$. The optimum intensity for maximum second harmonic response occurs near $1.4I_0$. In comparison to the fixed geometry case, the value of I' that produces the maximum harmonic response is less and the decline at large I'/I_0 is more rapid. This can be attributed to the fact that as I' increases for the constant power case, the irradiated area decreases, thereby reducing the number of atoms in the beam, whereas for the case of fixed geometry, the harmonic response is independent of area.

Fig. 2. Fundamental and Second Harmonic Signals of Saturated Two-Level Atomic System as Function of Peak-Modulated Laser Intensity for Fixed-Input Power

The implications of these results for improved atomic detection are quite exciting. Note that for $I' > I_0$, a_2 is a significant fraction of a_1 . Between intensities that produce relative maxima for a_1 and a_2 , i.e., $5I_0 < I' < 18I_0$, a_2/a_1 ranges between 0.4 and 0.5. Thus, very little signal is sacrificed by detection at $2f_0$ rather than at f_0 . For constant power, the relative responses at f_0 and $2f_0$ differ by only a factor of 4 in the vicinity of the maximum response at $2f_0$. In fact, compared to the unsaturated response at f_0 , only an order of magnitude reduction in absolute signal level occurs when detection is performed at $2f_0$ near $I' = I_0$. Consequently, for detection situations in which the major limitation is noise associated with scattered light, a dramatic improvement in the S/N ratio is anticipated by harmonic saturated spectroscopy.

B. EXPERIMENTAL APPARATUS

Atomic sodium was studied because it has been the subject of numerous other spectroscopic investigations, including atomic fluorescence and saturation studies.¹ In addition, sodium is readily excited with cw dye lasers.

The primary experimental apparatus is shown in Fig. 3. Laser radiation is supplied by a tunable cw dye laser (Spectra Physics 375) pumped by an argon ion laser (Coherent CR-12) operating at 5 W on all lines. The laser radiation was passed through a X4 beam expander and then mechanically chopped, typically at 200 Hz, by a slotted wheel with 5-mm slots. The resulting light was modulated approximately sinusoidally with its power varying between 1.4% and 98.6% of the power prior to chopping. (Note that 100% modulation is impossible because of the infinite spatial extent of a Gaussian beam.) A 250-mm focal length lens focused the modulated beam into an air-acetylene flame. Solutions were aspirated into the nebulizer and premix burner assembly (Perkin-Elmer 303-0352 and 303-0191, respectively). The burner head (Perkin-Elmer 303-0401) had three slots.

The emission was imaged by a 150-mm focal length lens onto a photomultiplier tube (EMR 9558B) after passing through two absorption filters

Fig. 3. Schematic of Experimental Apparatus

(Schott KG1,2) and an 0.8-nm bandpass interference filter with a 30% maximum transmission centered at 589.3 nm. The output of the photomultiplier tube was analyzed by a lock-in amplifier (Ithaco 391A) synchronized to the chopping frequency. A 12.5-sec output time constant (0.01-Hz bandpass) was used on the lock-in amplifier.

A NaCl/H₂O solution provided sodium for analysis. AlCl₃ was added to the solution to provide a high level of scattering interference so that precise and reproducible measurements could be performed in order to demonstrate the method. Aluminum is known to form a highly scattering refractory oxide upon combustion in the air-acetylene flame.^{26,15} Both the NaCl and the AlCl₃ were A.C.S. reagent grade supplied by MCB and J.T. Baker, respectively. To reduce its residual sodium content, the AlCl₃ was further purified by vacuum sublimation.

C. RESULTS AND DISCUSSION

1. HARMONIC CONTENT OF SATURATED FLUORESCENCE

Initially, the harmonic content of the laser beam modulated at 200 Hz was analyzed, because components of the incident light at harmonics above the fundamental will lessen scattering background interference rejection at these frequencies. The relative harmonic content of the incident laser light at f_0 , $2f_0$, $3f_0$, and $4f_0$ was 1.0, 0.02, 0.04, and 0.08, respectively. The second harmonic had the lowest magnitude relative to the fundamental. The origin of this component is of interest. If the laser beam's spatial intensity profile were purely Gaussian it would be symmetric above and below a horizontal plane that splits the beam. Chopping a symmetric beam by proceeding vertically along a line perpendicular to that plane yields a waveform devoid of even harmonic components. In these studies, the intensity profile of the laser beam was found by scanning a 10- μ m pin hole over the beam. While nearly Gaussian, a small asymmetry with respect to the horizontal plane was found. This spatial asymmetry introduces even harmonic components into the modulated laser light.

The fluorescence response of the optically saturated sodium with the incident beam modulated as previously described is shown in Fig. 4. These points were obtained at high sodium concentrations. The laser intensities were found by dividing the incident power, prior to chopping, by the average beam area over the portion of the laser beam imaged onto the photomultiplier tube. Over the approximately 2.5-cm region imaged on the photomultiplier tube, the cross sectional area of the beam varied from about $7.5 \times 10^{-5} \text{ cm}^2$ to $2.5 \times 10^{-5} \text{ cm}^2$ with an average area of $4 \times 10^{-5} \text{ cm}^2$. At low intensities the fundamental signal is an order of magnitude greater than the second harmonic signal. At intensities above 2 kW/cm^2 , the fundamental signals begin to level off while the second harmonic response continues to rise. Near 10 kW/cm^2 the signal at $2f_0$ is 50% of the signal at f_0 . The dashed curves on this graph are the theoretical responses at f_0 and $2f_0$ (Fig. 1) for $I_0 = 1.0 \text{ kW/cm}^2$. Very good agreement exists between the experimentally determined points and the theoretical curves.

2. SIGNAL-TO-NOISE IMPROVEMENTS

The powerful ability of harmonic saturated spectroscopy to reject background scattering and improve the S/N ratio is demonstrated in Fig. 5. The upper curve is the output of the lock-in amplifier tuned to f_0 as the dye laser wavelength was scanned over the sodium D_1 line at 0.01 nm/min . The lower curve is the signal at $2f_0$ multiplied by 10. The aspirated solution contained 0.1 ppm NaCl and $0.2\% \text{ AlCl}_3$, while the incident laser intensity was 6.8 kW/cm^2 . At f_0 a small signal is observed superimposed on the large scattering background with a signal to background (S/B) ratio of 0.2. At $2f_0$ the S/B ratio is 8.7, more than 40 times that at f_0 . The primary source of background at $2f_0$ was the $2f_0$ component of the incident laser light. More precise modulation will allow even better scattering background rejection. In addition to background rejection, an S/N ratio improvement of 5.3 was observed for detection at $2f_0$ as compared with detection at f_0 . (Here noise is defined as the rms variation of the background level.)

The improvement in the S/N ratio as a function of intensity for fixed input laser power was investigated. Figure 6 shows experimentally determined

Fig. 4. Fluorescence Signal at Fundamental and Second Harmonic from Sodium in Air-Acetylene Flame Versus Peak Incident Laser Intensity. The dashed lines are the theoretical curves for an ideal two-level atom with $I_0 = 1 \text{ kW/cm}^2$.

Fig. 5. Fluorescence Signals from 0.1 ppm NaCl and 0.2% AlCl_3 Aqueous Solution at f_0 and $2f_0$. The incident laser intensity of 6.8 kW/cm^2 was sinusoidally modulated at 200 Hz.

Fig. 6. Signal-to-Noise Ratios at f_0 and $2f_0$ as Function of Peak-Modulated Laser Intensity for Fixed-Incident Laser Power of 180 mW

S/N ratios at both f_0 and $2f_0$ as a function of laser intensity for a fixed power of 350 mW. From the experimental data it is seen that the S/N ratio for the signal detected at $2f_0$ increased as focusing began and reached a peak near 1 kW/cm^2 . Further focusing produced a diminished response. Note that the maximum response occurred near the value of I_0 that produces the best fit in Fig. 4. This is in good agreement with the predicted value of $1.4I_0$ obtained from Fig. 2, assuming that the noise is independent of beam diameter.

Another fact should be noted. At $I > 0.25 \text{ kW/cm}^2$, the S/N ratio for $2f_0$ is greater than at f_0 . However, below that intensity this is reversed and at $I = 25 \text{ W/cm}^2$, corresponding to unsaturated resonance fluorescence, the S/N ratio at f_0 is greater than the best S/N ratio at $2f_0$. This implies that in certain cases unsaturated resonance fluorescence detected at f_0 will be preferable to second harmonic detection, which requires intensities high enough to partially saturate the transition.

The audio spectral content of the noise is an important factor in consideration of the noise rejection capabilities of harmonic saturated spectroscopy. In our experiment the magnitude of the rms noise detected at f_0 was approximately 12 times that observed at $2f_0$, and this factor was relatively insensitive to chopping frequency. To clarify this difference in absolute noise levels, the rms scattering noise as a function of frequency was obtained in the flame environment and is shown in Fig. 7. For these studies, the incident laser beam was not modulated and the lock-in amplifier was tuned to the indicated frequencies using a bandwidth of 0.01 Hz. One observes that at frequencies below 400 Hz the noise displays "1/f" behavior.²⁷ In the present experiments the primary source of noise was fluctuations in scattering from nonvitalized components in the flame. Only a small component was caused by flame emission or other non-laser related sources.

The data in Fig. 7 are qualitatively similar to those presented by Hieftje and Bystroff²⁸ who studied sodium flame emission signals as a function of frequency. They also observed 1/f behavior at low frequencies and a "white" dependence at higher frequencies. The fact that the present scattering noise and the sodium emission noise display similar frequency dependences

Fig. 7. Noise Audio Spectrum of Air-Acetylene Flame. The bandwidth of the lock-in was 0.01 Hz.

indicates that a major source of these fluctuations may be the result of non-uniformity in the combustion process, for example, flame inhomogeneity both in composition and temperature along with aspiration and nebulization variations.

Harmonic saturated spectroscopy is particularly advantageous when the dominant noise source exhibits $1/f$ behavior. Consider a noise source $n(t)$ that has a Fourier transform given by $N(f)$. The response S at f_0 and $2f_0$ to $n(t)$ modulated by $m(t) = \cos 2\pi f_0 t$ is given by²⁹

$$S(f_0) = \frac{1}{2} N(0) + \frac{1}{2} N(2f_0) \quad (6)$$

$$S(2f_0) = \frac{1}{2} N(f_0) + \frac{1}{2} N(3f_0) \quad (7)$$

For white noise, i.e., $N(0) = N(f_0) = N(2f_0) = N(3f_0)$, the two signals are equal. However, it is readily seen from Eqs. (6) and (7) that for $1/f$ noise, i.e., $N(0) > N(f_0) > N(2f_0) > N(3f_0)$, $S(2f_0)$ is always less than $S(f_0)$.

3. EXCITATION WAVEFORM

Experiments were performed varying the modulation waveform in an attempt to increase the relative size of the signal at $2f_0$ to that at f_0 . If the laser beam is not beam expanded, a waveform more nearly squarewave in shape is obtained. A pure squarewave has no even harmonic components so that background signals at $2f_0$ should be almost entirely eliminated. Unfortunately, the profile of the saturated fluorescence response to incident squarewave modulation is squarewave; therefore, it will lack a $2f_0$ component. Squarewave modulation would seem to be less efficient than sinusoidal. Figure 8 displays the signals at f_0 and $2f_0$ for both nearly sinusoidal and squarewave modulations as functions of laser intensity. As expected the ratio of signal at f_0 to that at $2f_0$ is significantly less for the squarewave modulation.

There may be instances in which the beam diameter is much smaller than the slot width of the chopper wheel so that squarewave modulation is the only

Fig. 8. Sodium Fluorescence Signals at f_0 and $2f_0$ as Function of Peak Laser Intensity for Sinusoidal-Modulated Beam and for Squarewave-Modulated Beam.

option. We note that the saturated response to a squarewave is another squarewave and that this waveform possesses a strong third harmonic component.²⁵ Thus it may be advantageous to perform detection at $3f_0$.

4. DEPTH OF MODULATION

The dependence of the depth of modulation δ ,

$$\delta = \frac{I_{\max} - I_{\min}}{I_{\max}} \quad (8)$$

on the second harmonic signal was studied, where $I_{\max}$ is the maximum laser intensity and $I_{\min}$ is the minimum laser intensity. By varying δ , the nonlinear responses of different portions of the saturation curve are sampled. Variation of δ was accomplished by splitting the laser beam just prior to chopping. One beam was chopped, then both were recombined by focusing each beam into the flame in a coaxial counterpropagating configuration. Different δ 's were obtained by adjusting the intensity of each beam independently, subject to a fixed total maximum intensity.

For $I_{\max} = 3.0 \text{ kW/cm}^2$, the signal strengths at f_0 and $2f_0$ as a function of δ are presented in Fig. 9. Figure 9 shows that a maximum δ produces the greatest response at both f_0 and $2f_0$. The increase in signal at f_0 as δ is increased can be explained as follows. The dc portion of the incident light pushes the transition into saturation. The modulation in fluorescence because of the chopped portion of the incident beam will be relatively small. Maximizing the amount of incident modulation should result in maximizing fluorescence modulation. In addition to this consideration, an additional factor should be taken into account when viewing the behavior of the signal at $2f_0$. For small δ 's only a narrow region of the saturation curve is sampled. The saturation curve over this narrow region appears relatively linear minimizing the amount of $2f_0$ signal, which results from the nonlinear curve shape.

Fig. 9. Sodium Fluorescence Signals at f_0 and $2f_0$ as Function of Modulation Depth δ . The peak laser intensity was 3 kW/cm^2 .

D. CONCLUSIONS

These studies have shown that in atomic detection experiments for which saturation is desired or encountered, harmonic saturated spectroscopy is an extremely effective technique for the rejection of scattering of the incident exciting source. Under proper conditions, in contrast to synchronous detection at the fundamental the reduction in signal level at the second harmonic is minor compared with the reduction in noise at this harmonic, so a large improvement in S/N ratio is feasible. It was also found that detection of saturated fluorescence at twice the frequency of the amplitude-modulated laser intensity is inherently subject to less noise than typical fluorescence detection at the modulation frequency because of the audio spectral nature of noise sources found in common detection situations. It is concluded that under conditions of saturation, fluorescence detection by harmonic saturation spectroscopy is an effective means to reduce scattering interference and thereby provide for sensitive atomic detection.

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III. COLLISIONAL ENERGY TRANSFER IN TIN BY DIATOMICS AND RARE GASES

The collisional transfer of electronic energy to vibrational, rotational, and translational degrees of freedom is of continuing fundamental interest. Much experimental and theoretical work has been applied to gaining an understanding of these processes. One aspect of particular interest is the possible enhancement of rates of energy transfer resulting from the existence of near-resonant pathways.³⁰⁻³⁵ A resonant pathway is said to exist when the energy difference between electronic levels in one species closely matches the vibrational-rotational spacings in the other colliding species. This matching of energy differences minimizes the amount of energy transferred to translational motion, termed the energy defect, by exchanging electronic, rotational, and vibrational energy directly. Examples can be found where minimizing the energy defect appears to enhance the rate of energy transfer.³⁰ However, other examples can be cited where a small energy defect does not result in improved energy transfer.³⁰

In an effort to better understand the significance of near resonant pathways, we have studied the nonadiabatic energy transfer between very simple pairs of collision partners. Tin was laser excited to two different electronic states, $6s^3P_2^0$ and $6s^3P_0^0$, in the presence of five buffer gases: He, Ar, H_2 , D_2 , and N_2 . An energy level diagram for tin is given in Fig. 10. Tin was selected as the atomic species because, as can be seen in Fig. 10, it has a number of levels in which fluorescence can be monitored. Furthermore, several of these levels present a good opportunity to investigate the role of resonance effects in energy transfer, because they are separated from the initially excited level by energies approximately equal to the vibrational spacing of H_2 . Also, tin has a sufficiently low density of levels so that a series of sequential electronic to translational transfers could not populate all the levels and obscure resonant effects.

Nonresonance radiation originating from collisionally populated tin levels was monitored, allowing determination of the relative populations of

Fig. 10. Energy Level Diagram for Tin. The arrows represent the energy of the exciting laser photon.

the various levels. These populations were carefully examined to ascertain whether they were influenced by the existence of near-resonant pathways. Vastly different collisional deactivation behavior was observed for two laser excited levels separated by less than 4000 cm^{-1} .

In addition to its fundamental interest, collisional energy transfer is also of practical concern. In areas of laser trace detection of atomic species,^{3-5,36} nonresonance fluorescence induced by energy transfer processes may result in smaller detection limits than resonance fluorescence. It is then very important to optimize the transfer of excited state population from the initially excited level to other radiating levels. This optimization requires selection of the correct emitting level and the most efficient buffer gas. That information is supplied by studies such as that detailed in this report.

Previous energy transfer studies performed on tin have been limited to the study of low-lying spin-orbit split states of the ground electronic term.³⁷ As can be seen in Fig. 10, excitation of higher levels permits the study of a greater number of nearby states separated from the initially populated level by numerous different energies. Elevated temperatures ($\sim 1300\text{ K}$) are required to obtain tin vapor pressures that generate sufficient emission so that precise measurements can be made. At these temperatures, not only $E + V$, R processes, but also the weaker V , $R + E$ processes that populate tin levels at energies higher than the laser excited states have been observed.

A. EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Fig. 11. The output of a QIK-4 frequency-doubled dye laser is directed through a flameless furnace containing tin vapor. The laser dyes employed for excitation of tin were Rhodamine 590 for 303.4 nm excitation and Fluorol 555 for 270.6 nm . The laser repetition rate was 15 Hz with 10^{-6} sec pulse duration. The excitation linewidth was approximately 0.3 cm^{-1} . The peak laser intensity in the furnace was 0.85 kW/cm^2 at 303.4 nm and 1.15 kW/cm^2 at 270.6 nm .

Fig. 11. Experimental Apparatus for Collisional Transfer Studies

The cell through which the laser beam was directed contained a tube-shaped 5-mm-diameter furnace made of 0.002-inch thick rhenium foil, the inner surface of which was coated with approximately 40 mg of tin. The temperature of the electrically heated furnace was set at 1343 ± 5 K by a 10-V, 500-A Perkin-Elmer HGA-2000 power supply/controller, and this temperature was monitored with an optical pyrometer. It was experimentally determined that the temperature 1343 K fell in the middle of the temperature range, 1320 to 1370 K, required to optimize rhenium furnace life and tin fluorescence intensity. The tin vapor pressure at 1343 K is approximately 5×10^{-4} Torr. A Wallace and Tiernan pressure gauge attached to the cell measured the buffer gas pressure. A slit cut in the tubular rhenium furnace allowed the tin fluorescence to be imaged on the entrance slit of a spectrometer and to be viewed perpendicular to the direction of propagation of the laser beam.

The spectrometer consisted of two 1/4-m Jarrell-Ash Model 82-410 monochromators connected in tandem. The slit width was 500 μ m. The fluorescence was monitored by an EMR 6256S photomultiplier tube and recorded with a PAR Model 160 boxcar integrator with gate width set at an interval of 10^{-6} sec. All experiments were carried out under saturation conditions to maximize the fluorescence emission and to minimize the effect of laser intensity fluctuations on the fluorescence intensities.⁴

Tin emission lines were recorded that were intense enough for detection and did not undergo serious overlap by strong adjacent lines. Approximately 10 measurements for each tin line were recorded during a given experiment. Averages and standard deviations were calculated. When the fluorescence intensity of a tin line was an order of magnitude greater than the minimum detection level, an experimental uncertainty of less than $\pm 10\%$ was usually obtained. When the fluorescence intensity was close to the minimum detection level, an uncertainty of $\pm 20\%$ to $\pm 30\%$ was commonly observed. After correcting fluorescence line intensities for the wavelength response of the photomultiplier tube and the two spectrometer gratings, relative atomic state

populations were obtained for each line by dividing the fluorescence intensities by the appropriate value of transition oscillator strength.*

Measurements were carried out with five buffer gases. For H_2 , D_2 , N_2 , and Ar, pressures of 100 Torr were used. In an attempt to make the relative level populations more reflective of thermally-averaged energy-transfer cross sections, a second set of measurements was performed. The rate of collisions leading to a particular observed energy transfer process is approximately proportional to the average relative velocity of the collision partners, their concentrations, and the thermally averaged cross sections for the process.³⁸ Buffer gas pressures were selected so that their products with the relative velocities were the same in each case. Collision rates, which lead to relative level populations, are then proportional to the thermally averaged cross sections for energy transfer. For a pressure of 100 Torr of H_2 the other buffer gas pressures are: D_2 -140, N_2 -338, Ar-338, and He-140 Torr. Because the vibrational-rotational energy spacings of H_2 and D_2 are large, the effect of energy resonances of H_2 and D_2 with atomic tin is of great interest. Nitrogen exhibits a continuum of closely spaced rotational levels, and Ar and He, of course, display neither vibrational nor rotational structure.

B. RESULTS AND DISCUSSIONS

The relative level populations for constant pressure and for the pressure resulting from normalized relative velocity are reported in Table 1. Constant pressure studies are indicative of rate constants of energy transfer, whereas variable pressure studies are more reflective of the thermally-averaged cross sections. It can be seen from Table 1 that data from both studies are qualitatively quite similar. Consequently, the results will be discussed simultaneously.

Whenever possible, the relative populations of a given level derived from radiative transitions originating at the level but terminating in different lower levels were measured. The data only for emission terminating a level

*The gf values were supplied by Dr. G. A. Martin, National Bureau of Standards, Boulder, Colorado.

Table 1. Collisionally Induced Tin Populations Relative to Laser Excited Level

Laser Excited Level (cm ⁻¹)	Transition Energies (cm ⁻¹)	ΔE (cm ⁻¹)	H ₂ (100 Torr)	D ₂ (100 Torr)	H ₂ (100 Torr)	Ar (100 Torr)	D ₂ (140 Torr)	H ₂ (355 Torr)	Ar (383 Torr)	He (140 Torr)
34640.8										
	34914.2 - 3427.7	+ 273.4	3.0×10^{-3}	2.0×10^{-3}	1.8×10^{-3}	2.1×10^{-5}	2.5×10^{-3}	2.1×10^{-3}	2.6×10^{-5}	2.5×10^{-4}
	38628.8 - 8613.0	+ 3988.0	2.0×10^{-4}	1.7×10^{-6}	7.1×10^{-5}	9.3×10^{-7}	2.0×10^{-6}	7.9×10^{-5}	1.1×10^{-6}	7.9×10^{-7}
	39257.1 - 8613.0	+ 4616.3	4.5×10^{-5}	3.2×10^{-5}	2.2×10^{-5}	1.0×10^{-6}	4.2×10^{-5}	3.3×10^{-5}	1.5×10^{-6}	4.0×10^{-7}
38628.8										
	39257.1 - 8613.0	+ 428.3	1.2×10^{-1}	1.0×10^{-1}	3.7×10^{-2}	3.1×10^{-2}	1.2×10^{-1}	5.0×10^{-2}	8.1×10^{-2}	1.4×10^{-1}
	39625.5 - 3427.7	+ 996.7	2.2×10^{-2}	2.3×10^{-2}	1.0×10^{-2}	1.3×10^{-2}	2.6×10^{-2}	1.4×10^{-2}	2.8×10^{-2}	5.5×10^{-2}
	43683.0 - 3427.7	+ 5054.2	8.0×10^{-5}	8.7×10^{-5}	7.5×10^{-5}	9.5×10^{-5}	1.0×10^{-4}	8.1×10^{-5}	2.1×10^{-4}	1.4×10^{-4}
	44144.6 - 1691.8	+ 5515.8	1.7×10^{-5}	2.5×10^{-5}	1.9×10^{-5}	7.9×10^{-6}	2.5×10^{-5}	3.1×10^{-5}	3.1×10^{-5}	3.4×10^{-5}
	44576.1 - 3427.7	+ 5947.3	2.2×10^{-5}	2.2×10^{-5}	2.1×10^{-5}	5.6×10^{-6}	2.7×10^{-5}	2.7×10^{-5}	1.6×10^{-5}	1.2×10^{-5}
	34914.2 - 3427.7	- 3714.6	1.2×10^{-1}	1.7×10^{-1}	4.7×10^{-2}	1.6×10^{-3}	2.3×10^{-1}	7.9×10^{-2}	2.0×10^{-3}	1.0×10^{-3}
	34640.8 - 1691.8	- 3988.0	1.7×10^{-1}	1.5×10^{-1}	7.2×10^{-2}	1.9×10^{-3}	1.7×10^{-1}	1.0×10^{-1}	2.6×10^{-3}	1.2×10^{-3}

farthest above the ground state appear in Table 1. Differences in derived populations were calculated in several instances when the emissions from the same upper level but differing lower levels were compared. This discrepancy arises primarily from two sources. The first relates to the uncertainties of the gf values ($\pm 50\%$) by which our experimental intensities were divided, while the second is attributed to effects of self-absorption.^{39,40} Self-absorption can be important if the levels in which the radiative transitions terminate have significant populations. In the present studies, this effect was observed to be important for transitions terminating in the ground, $5p^2\ ^3P_0$, level. These transitions resulted in calculated populations typically 30% to 70% below the values calculated from transitions terminating in higher levels. Transitions terminating in the $5p^2\ ^3P_1$ level (1691.8 cm^{-1}) also displayed a small amount of self-absorption with calculated populations about 10% below those found by using transitions terminating on higher levels. Emission from transitions terminating on the $5p^2\ ^3P_2$ (3427.7 cm^{-1}) and higher levels showed no self-absorption. For the majority of levels studied, relative populations were determined from transitions that terminated on these levels. However, for two levels only transitions terminating on the $5p^2\ ^3P_1$ level were available. There are a variety of techniques for correcting emission intensities for self-absorption.⁴¹ However, it was determined that their application did not reliably improve the populations for the levels in question. Considering the uncertainties in the gf values used to calculate the level populations, the self-absorption effects are not considered a significant problem for the two states of concern.

Figures 12 and 13 show the relative level populations from Table 1 plotted as functions of the energy transferred to or from the tin atoms. It can be seen from these figures that diatomics transfer energy to certain levels approximately two orders of magnitude more efficiently than the rare gases. In particular, this is the case for the populations transferred from the $6s\ ^3P_0^o$ level to the $6s\ ^3P_1^o$, $6s\ ^3P_2^o$, and $6s\ ^1P_1^o$ levels (Fig. 12) and for populations transferred from the $6s\ ^3P_2^o$ level to the $6s\ ^3P_0^o$ and $6s\ ^3P_1^o$ (Fig. 13).

Fig. 12. Relative Level Populations of Tin . The laser-excited level ($\Delta E = 0$) is the $6s^3P_0$ level at 34640.8 cm^{-1} .

Fig. 13. Relative Level Populations of Tin. The laser-excited level ($\Delta E = 0$) is the $6s^3P_2^o$ level at 38628.8 cm^{-1} .

Note that the reciprocal energy processes $6s^3P_0^o + 6s^3P_2^o$ and $6s^3P_2 + 6s^3P_0^o$ both display the same behavior as that expected from detailed balancing.⁴² For energy transfer processes connecting the $6s^3P_2^o$ to the $6s^1P_1^o$, $5p^3S_2$, $5d^3F_2^o$, and $5d^3D_{2,3}^o$ levels, diatomics and rare gases transfer populations with nearly equal efficiency (Fig. 13).

These results are consistent with two different energy transfer mechanisms. It is likely that rotational-vibrational resonance effects dominate in the cases where diatomics transfer energy more efficiently than rare gases. Where they transfer with nearly equal probability, resonance effects are not believed to be important. In these cases curve crossing mechanisms,^{31,43-45} as might be described within the Landau-Zener formalism, may be dominant.

At the 1343 K experimental temperature, sufficient numbers of rotational and vibrational energy levels are populated so that near resonant pathways, arbitrarily defined as within kT ($\sim 1000 \text{ cm}^{-1}$) of resonance, exist for each tin level in the presence of each diatomic buffer gas. However, the current results indicate that near resonant pathways are important only in specific cases. This indicates that whereas existence of these pathways is a necessary condition for resonant energy transfer, it is not sufficient to ensure the dominance of these pathways.

When the relative level populations induced by the diatomic buffers are considered, very little difference is observed between H_2 and D_2 . This similarity is interesting because of their different vibrational frequencies H_2 , $\omega_e = 4395 \text{ cm}^{-1}$; D_2 , $\omega_e = 3118 \text{ cm}^{-1}$.⁴⁶ However, the existence of a large number of populated rotational levels would tend to smear out purely vibrational effects. Typically, N_2 transferred population less efficiently than either H_2 or D_2 . Nitrogen has much more closely spaced rotational levels than either H_2 and D_2 ; consequently, larger changes in rotational quantum number J are required for the exchange of similar amounts of energy. Resonant pathways that require large changes in J would be expected to be less efficient in transferring energy than those with smaller changes in J .^{30,44,47}

For nonresonant cases, there is another reason to expect N_2 to transfer energy less efficiently than H_2 or D_2 . Within the curve crossing formalism, energy exchange can be expected to occur if the energy difference between the two potential curves is less than the energetic uncertainty of the collision. This energetic uncertainty ΔE is related to the time T required to traverse the crossing region of the potential energy surfaces by $\Delta E = h/T$.^{31,43,45} As the relative velocity of the collision partners increases so will ΔE , thus facilitating energy transfer. Since H_2 and D_2 are significantly lighter than N_2 they should transfer energy more efficiently by means of this nonresonant mechanism. A similar effect would also be expected for He compared to Ar, but no systematic difference is apparent.

Finally, we consider the significance of the current results to elemental analysis by laser-induced nonresonant fluorescence spectrometry. Under conditions of saturation of the pumping transition, the population of the initially excited level is maximized and independent of quenching.⁴ It is of analytical importance to determine the fraction of this population that may be transferred to other states, resulting in nonresonant emission. The current results demonstrate that it is possible to transfer more than 10% of the population of the initially excited level to states several hundred cm^{-1} higher in energy, whereas states lying well below (at least 4000 cm^{-1}) the initially excited level may be populated to a similar extent. Population is transferred more readily to levels at lower energies, because all collision partners can accept energy from tin; however, because of their vibrational and rotational degrees of freedom, diatomics are more likely to accept energy than rare gases.

These studies also indicate that population transfer to specific levels can be significantly affected by the buffer gas and the specific level to which population is to be transferred. For example, with an H_2 or D_2 buffer gas, the $6s^3P_{0,1}^o$ levels may have nearly 20% of the $6s^3P_2^o$ level population transferred to them. If Ar had been chosen as buffer gas the relative population would have dropped 0.2%. Clearly, this results in an undesirable and

unnecessary decrease in analytical detection efficiency. Currently no simple theory predicts a priori which buffer gas will transfer to which level most efficiently. These parameters must be determined experimentally.

C. SUMMARY

In summary, we obtained the relative populations of numerous tin levels populated by collisional energy transfer from an initially laser pumped level. These populations yield information concerning the relative rates of energy transfer for the various buffer gases studied. The results indicated two distinct energy transfer behaviors. First, for certain tin levels diatomic collision partners produce populations nearly two orders of magnitude higher than when rare gases are present. This behavior is attributed to the effects of near-resonant energy transfer pathways for the $E + V/R$ and $V/R + E$ processes found in the diatomic collision partners. Second, for other tin levels, diatomics and rare gases transfer population approximately at the same rates and more efficiently than in the former case. For these levels the near-resonant pathways can be obscured by means of a more effective energy transfer channel common to both diatomics and rare gases such as by curve crossing mechanisms.

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