

**TWO-PHOTON ABSORPTION, LASER-INDUCED FLUORESCENCE DETECTION OF Cl ATOMS**

Michael HEAVEN, Terry A. MILLER, Richard R. FREEMAN

*Bell Laboratories, Murray Hill, New Jersey 07974, USA*

and

J.C. WHITE and Jeffrey BOKOR

*Bell Laboratories, Holmdel, New Jersey 07733, USA*

Received 4 December 1981

Laser-induced fluorescence has been observed from Cl following pumping of a two-photon allowed transition at 210 nm. The detection technique reported here is not intrusive, highly selective and has good spatial and temporal resolution. Titration of the Cl with Br<sub>2</sub> indicates a detection sensitivity of  $<1 \times 10^{13}$  Cl/cm<sup>3</sup>.

**1. Introduction**

There are a number of "light" atoms, e.g. H, N, O, and the lighter halogens, which are particularly important in numerous gas-phase chemical reactions. The reactions of these atoms control the chemistry of the stratosphere, play key roles in all of combustion and electrical discharge chemistry, are central to the operation of chemical lasers, e.g. HF, HCl lasers, and are participants in the simplest and most fundamental of chemical reactions. Because of the ubiquity and significance of these atomic reactions, much effort has been expended upon developing means of detecting these atoms.

Ideally such a detection technique should be highly selective and have high sensitivity because the rapidity of the atomic reactions restrict the steady-state concentration of these species to low levels. As with any detection scheme it should be non-intrusive; in addition it should also be in situ because rapid wall and background gas reactions render sampling techniques immediately suspect. For many, but not all, applications, the detection capability should be absolute. Finally, any ideal detection scheme should combine three-dimensional spatial resolution with rapid temporal resolution.

Not surprisingly, none of the techniques developed

so far fulfill all of the above attributes of an ideal detector for even one, much less all, of the "light" atoms. Mass spectrometry is hampered by sampling problems. Electron paramagnetic and laser magnetic resonance require the sample to be immersed in a large magnetic field which can alter the environment and severely restrict spatial and temporal resolution. Also some environments adversely affect their sensitivity. Chemical titrations and chemiluminescence reactions have played important roles in determining atomic concentrations, particularly absolute ones, but are clearly intrusive techniques.

It would appear that a technique that involves only the absorption and/or emission (or scattering) of an easily detected visible or near UV photon would be the best. However, the generic energy level diagram applicable to these light atoms, as shown in fig. 1, illustrates the difficulty of this approach. The lowest excited state is typically  $\geq 80000$  cm<sup>-1</sup> above the ground electronic state. This means that any (laser) Raman scattering technique is going to be non-resonant and of relatively low sensitivity [1] ( $\approx 10^{16}$  atoms/cm<sup>3</sup>). Similarly standard laser-induced fluorescence techniques are impractical due to the short wavelength ( $\lambda < 125$  nm) of these transitions.

Previous work on spectrophotometrical detection of these light atoms has eschewed laser techniques, and

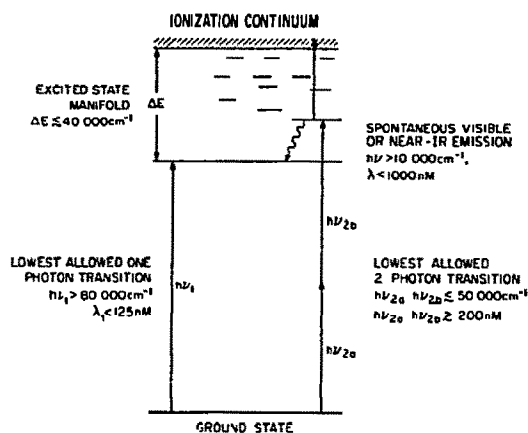


Fig. 1 Schematic energy level diagram for "light" atoms. On the left hand side a one-photon transition is illustrated, on the right a two-photon transition. This energy level diagram applies to H, N, O, C, F, Cl, Br and other "light" atoms. As shown in the explicit listing in table 1, the only exception to the stated energy intervals is for F atoms.

their inherent advantages, for atomic resonance lamp sources<sup>‡</sup>. Using a resonance lamp one can do simple optical absorption (with relatively low sensitivity) and resonance fluorescence with increased sensitivity. Indeed atomic resonance lamp spectrophotometry is probably today the single most popular technique for light atom detection. However, it is a very difficult technique requiring considerable experimental skill. Processes like self-reversal in the lamp can alter the emission line and hence absorption profile, similarly radiation trapping by the sample can make fluorescence measurements difficult, at best, to interpret.

In this paper we describe a new approach to the detection of "light" atoms (which we now define as ones with their first excited state in the vacuum UV) which, in principle, satisfies almost all the criteria earlier set forth for the ideal detector. In an earlier publication [3], we demonstrated the technique for H atoms and a brief report on N and O atom detection has appeared [4]. In this paper we apply this technique to the more chemical, and difficult, problem of Cl atom detection. Based upon our experimental results with Cl and our previous experience with H we present schemes whereby all the halogen atoms can be detected.

<sup>‡</sup> For an excellent review of traditional detection techniques, see ref. [2].

The technique is schematically set forth on the right hand side of fig. 1. Rather than trying to drive atoms to the lowest excited state using a one-photon pump, we drive them to the (usually) second lowest excited state via a two-photon transition. This shifts the wavelength requirement on the pump from the vacuum, usually windowless, UV to wavelengths typically greater than 200 nm. The production of high spectral quality, relatively high power, tunable radiation between 200 and 250 nm is not routine, but neither is it as difficult as would be the production of coherent light at wavelengths less than 125 nm. We describe briefly our procedures for generating the pump radiation in the experimental section.

Once atoms have been pumped to the two-photon resonance state they have available three means of decay. They can (i) decay non-radiatively (collisionally) in process (ii) the atom can absorb a third photon and ionize. It would indeed be possible to detect the atoms by monitoring their ion production. In fact such multi-photon ionization techniques have been widely used for atomic detection [5]. These techniques are highly sensitive, but have the disadvantage of requiring electrodes in the sample. The method we have employed for detection involves the third (iii) decay mode whereby the atom spontaneously emits a visible or near IR photon and decays to a lower excited state. This process we call two-photon absorption, laser induced fluorescence (TALIF).

We will show that the sensitivity of TALIF can be expected to range from  $10^{13}$  to  $10^9$  atoms/cm<sup>3</sup> for all the light atoms with the possibility of absolute concentration determination. Since TALIF does not involve a one-photon resonance terminating in the ground state, problems such as radiation trapping and self absorption are completely avoided. It is a non-intrusive, in situ technique with high temporal resolution i.e. the pulse duration of the lasers (typically less than 5 ns). Using 2 photons of the same frequency, i.e. one beam, the spatial resolution is defined (with no spatial discrimination in the detector) by the beam waist wherein the power density is sufficient to induce two photon transitions, typically roughly a cylinder of a mm or two diameter and a few mm long. If one crosses two focused beams of different frequencies whose sum equals the two-photon frequency one can attain a resolution corresponding to a volume of  $\ll 1$  mm<sup>3</sup>, as has been demonstrated [3] in the remote detection of H and D atoms.

## 2. Theory

It is extremely useful to have an expression for the number of detectable, visible or near IR photons emitted as a function of such variables as ground-state population, laser power, etc. In general the off-diagonal elements of the density matrix may be neglected, and a simple rate equation approach suffices. At any given point in time, the emitted photon flux will be proportional to the two-photon resonance excited state population,  $[N^*]$ .  $[N^*]$  will obey a rate equation of the form [6] (as long as  $[N_0]$  is not depleted)

$$\begin{aligned} d[N^*]/dt = W[N_0] - [N^*]\sigma_t I - [N^*]\tau_{rad}^{-1} \\ - [N^*]k_c[C], \end{aligned} \quad (1)$$

where  $W = \alpha I^2/\hbar\omega$ ,  $I$  is the laser power,  $\alpha$  the two-photon cross section for excitation from the ground state,  $\sigma_t$  the cross section for ionization from the two-photon resonance state,  $\tau_{rad}$  the radiative lifetime for spontaneous emission from the two-photon excited state, and  $k_c$  the rate coefficient for collisional deactivation by the gas (or gasses) with concentration  $[C]$ . If we integrate this equation assuming a square laser pulse of length  $T_p$ , then

$$[N^*] = (W[N_0]/B)(1 - e^{-Bt}), \quad 0 \leq t \leq T_p, \quad (2)$$

with

$$B = \tau_{eff}^{-1} + \sigma_t I/\hbar\omega \quad (3)$$

and

$$\tau_{eff}^{-1} = \tau_{rad}^{-1} + k_c[C]. \quad (4)$$

Once the laser pulse is over,  $t > T_p$ , the excited state, and the detected fluorescence emission, decays exponentially as

$$[N^*] = [(W[N_0]/B)(1 - \exp(-BT_p))] \exp(-t/\tau_{eff}). \quad (5)$$

Integrating the last equation from  $T_p$  to  $\infty$  gives the total number of detected fluorescence photons/pulse,  $I_T$ ,

$$\begin{aligned} I_T = (K\omega[N_0]\tau_{eff}/B) \exp(-T_p/\tau_{eff}) \\ \times [1 - \exp(-BT_p)], \end{aligned} \quad (6)$$

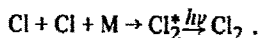
where  $K$  is a proportionality constant depending upon response, solid angle, etc.

## 3. Experimental

By inserting reasonable [6,7] numerical values into the above equations it is clear that for a  $1 \text{ cm}^{-1}$  bandwidth laser focusable to  $\approx 10^{-3} \text{ cm}^3$ , 1–10 mJ/pulse energies are required to excite a reasonable fraction of atoms (0.1%). Such a source has recently been developed [8] and we have used it in this work with only minor modification. We describe it very briefly here. The output of YAG-pumped rhodamine 6G dye laser is frequency doubled in a KDP crystal. This radiation is converted to the ArF amplifier band pass as the fourth anti-Stokes line in a  $\text{H}_2$  Raman cell. This low power coherent radiation is amplified in two stages by ArF excimer lasers. The resulting output at 10 pps has an energy of 125 mJ/pulse, a spectral width of  $\leq 2 \text{ cm}^{-1}$ , and a tunability over  $\approx 300 \text{ cm}^{-1}$  between 192.8 and 193.9 nm. The output of this source can again be Raman shifted in a  $\text{H}_2$  ( $\text{D}_2$ ) cell with  $\approx 10\%$  efficiency on the first Stokes line.

The Cl atom has a two-photon allowed transition [9] from the  $3p \ ^2P_{3/2}$  ground state to the  $4p' \ ^2F_{7/2}$  state at  $95180 \text{ cm}^{-1}$  ( $h\nu/2 = 47590 \text{ cm}^{-1}$  or  $\lambda = 210.1 \text{ nm}$ ). This transition lies nicely within the tuning range of the first Stokes shifted ArF output ( $\approx 47450$ – $47650 \text{ cm}^{-1}$ ). The  $4p' \ ^2F_{7/2}$  state has as its shortest wavelength decay channel a transition to the  $4s' \ ^2D_{5/2}$  state at  $9041 \text{ \AA}$ , which we monitored with an RCA C31034 phototube. Unwanted chemiluminescence was partially blocked by a combination of color filters.

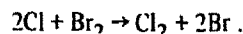
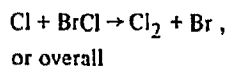
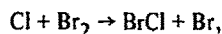
The Cl atoms were produced with a microwave discharge through a  $\approx 3\%$  mixture of  $\text{Cl}_2$  in  $\approx 2$  Torr of Ar. Approximately 150 W of microwave power was supplied to the discharge by an Electrochemical Supplies discharge unit. The atom transversed a distance of  $\approx 20 \text{ cm}$  between the discharge and detection region with one right angle bend, fitted with a Wood's horn, in the distance of travel. This portion of the pyrex discharge tube was treated, prior to use, with phosphoric acid. The presence of Cl atoms in the detection region could be established by the existence of a red glow from the reaction [10],



It was found that the intensity of this emission, judged by eye or photomultiplier current, was very reproducible as a function of Cl pressure or discharge current.

To establish the sensitivity of the TALIF experi-

ment, it was necessary to independently establish the concentration of Cl atoms in the detection region. We choose to titrate [11] the TALIF signal by the addition of Br<sub>2</sub>. The reaction sequence is



Both of these Cl atoms reactions are known to be fast [12,13]. Clearly the overall reaction removes two Cl atoms for every Br<sub>2</sub> molecule added, i.e.  $[\text{Cl}]_0 = \frac{1}{2}[\text{Br}_2]_{\text{endpoint}}$ . Interestingly, the amount of chemiluminescence emitted from the system was little changed by the titration reaction due to recombination emission from BrCl\* and Br<sub>2</sub>\*. However, the Cl atom TALIF was clearly titratable evidencing the selectivity of the TALIF method.

Typically, strong TALIF signals were observed with a total pressure of 2–3 Torr in the fluorescence cell, as measured by a Baratron capacitance manometer. The flow velocity in the system was determined by combining total pressure measurements and flow rates measured by a Matheson 604 flowmeter in the Ar line. With an initial Cl<sub>2</sub> concentration of  $\approx 2.5 \times 10^{15}$  molecules/cm<sup>3</sup> passing through the discharge, a Cl atom concentration of  $7.5 \times 10^{14}$  atoms/cm<sup>3</sup> was determined in the fluorescence cell by the Br<sub>2</sub> titration. This corresponds to  $\approx 15\%$  of the Cl<sub>2</sub> molecules being dissociated into Cl atoms in the detection region, a very reasonable figure.

#### 4. Results and discussions

Fig. 2 shows a frequency scan over the region of the two-photon  $3p^2P_{3/2} \leftrightarrow 4p^2F_{7/2}$  Cl atom resonance. The resulting TALIF signal is clearly visible with a  $S/N \approx 50$ . For this signal the Cl atom concentration was  $\approx 7 \times 10^{14}$  atoms/cm<sup>3</sup>. This particular trace was obtained with boxcar detection and a 2 s time constant. Consistent  $S/N$  was often observed on a single shot basis with an oscilloscope. Under these conditions the limiting detectability of Cl atoms would be  $\approx 1 \times 10^{13}$  atoms/cm<sup>3</sup>. Increasing the modest integration time on the experiment would place one in the  $10^{12}$  atoms/cm<sup>3</sup> range.

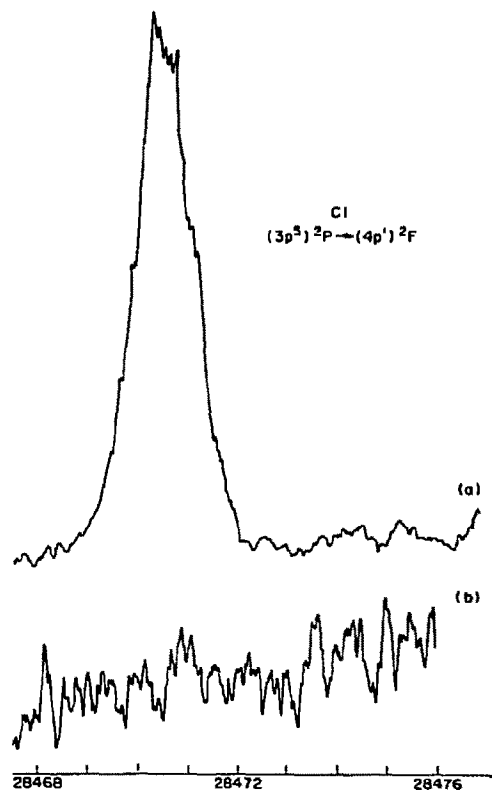


Fig. 2. Frequency scan of TALIF signal of Cl atoms. The frequency markers at the bottom of the trace correspond to the grating drive ( $f$ ) of the dye laser. To obtain the true frequency  $F$  of the photons interacting with the Cl atoms, use  $F = 10^9/f + 3 \times 4155 \text{ cm}^{-1}$ . Trace a corresponds to the TALIF signal observed on the 904 nm emission from the  $4p^2 2I_{7/2} \leftrightarrow 4s^2 2D_{5/2}$  transition. Trace b gives the intensity of the first Stokes shifted emission from the Ar<sup>+</sup> amplifier.

Interestingly, in this experiment the noise was created by the chemiluminescence background from Cl recombination. Since this signal is proportional to  $[\text{Cl}]^2$ , the noise should actually decline more rapidly than the TALIF signal for lower  $[\text{Cl}]$ , assuming the noise is due to amplitude fluctuations. Efforts to test this hypothesis were inconclusive as at significantly lower  $[\text{Cl}]$ , laser scattering from the apparatus (or fluorescence induced thereby) became the limiting noise. Better baffeling and/or increased filtering of the chemiluminescence should improve this noise factor. However, we believe the ultimate sensitivity for Cl atoms with this laser on this transition with this level of chemiluminescence, would be in the low  $10^{12}$  atoms/cm<sup>3</sup> range.

Table 1  
Examples of two-photon allowed transitions and resulting fluorescence emissions in "light" atoms

Atom	Two-photon transition <sup>a)</sup>	$h\nu/2$ <sup>b)</sup>	Fluorescence transition	$h\nu$ <sup>b)</sup>
H	$1s^2S-3d^2D$	205	$3d^2D-2p^2P$	656
N	$2p^3^4S-3p^4D$	211	$3p^4D-3s^4P$	871
C	$2p^2^3P-3p^3P$	280	$3p^3P-2p^3P^0$	910
O	$2p^4^3P-3p^3P$	225	$3p^3P-3s^3S$	844
I	$2p^5^2P-3p^2P^0$	168	$3p^2P^0-3s^2P$	703
Cl	$3p^5^2P-4p^4^2I$	210	$4p^4^2I-4s^4^2D$	904

<sup>a)</sup> See ref. [15] for calculations of two-photon transition rates for N, O, and Cl

<sup>b)</sup> Often these transitions have several fine structure components, so the listed wavelength simply approximates the individual transition frequencies

This is about a factor of 300 less sensitivity than was estimated for H atoms using a similar apparatus. If the chemiluminescence were removed, the  $S/N$  for the Cl experiment would obviously be improved, probably by an order of magnitude. However, the ultimate Cl sensitivity is less than for H because of two factors. The Cl sensitivity is limited because of the inefficiency of detecting the 910 nm radiation from the Cl excited state, as well as it being only one of several decay channels. It is also true that the two-photon excitation cross section is estimated [14,15] to be about an order of magnitude smaller for Cl than for H; indeed the TALIF signal showed no signs of saturation.

In table 1, we list a number of light atoms, which we believe can easily be detected by the present laser system or other near-UV generating systems. Based upon our experience we conservatively expect the limits of detectability for all these atoms would be in the  $10^{10}-10^{12}$  atoms/cm<sup>3</sup>. One distinct advantage of a Raman shifted system is that if one demonstrates TALIF detection with the  $n$ th (anti) Stokes line, then one is guaranteed of being able to do two-beam TALIF, with its high spatial resolution, with the  $n-1$  and  $n+1$  (anti) Stokes frequencies.

## 5. Conclusions

We have applied a novel two-photon laser-induced

fluorescence detection technique to observe free Cl atoms. This TALIF technique has extremely high inherent temporal and spatial resolution, and high sensitivity. This technique should be applicable to the remote detection of essentially any light atom with presently available laser technology.

## Acknowledgement

We gratefully acknowledge discussions with W.K. Bischel and the expert technical assistance of R.H. Storz and L. Etchner

## References

- [1] J.C. Cummings and D.P. Aeschliman, *Opt. Commun.* 31 (1979) 165.
- [2] M.A.A. Clyne and W.S. Nip, in *Reactive intermediates in the gas phase*, ed. D.W. Setser (Academic Press, New York, 1979) p. 1
- [3] J. Bokor, R.R. Freeman, J.C. White and R.H. Storz, *Phys. Rev. A* 24 (1981) 612.
- [4] W.K. Bischel, B. Perry and D.R. Crosley, *Bull. Am. Phys. Soc.* 26 (1981) 23; *Chem. Phys. Letters* 82 (1981) 85
- [5] G.S. Hurst, M.G. Payne, S.D. Kramer and J.P. Young, *Rev. Mod. Phys.* 51 (1979) 767.
- [6] W.K. Bischel, J. Bokor, D. Kligler and C.K. Rhodes, *IEEE J. Quantum Electron.* QE-15 (1979) 380
- [7] J. Bokor, Ph. D. Thesis, Stanford University (1979)
- [8] J.C. White, J. Bokor, R.R. Freeman and D. Henderson, *Opt. Letters* 6 (1981) 293.
- [9] S. Bashkin and J.O. Stoner Jr., *Atomic energy-level and grottrian diagrams*, Vol. 2 (North-Holland, Amsterdam, 1978).
- [10] M.A.A. Clyne and D.H. Stedman, *Trans. Faraday Soc.* 64 (1968) 1816.
- [11] M.A.A. Clyne and D.J. Smith, *J. Chem. Soc. Faraday Trans. II* 74 (1978) 263.
- [12] M.A.A. Clyne and H.W. Cruse, *J. Chem. Soc. Faraday Trans. II* 68 (1972) 1377.
- [13] P.P. Bernard and M.A.A. Clyne, *J. Chem. Soc. Faraday Trans. II* 71 (1975) 1132.
- [14] G. Bassani, J.J. Forney and A. Quattropiani, *Phys. Rev. Letters* 39 (1977) 1070.
- [15] K. Omidvar, *Phys. Rev. A* 22 (1980) 1576