Intense Vacuum Ultraviolet Atomic Line Sources

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Intense atomic lines (O, N, S, C, Br, Cl, H, Se, Kr) have been produced by microwave excitation of mixtures of various gases in helium under flow conditions. The intensities generally obtained are greater than 10^{14} quanta/sec and are suitable for atomic emission studies and as photochemical light sources in the vacuum uv. Conditions for producing these high purity line sources are discussed.

Introduction

We have previously described a method[1] for measuring very low concentrations of hydrogen atoms by following the absorption and subsequent emission of the hydrogen Lyman-α resonance line. In a now successful attempt at extending this method to the measurement of concentrations of other atoms in their ground electronic states, as well as metastable states, we developed a need for producing moderately high intensity ($>10^{14}$ quanta/sec) atomic line sources that were (1) free of impurity lines, (2) easy to fabricate, and (3) of constant intensity over extended periods of time. The sealed-off gettered lamps[2] that were so highly successful for producing both clean as well as intense rare gas and hydrogen Lyman-α lines were found unsuitable for producing clean, high intensity atomic emissions from other atoms, e.g., Cl, Br, C, N, O, and S.

Harteck et al.[3,4] have produced intense iodine and bromine lamps using an electric discharge through a flowing mixture of iodine and bromine in argon. This flow method appears to reduce the buildup of impurities within the lamp, thus minimizing molecular as well as other atomic emissions. Using a similar flow method, we have been able to produce several new intense line sources by microwave excitation of various gas mixtures using a lamp of very simple design. For comparison purposes, a number of atomic lines previously reported in the literature,[2,5-8] produced from lamps of different design, have also been investigated here using the present procedure. The various atomic line sources investigated are described below.

Lamp Construction and Operation

The design of the electrodeless discharge lamp is shown in Fig. 1. The lamp length is 17.8 cm with two 7-mm o.d. inlet and outlet tubes attached. Swagelock

to Kovar-Kovar to glass is the method used to connect flexible precision 6.35-mm polyethylene tubing to both the inlet and outlet ports of the lamp. A LiF window 1.5 mm thick and 28 mm in diameter is sealed with an epoxy resin to 28-mm o.d. glass tubing as shown. This tubing is constricted at the end to provide a means of making a completely external seal between the windows and lamp. This window sealing method has been previously described by Bass[9] and has the advantage that the discharge is confined to the inner 13-mm o.d. tube and does not come in contact with the cement. The front of the lamp fits tightly into a Veeco* O-ring quick-connect 2.85-cm diam, which provides a convenient means of connecting the lamp to a reaction cell or to the entrance slit of a vacuum monochromator. The lamp is pumped from the backside or outlet side with a mechanical forepump (1.2 liter/sec) with a liquid nitrogen cold trap in between. The cold trap is isolated from the connecting tubing and lamp by means of a vacuum stopcock which is closed whenever liquid nitrogen is not maintained in the trap. This prevents oil from diffusing back into the line and lamp. (Pump oil contamination is the major source of window transmission loss, and this is a necessary precaution.) The gas pressure, which is a measure of the gas flow rate, is monitored at the outlet side of the lamp by means of a Piranni gauge connected into the flexible tubing using a Swagelock T. The inlet side of the lamp is connected through flexible tubing to a Swagelock needle shut-off valve and an O-ring joint. Different gas mixtures are prepared in 2-liter bulbs and these bulbs are separately attached to the O-ring joint.
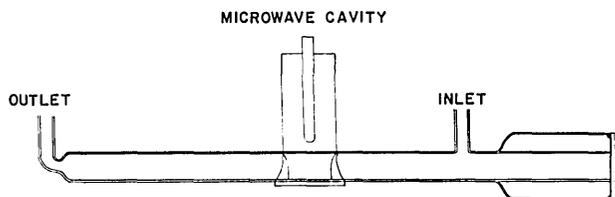
Fig. 1. Schematic drawing of flow lamp (dimensions in text).

A bulb containing a gas mixture is attached to the lamp inlet, the lamp and tubing are evacuated to a pressure of about 1 μ and then the gas flow is adjusted to a pressure of about 1 torr, which in this arrangement corresponds to a flow rate of 0.3 liter atm/h.

A commercial 125-W, 2450-MHz microwave generator coupled to a 2.5-cm diam × 5-cm long cylindrical

Evenson-Broida cavity is used to excite a discharge in the lamp. This type of resonant cavity, described in detail in the literature[10] was found to be best suited to producing intense discharges in our gas mixtures.

All of the gases used are reagent grade. Helium, the gas used in largest amount, is taken from a large cylinder. Helium oil-free-grade is adequate for making flow lamps.

Lamp Intensity and Spectral Characteristics

All emission spectra are taken with a $\frac{3}{4}$-meter f-11 vacuum monochromator (Ebert) with 50-μ slits at a scanning speed of 100 Å/min. The spectral slit width is approximately 1 Å, and, therefore, multiplet splitting is often not resolved, nor is it possible to determine the extent of line self-reversal. These factors are rela-

Table I. Atomic Lines Produced by Microwave Excitation in a Flow Lamp

Atomic specie	Gas mixture	Emission line (Å)	Transition		Relative intensity	Absolute intensity × 10^{-15}
H	2% H_2 in He	1215.7	$(2p)^2P_{1/2}$	$\rightarrow (1s)^2S_{1/2}$		[a]0.76
Xe	3% Xe in He	1469.6	$(5p^56s)^2P_{3/2}$	$\rightarrow (5p^6)^1S_0$		[a]1.00
Kr	3% Kr in He	1235.8	$(4p^55s)^2P_{3/2}$	$\rightarrow (4p^6)^1S_0$	1.00	[a]1.20
		1164.9	$P_{1/2}$	$\rightarrow S_0$	0.20	
O	10% O_2 in He	1302.2	$(2p^33s)^3S_1^0$	$\rightarrow (2p^4)^3P_2$	0.61	[a]0.20
		1304.9	$^3S_1^0$	$\rightarrow ^3P_1$	0.97	
		1306.0	$^3S_1^0$	$\rightarrow ^3P_0$	1.00	
N	1% N_2 in He	1745.2	$(2p^23s)^2P$	$\rightarrow (2p^3)^2P^0$	0.78	[b]1.40
		1742.7			1.00	
		1494.7	^2P	$\rightarrow ^2D^0$	0.15	[a]0.35
		1492.6			0.30	
		1411.9	^2D	$\rightarrow ^2P^0$	0.06	
Cl	0.1% Cl_2 in He	1396.5	$(3p^44s)^4P_{3/2}$	$\rightarrow (3p^5)^2P^0_{1/2}$	0.35	[a]1.04
		1389.9	$^4P_{1/2}$	$\rightarrow ^2P^0_{1/2}$	1.00	
		1379.6	$^4P_{3/2}$	$\rightarrow ^2P^0_{3/2}$	0.13	
		1363.5	$^2P_{3/2}$	$\rightarrow ^2P^0_{1/2}$	0.17	
		1351.7	$^2P_{1/2}$	$\rightarrow ^2P^0_{1/2}$	0.05	
		1347.3	$^2P_{3/2}$	$\rightarrow ^2P^0_{3/2}$	0.03	
Br	0.1% Br_2 in He	1633.6	$(4p^45s)^4P_{3/2}$	$\rightarrow (4p^5)^2P^0_{1/2}$	1.00	[b]1.20
		1582.4	$^4P_{1/2}$	$\rightarrow ^2P^0_{1/2}$	0.50	
		1576.5	$^4P_{5/2}$	$\rightarrow ^2P^0_{3/2}$	0.92	
		1540.8	$^4P_{3/2}$	$\rightarrow ^2P^0_{3/2}$	0.25	
		1575.0	$^2P_{3/2}$	$\rightarrow ^2P^0_{3/2}$	0.46	
		1531.9	$^2P_{1/2}$	$\rightarrow ^2P^0_{1/2}$	0.17	
		1488.6	$^2P_{3/2}$	$\rightarrow ^2P^0_{1/2}$	0.15	
		1449.9	$^2P_{1/2}$	$\rightarrow ^2P^0_{3/2}$	0.03	
		1384.6	$^4P_{1/2}$	$\rightarrow ^2P^0_{1/2}$	0.01	
C	1% CH_4 in He	1930.9	$(2s^22p^3s)^1P^0_1$	$\rightarrow (2s^22p^2)^1D_2$	1.00	[b]0.98
		1658.1	$^3P^0$	$\rightarrow ^3P$	0.52	
		1657.0				
		1656.3				
		1560.3	$^3D_0$	$\rightarrow ^3P$	0.58	
		1560.7				
		1561.4				
S	0.2% H_2S + He	1914.9	$(3p^34s)^5S^0_2$	$\rightarrow (3p^4)^3P_1$	0.16	
		1900.3	$^5S^0_2$	$\rightarrow ^3P_2$	0.52	
		1826.3	$^3S^0_1$	$\rightarrow ^3P_0$	1.00	[b]0.50
		1820.4	$^3S^0_1$	$\rightarrow ^3P_1$	0.64	
		1807.3	$^3S^0_1$	$\rightarrow ^3P_2$	0.18	
		1667	$^1D^0_2$	$\rightarrow ^1D_2$	0.13	

[a] Line intensity determined by CO_2 actinometry

[b] Line intensity determined from monochromator traces.

1930.9
1657
1560
CARBON
1216

(a)

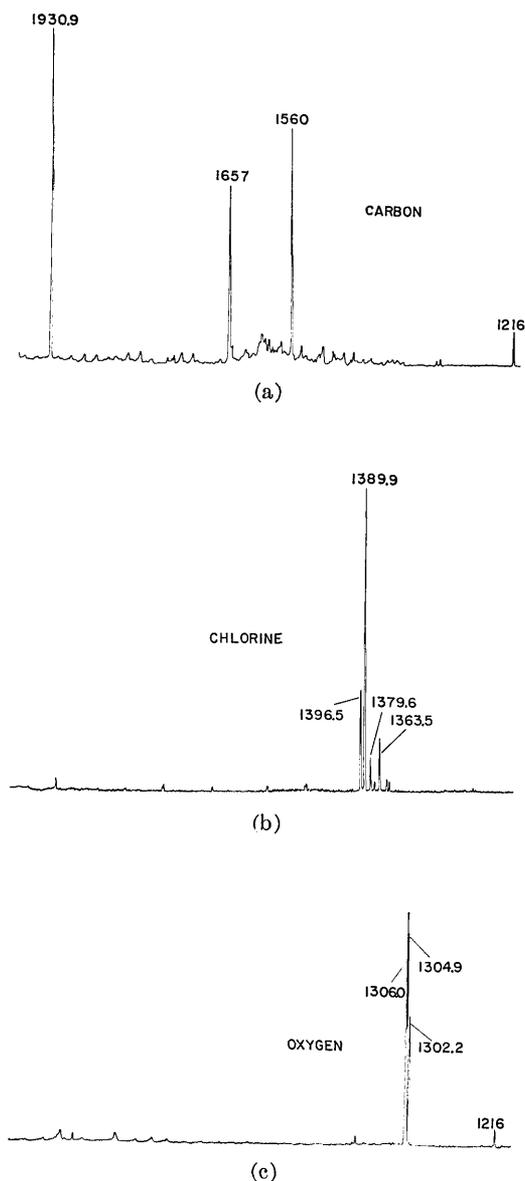1389.9
CHLORINE
1396.5
1379.6
1363.5

(b)

1304.9
1306.0
OXYGEN
1302.2
1216

(c)

Fig. 2. (a) Monochromator tracing of carbon lamp between ∼ 1200 Å and 2000 Å. (b) Monochromator tracing of chlorine lamp between ∼ 1200 Å and 2000 Å. (c) Monochromator tracing of oxygen lamp between ∼ 1200 Å and 1800 Å.

tively unimportant if the spectral lines are used as photochemical light sources, but are important if the lines are used for spectral calibrations or to excite atomic fluorescence. The EMR ASCOP photomultiplier tube used in these measurements contains a LiF window and a semitransparent cesium telluride photocathode. This surface has a flat spectral response between 1200 Å and 2600 Å. In the few cases (Br, C, and S lamps) in which line intensity measurements are determined from spectral traces, they are compared directly with the Xe 1470-Å line making the justifiable assumption that the spectral response is independent of the wavelength above 1350 Å, where the LiF windows transmit most of the radiation.

Carbon dioxide actinometry is used to determine the absolute intensities of the various lines. The quantum yield of CO production is assumed to be unity.[11,12] The pressure of CO_2 in the absorption cell is held constant, and the extent of light absorption is calculated from the extinction coefficient of CO_2 at the particular wavelength of the measured line (or multiplet). For each of the lamps, the discharge is brought almost into contact with the LiF window. The microwave power level is generally about 60%. If the front of discharge is brought to the same distance from the absorption cell, the lamp output is found to be relatively insensitive to the length of the discharge or the microwave power level. For intensity comparison purposes, actinometry measurements have been made in a similar way to that of Okabe.[2] The effective aperture is 13 mm and the CO_2 actinometry cell is brought into contact with the lamp window. The actinometry results of the flow lamps therefore can be directly compared with the sealed-off gettered lamps.[2]

The results of both relative and absolute intensity measurements on the various atomic line sources investigated are listed in Table I. Also indicated in this table are the gas mixtures used to generate each of the line sources. Although only a single mixture is listed for each lamp this should not be taken to mean that this mixture is necessarily optimized. In the case of the rare gas lamps, for example, a change in composition of 0.5% to 10% results in no significant change in intensity or spectral purity. Other lamps such as N, O, C, and S are considerably more sensitive to composition. In these lamps, the additive gas concentration cannot be varied by more than a factor of 3 or 4 without noticeably affecting lamp performance. The chlorine, bromine, and hydrogen resonance lamps are of intermediate sensitivity, gas compositions being variable over a range of 7 or 8 without significantly affecting spectral purity or intensity. Flow conditions for the rare gas lamps are not critical. Slow flow and fast flow conditions produce spectrally pure and intense lines. For the other atomic lines, however, a flow rate somewhat higher than that required to maintain a stable discharge is generally required to obtain minimum molecular impurity emissions. Under conditions of minimum flow, the discharges are generally very bright. It has been our experience that when the flow rate is adjusted so that the discharge intensity becomes somewhat dull in color, the best spectral purity is obtained. Increasing the flow rate beyond this point produces no noticeable improvement in intensity or spectral purity and only shortens the time that a given gas mixture reservoir can be used. Typical flow rates were about 0.3 liter atm/h when operating at a pressure of 1 torr. At this flow rate, the gas compositions listed in Table I generally lead to optimum results.

Emission spectra from three line sources, C, Cl, and O are shown in Fig. 2 as typical examples. In the case of the chlorine and oxygen lamps, it can be seen that relatively few impurity lines are present. The carbon lamp, on the other hand, contains somewhat higher levels of impurity emission particularly between 1680–1530 Å. Impurity lines in this region are due primarily

to molecular H_2 emissions. The other atomic line sources (spectra not shown) have a spectral purity comparable with or better than that of the chlorine atom lamp.

A number of other gases were also tried as possible sources for carbon, nitrogen, and sulfur lines, e.g., CCl_4, CO_2, N_2O, NO, and CS_2. In each case, the rapid buildup of polymeric impurities or the presence of moderately intense impurity bands rendered these gas mixtures less advantageous than those listed in Table I.

The carbon and sulfur sources listed in Table I were the cleanest sources that we were able to find. These sources do, however, eventually result in the buildup of polymeric deposits in the flow lamp, which is not the case for all of the other gas mixtures listed in Table I. These polymeric deposits can be rapidly removed in a matter of a few minutes. The procedure is to flow oxygen through the lamp and subject it to a microwave discharge.

Conclusions

The intensities of the nitrogen, hydrogen, and oxygen lines produced in the flow lamps are one order of magnitude more intense than the sealed-off gettered lamps described in the literature.[2] The spectral purity has been found also to be greatly improved. The rare gas line sources are of intensity equal to the sealed-gettered lamps. They are also as free of impurities and have the distinct advantage over the gettered lamps of being easier to construct and are more reproducible. They do not have to be checked for spectral purity from time to time since they appear to have unlimited operating time.

Previously, the well-known often used light sources in the vacuum uv used as photolysis sources included the argon (Ref. 13) 1065-Å, Kr 1165-Å, H 1216-Å, Kr 1236-Å, Xe 1205-Å Xe 1470-Å (Refs. 6 and 7), and Hg 18 49-Å, lines. The more recent additions C 1930 Å (Ref. 14), bromine 1633 Å (Refs. 3,4), and 2062 Å (Ref. 3) helped fill some of the gaps in the vacuum uv wavelength span between the LiF cutoff of 1050 Å and the quartz limit at about 2000 Å. A number of the newer lamps described here help fill in the remaining gaps, namely, O 1303 Å, Cl 1390 Å, Br 1489 Å, Br 1575 Å, N 1493 Å, N 1745 Å, C 1560 Å, C 1650 Å. Many of these lines are routinely produced in spectroscopy laboratories by means of discharges through various gases.[8] However, line intensities from these sources are usually 10^{13} quanta/sec or less, and in most cases are inadequate as photochemical light sources. In the lamps described here the oxygen, chlorine, bromine, nitrogen, and carbon lines listed above all have intensities greater than 10^{14} quanta/sec.

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