Conf-820949--2

LA-UR -82-2452

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TITLE MULTIPLE-PHOTON LASER-INDUCED FLUORESCENCE

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SUBMITTED TO To be presented at the First International Congress on Applications of Lasers and Electro-Optics, September 21-23, 1982, Boston, MA. This talk will also be published in the Conference Proceedings

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Multiple-photon laser-induced fluorescence

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Abstract

The technique of multiple-photon laser-induced fluorescence has been used to study the spectroscopy and dynamics of atoms, molecules, and free radicals. Among the species investigated were iodine atoms (I), carbon monoxide (CO), molecular iodine (I_2), and HS and DS radicals.

Introduction

The spectroscopy and dynamics of numerous high-lying electronic transitions of atoms, molecules, and free radicals are, in many instances, poorly understood due to the lack of excitation sources possessing the appropriate spectral output or temporal characteristics. However, with the availability of spectrally-intense, continuously-tunable lasers providing radiation in the ultraviolet-visible spectral regime, high-lying electronic states can be probed via a multiple-photon excitation and fluorescence detection approach. Moreover, certain transitions which are single-photon forbidden can be accessed by multiple-photon processes. The subsequent time-resolved fluorescence spectrum provides useful spectroscopic and kinetic information concerning the excited states.

Several recent studies have demonstrated the utility of the multiple-photon excitation scheme. The spectroscopy of high-lying electronic transitions of O, N, Cl, H, and D atoms[1-3] has been elucidated. In addition, the $A^2\Sigma^+$ state of NO[4] and the $A^1\Pi$ state of CO[5] have been probed via two-photon excitation.

In the present investigation we have used two-photon processes to excite several states (between approximately 65,000 cm^{-1} and 73,000 cm^{-1} above the ground state) in iodine atoms, the $A^2\Sigma^+ - X^2\Pi$ transitions of HS and DS, and the $B^1\Sigma^+ - X^1\Sigma^+$ transitions of CO. In addition, the $I^1\Sigma_u^+$ state of molecular iodine (I_2) has been probed via three-photon excitation.

Experimental

To perform the multiple-photon laser-induced fluorescence studies, the experimental apparatus shown in Fig. 1 was used. The basic probe laser is a Nd:YAG laser-pumped dye laser providing spectral coverage from approximately 400 nm to 700 nm. The fundamental output from the dye laser is either frequency doubled or mixed with the 1.06-μm output of the Nd:YAG laser to provide ultraviolet wavelengths as short as 220 nm. The pulse width from the dye laser is approximately 10 ns (FWHM). For generating free radicals of interest, a uv excimer laser operating at either 193 nm (ArF) or 248 nm (KrF) is used to photodissociate appropriate precursor molecules. A digital delay generator is used to trigger the Nd:YAG laser at a predetermined time after the excimer laser is fired. The photolysis and probe laser beams overlap spatially within the observation zone. The fluorescence signals are monitored at right angle to the laser beams. The detection system is comprised of a 1/4-m monochromator, band-pass filters, light-collection optics, and photomultiplier tube. For recording either the fluorescence emission or fluorescence excitation spectrum, a boxcar averager and chart recorder are used to process the laser-induced fluorescence signals, while for time-resolved studies a transient digitizer and minicomputer combination is employed.

Results

Two-photon excitation of HS and DS

The spectroscopy of the $A^2\Sigma^+ - X^2\Pi$ transitions of the HS and DS radicals has been extensively investigated by the single-photon laser-induced fluorescence technique.[6] Furthermore, this approach has been applied to DS to study the quenching of the A-state. Since a substantial data base regarding these free radicals was available, it was felt that the analysis of two-photon spectra would be simplified. Furthermore, the fluorescence from the A-state occurs in the region around 325 nm, while two-photon excitation is accomplished with laser wavelengths near 650 nm. Consequently, rejection of scattered laser light is straightforward.

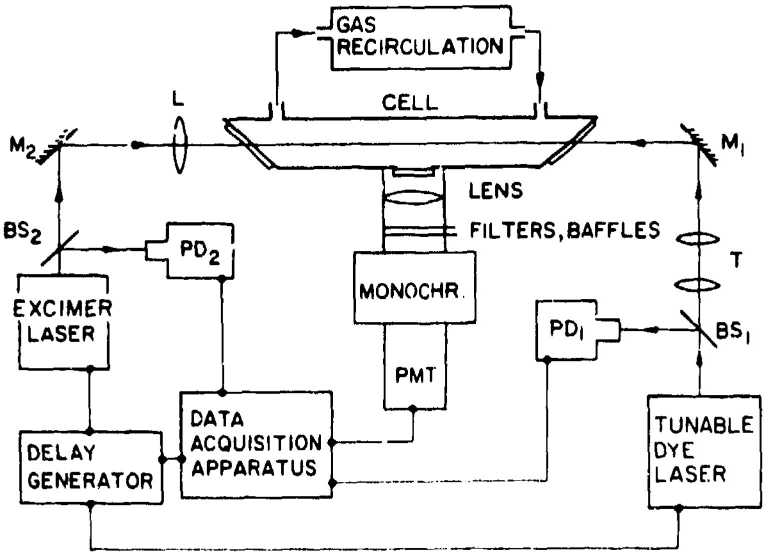
LASER-INDUCED FLUORESCENCE EXPERIMENTAL APPARATUS

Figure 1

The HS and DS radicals were generated by the 193-nm photolysis of H_2S and D_2S, respectively. The two-photon fluorescence excitation spectrum of HS is shown in Fig. 2. The dye laser was scanned between 644 nm and 650 nm and fluorescence monitored at 327.5 nm. In a similar manner the excitation spectrum of DS was recorded, as shown in Fig. 3. In both cases the laser bandwidth was sufficiently narrow to permit rotational lines belonging to O, P, Q, R, and S branches to be resolved.

Spectroscopy and quenching of I atoms

As indicated previously, high-lying electronic states of chlorine atoms have been probed via a two-photon excitation/fluorescence detection scheme. In a similar fashion we have excited several transitions in the 6p manifold of iodine atoms. Photodissociation of either CH_3I or CF_3I by KrF-laser irradiation produces both $I(5p\,^2P^\circ_{3/2})$ and $I(5p\,^2P^\circ_{1/2})$. From the former, two-photon resonances allow excitation of the $^2D^\circ_{5/2}$ or $^4D^\circ_{7/2}$ levels, while from the latter the $^2D^\circ_{3/2}$ state is accessible. These transitions are shown in the energy level diagram of Fig. 4. The two-photon fluorescence excitation spectrum of Fig. 5 clearly shows the three transitions.

The quenching of the electronic excitation of I atoms by argon has also been studied. Upon two-photon excitation of the $5p\,^2P^\circ_{1/2} - 6p\,^2D^\circ_{3/2}$ transition (dye laser wavelength at 3066.4 Å) visible emission is observed from the $^2D^\circ_{3/2}$ state, as well as several nearby levels, to various opposite parity states. This behavior is shown in Fig. 6. By spectrally and temporally resolving the emission from each of these transitions, it is possible to obtain kinetic information regarding both internal conversion among the close lying levels ($^2D^\circ_{3/2}$ to $^2P^\circ_{3/2}$, $^4D^\circ_{5/2}$, and $^4D^\circ_{3/2}$) and the quenching rate from each of these levels. The rise-times of the fluorescence signals were too fast to detect within the constraints imposed by our laser pulse width. Consequently, we were unable to derive values for the rates of internal conversion.

For the four fluorescent transitions indicated in the right-hand portion of Fig. 4, plots of the inverse lifetimes for fluorescence decay as a function of added argon pressure revealed that the slopes were identical within experimental error. A quenching rate constant of 5.5×10^6 $torr^{-1}s^{-1}$ was derived. The observation that all of the states are quenched at the same rate is not surprising, since internal conversion among the states is much more rapid than the quenching process.

Multiple-photon processes in CO

The two-photon excitation scheme for the $B^1\Sigma^+ - X^1\Sigma^+$ transition in CO is depicted in Fig. 7. The dye laser excitation wavelength is near 230 nm, and fluorescence is detected

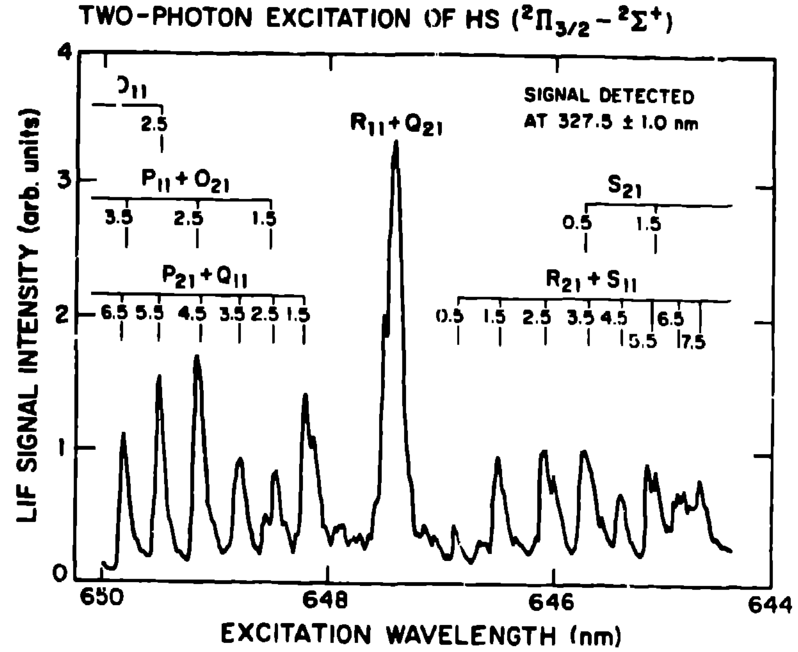

Figure 2

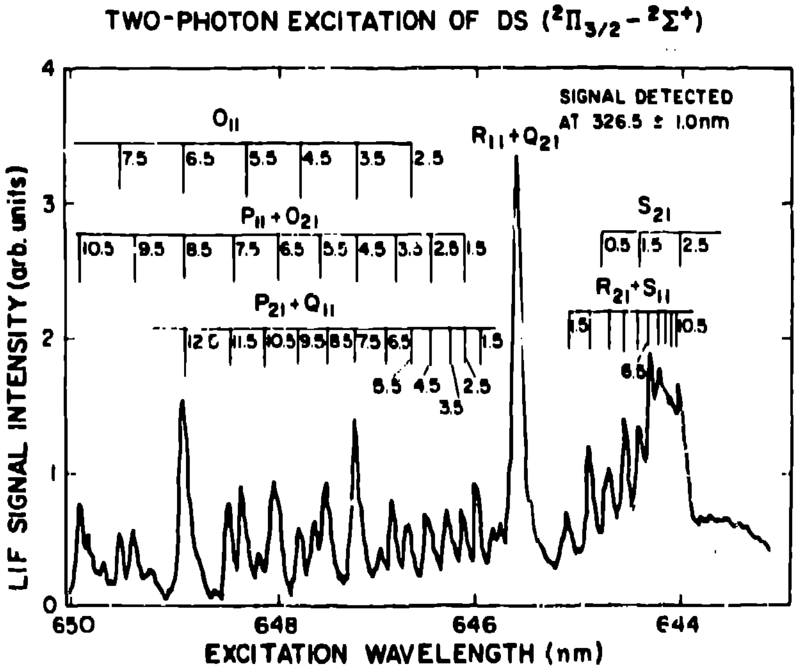

Figure 3

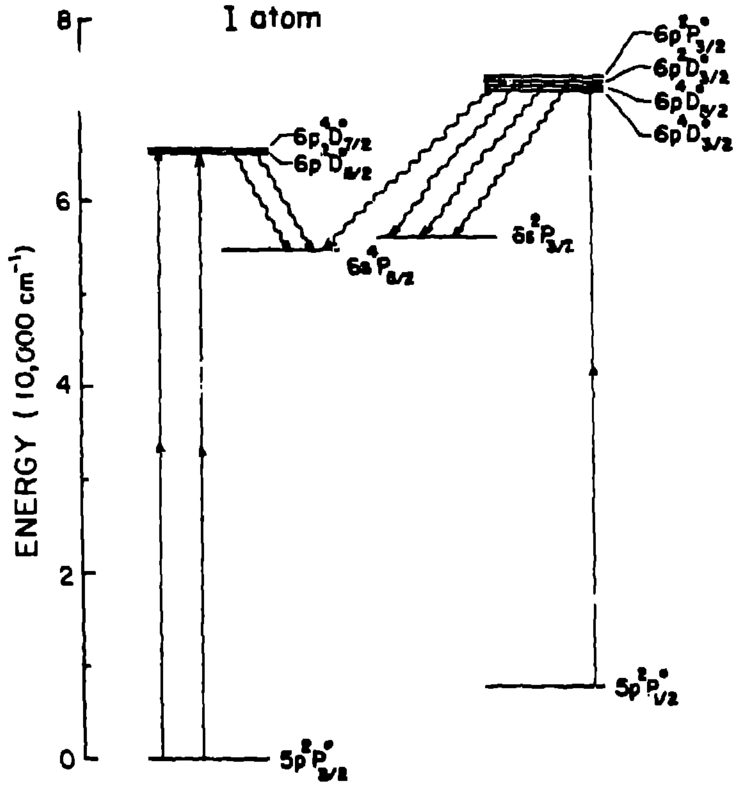

Figure 4

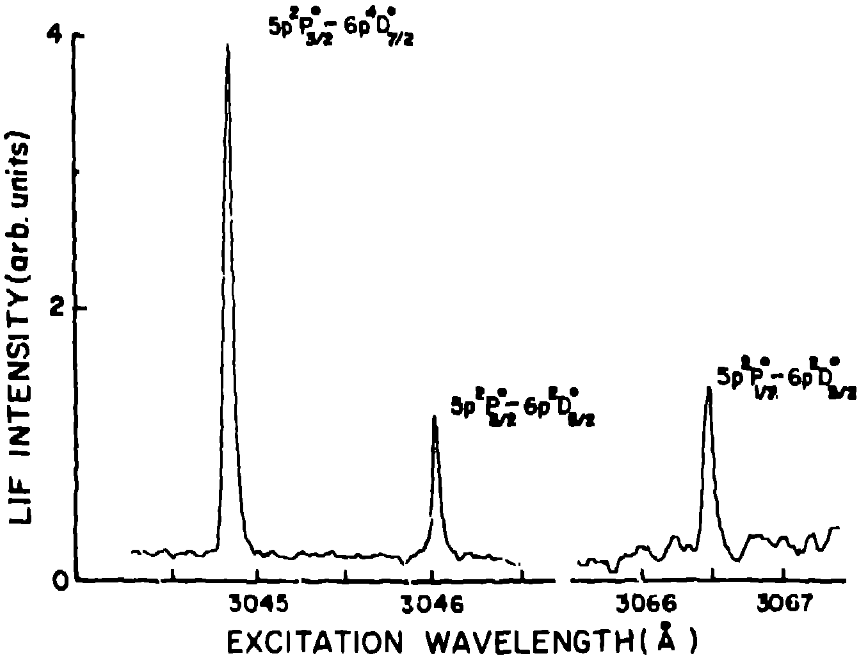

Figure 5

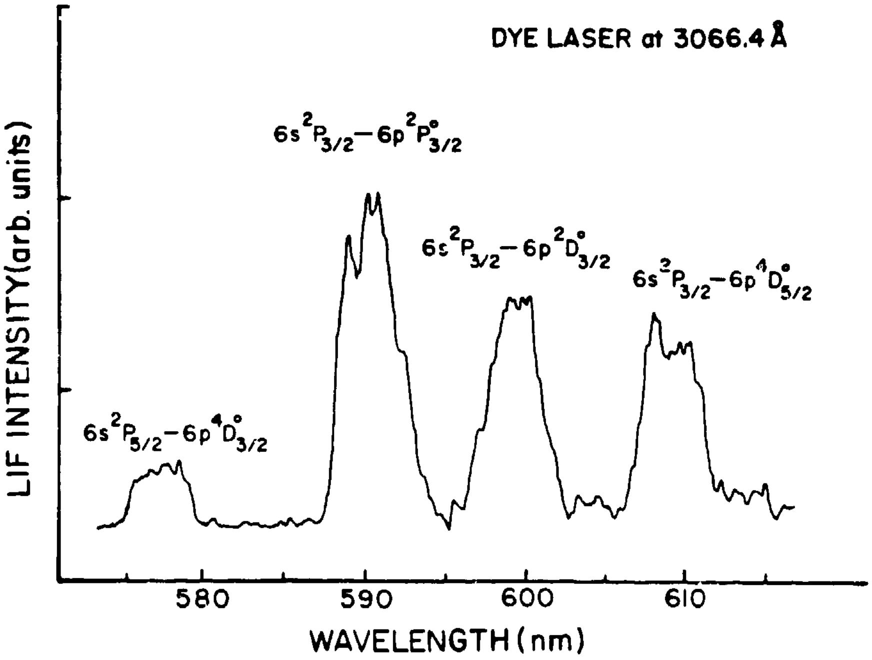

Figure 6

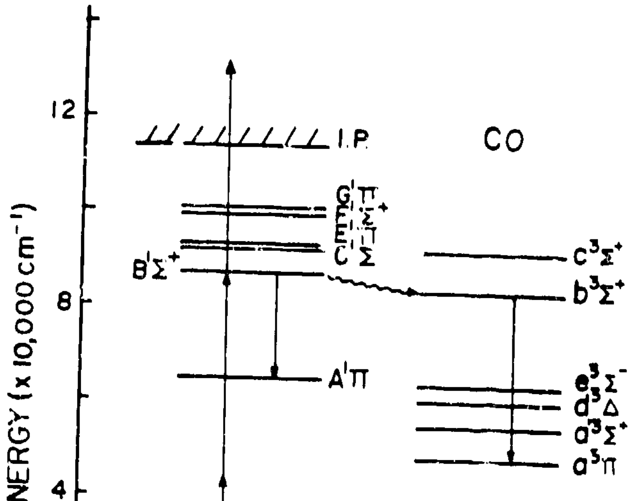

Figure 7

from the $B^1\Sigma^+ - A^1\Pi$ transition between 450 nm and 700 nm. Time-resolved studies of this emission permitted the rate constants for both CO self-quenching and quenching by N_2 to be determined. A Stern-Volmer plot of the data for neat CO is shown in Fig. 8. The rate constant determined from the slope is 5.9×10^6 torr^{-1}s^{-1}. In a similar manner the rate constant for quenching by N_2 was found to be 1.9×10^6 torr^{-1}s^{-1}.

The quenching of the $B^1\Sigma^+$ state of CO appears to involve primarily collisionally-induced intersystem crossing (see Fig. 7). Concommitant with the $B^1\Sigma^+ - A^1\Pi$ fluorescence, emission is also observed from the $b^3\Sigma^+ - a^3\Pi$ transition. An example of this behavior is shown in Fig. 9 for a 10-torr sample of CO. The triplet-triplet emission is in the 280- to 370-nm region. The intensity of this fluorescence becomes more intense with increasing gas pressure, indicative of a collisionally-induced process. The rate constant for the self-quenching of the triplet emission was found to be 3.1×10^6 torr^{-1}s^{-1}.

The fluence dependence of the fluorescence intensity of the $B^1\Sigma^+ - A^1\Pi$ transition was also studied. It was found that the functional dependence did not exhibit quadratic behavior as expected for a two-photon process. Since absorption of an additional 230-nm photon from the B-state can promote CO above its ionization limit, we made measurements of the ion current produced upon irradiation of CO. Ions were indeed detected. It appears that three-photon ionization is the dominant channel, while fluorescence from the B-state is of lesser importance.

Three-photon excitation of $I_2(I^1\Sigma_u^+ - X^1\Sigma_g^+)$

Preliminary studies of the three-photon excitation of the $I^1\Sigma_u^+ - X^1\Sigma_g^+$ transition of I_2 have been performed. The I-state lies approximately 185 nm above the ground state and is accessed with dye-laser output around 560 nm. Fluorescence from the I-state back to the ground state is detected in the vacuum uv (170 nm to 195 nm). Three-photon excitation spectra indicate that the $X^1\Sigma_g^+(v'' = 0) \rightarrow I^1\Sigma_u^+(v' = 17, 18)$ transitions are being excited.

Conclusion

Multiple-photon laser-induced fluorescence is a powerful technique for studying high-lying and single-photon forbidden transitions of radicals and molecules. For spectroscopic studies this technique ameliorates the difficulties associated with conventional vacuum ultraviolet sources and related equipment. In addition, the short pulse lengths available from tunable lasers permit the dynamics of the excited states to be investigated. The application of the multiple-photon laser-induced fluorescence approach to the transient and stable species discussed herein clearly reveals these attributes.

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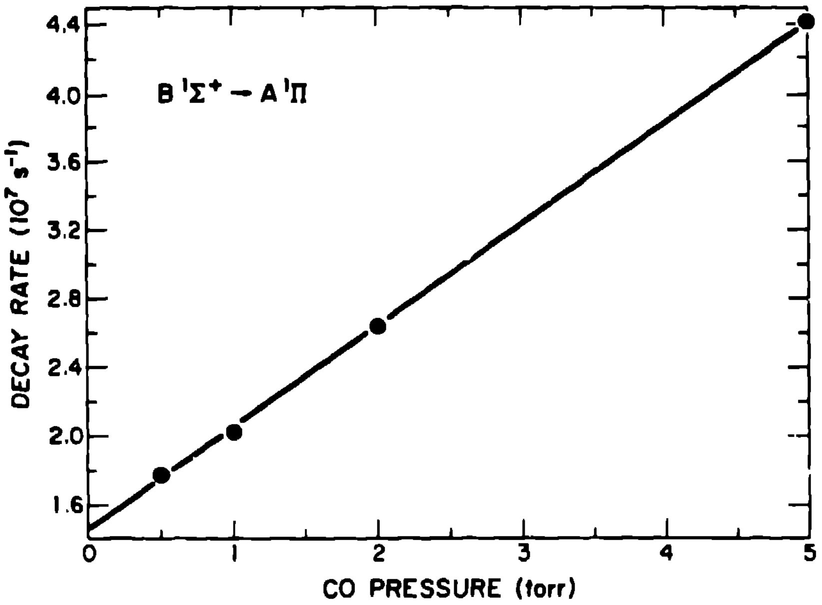

Figure 8

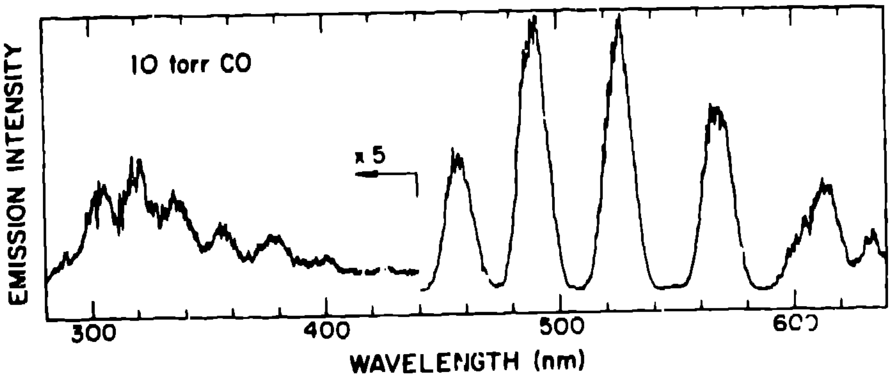

Figure 9