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MOLECULAR FLUORESCENCE AS A MONITOR OF MINOR STRATOSPHERIC CONSTITUENTS

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16. Abstract

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In addition, this report constitutes somewhat of a handbook for molecular fluorescence and includes a compilation of all reported studies for simple molecules using line source excitation.

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SYMBOLS AND CONVERSION FACTORS

$1 \text{ atm} = 760 \text{ torr}$

$= 1.01325 \times 10^{5} \text{ N m}^{-2}$

$= 7.3398 \times 10^{21} / T \text{ particles cm}^{-3}$

$1 \text{ cal} = 4.1840 \text{ J}$

$1 \text{ cm}^{-1} = 2.85912 \text{ cal mole}^{-1}$

a_F	Cross-sectional area of lens used to collimate the exciting source, cm^2
a_L	Cross-sectional area of laser beam, cm^2
a_s	Surface area of light source, cm^2
A_T	Total absorption factor, sec^{-1}; fraction of the incident radiation that is absorbed
b	Effective refractive index of an interference filter material
C	Detector photocathode radiant sensitivity, amp watt^{-1}
ϵ_J	Energy of the J rotational level above the ground state
f	Fraction of the total fluorescence monitored
$f_{\upsilon' \upsilon''}$	Vibrational transition probability for the $(\upsilon' \upsilon'')$ band
FWHM	Full linewidth at half peak intensity
G	Photodetector gain
g_e	Degeneracy of an electronic state
$g_e^{J''}$	Electronic degeneracy associated with a particular rotational level
θ	Transmission factor for the detector filter system
i_{an}	Photodetector anode dark current noise
i_{cd}	Photodetector cathode dark current
i_s	Photodetector signal anode current

I_a	Total radiant energy absorbed over full bandwidth
I_a^{ν}	Intensity of the radiation absorbed at the frequency ν
$I_{continuum}^{0}$	Amplitude of the continuum radiant intensity, watts - sec cm^{-2} $ster^{-1}$
I_f	Intensity of the fluorescence, watts
I_L	Intensity of laser beam, watts cm^{-2} or watts
I_{ν}	Intensity of the transmitted radiation at frequency ν
I_{ν}^{o}	Intensity of the incident radiation at frequency ν
I_s	Radiant intensity of source, watts cm^{-2} $ster^{-1}$
I_{scatt}	Intensity of scattered radiation
k_{d}, k_{q}	Rate constants for dissociation and quenching processes
k_f	Rate constant for fluorescence, sec^{-1}; equal to the inverse of the natural radiative lifetime, τ
k_{ν}	Absorption coefficient, cm^{-1} NTP^{-1}, base e
ℓ	Path length of interest, cm
$\lambda_{J'J''}$	Wavelength of the transition between J' and J'' rotational levels
λ_N	Wavelength of the peak transmission of an interference filter for radiation at normal incidence
$\lambda_{\upsilon'\upsilon''}$	Wavelength of the band origin of the ($\upsilon'\upsilon''$) band
λ_{φ}	Wavelength of the peak transmission of an interference filter for radiation at an angle of incidence φ
n	Total number density of absorbing or scattering species, cm^{-3}
n_i	Total number density of species in the i^{th} absorbing level, cm^{-3}
N	Equivalent noise input of a detector, watts
$\Delta\nu_D$	Doppler line half-width (FWHM), sec^{-1}
$\Delta\nu_L$	Lorentz, or pressure-broadened line half-width (FWHM), sec^{-1}
$\Delta\nu_N$	Natural line half-width (FWHM), sec^{-1}
$\Delta\nu_s$	Source line half-width (FWHM), sec^{-1}

$\Delta\nu_{voight}$	Voight line half-width (FWHM), sec^{-1}
ppb	Parts per billion by volume
Q_{rot}	Rotational partition function
Q_{vib}	Vibrational partition function
σ_{ν}	Absorption or scattering cross-section, cm^2, at frequency ν
σ_o	Absorption cross-section at a line center, cm^2
σ_s	Absorption cross-section at the source freqency, cm^2
$S_{J'J''}$	Line strength of a rotational line transition
τ	Radiative lifetime, sec
υ	Vibrational quantum number
ϖ	Angle of incidence, measured from the normal
Ω_F	Detector effective solid angle, steradians
Ω_s	Effective solid angle of source radiation, steradians

INTRODUCTION

The National Aeronautics and Space Administration is implementing a program to monitor the temperal and spatial concentrations of particulates and trace gas constituents in the upper troposphere and the stratosphere. Boeing 747 airliners are in use together with such supersonic aircraft as the Concorde and a U2 plane capable of attaining high altitudes but somewhat limited in its payload. Growing concern over the possible deleterious effects on the environment by SST and Space Shuttle engine exhaust emissions, particularly in the stratosphere, necessitates the collection of a reliable data base of current atmospheric concentration levels at these altitudes. Such data also is required to validate and refine more sophisticated atmospheric models to permit reliable assessments of any potentially harmful effects and hopefully illustrate methods for their minimization. The Climatic Impact Assessment Program of the US Department of Transportation has assumed this overall responsibility.

The generally low concentrations of many of the minor constituents in the stratosphere, most often measured on a parts per billion by volume (ppb) scale have made their monitoring a very demanding task. Several systems are being assessed as to their potential and for their feasibility as fully automated flight hardware. Currently, data are being obtained for NO using the chemiluminescent detector (detection limit 0.02 ppb, Ridley et al., 1974) and for O_3 by uv absorption (detection limit 3 ppb). A $C^{16}O$, $C^{18}O$ fluorescent source NDIR detector (detection limit 200 ppb) is being further refined in an attempt to sufficiently increase its sensitivity to the required 30 to 120 ppb range (McClatchie, 1972). Extensive data already have been collected for NO and O_3. Infrared emission and absorption techniques under high resolution conditions, the latter using the sun as a source, have been instrumented for balloon or aircraft platforms (Farmer, 1974). Such methods give an integral measure of a minor constituents concentration and require a more sophisticated analysis to provide its distributions as a function of altitude. Spectrometers and interferometers are being used in the 1 to 8 μm region (Farmer et al., 1972b; Ackerman and Muller, 1972a, b), 1 to 30 μm (Murcray et al., 1972), 50 to 300 μm (Baluteau et al., 1972), and 300 to 3000 μm (Harries, 1973). As a result of the growing concern for environmental quality, various new approaches have been considered for their suitability as pollution monitors. Line center absorption appears to be one that holds promise for detection at low concentration levels (Lowder et al., 1971; McGregor et al., 1972; Sulzmann et al., 1973). Another, using very sensitive opto-acoustic detectors reportedly can monitor CO, CO_2, or spin-flip Raman infrared laser absorptions by species at the parts per billion level (Kreuzer and Patel, 1971; Kreuzer, 1971; Kreuzer et al., 1972; Dewey et al., 1973; Rosengren et al., 1974). Gelbwachs (1974) has considered the extent to which water vapor absorptions will interfere and limit the sensitivity of such detectors. A total sulfur flame chemiluminescent detector, that monitors the S_2 band emission at 394 nm, has been reported to have a detection limit of 4 ppb (Krost et al., 1973). The enhanced absorptions noted if a species is inserted within a laser cavity is yet another area open to extensive exploitation (Chackerian and Weisbach, 1973; Atkinson et al., 1973). However, other techniques, ideally simple in nature and free from interferences also need to be developed. This report considers in detail, the feasibility of one such approach which is only now beginning to be exploited to its full analytical potential. Namely, molecular fluorescence, such an approach has been largely disregarded. However, solar induced fluorescence has been monitored for many years in the upper atmosphere by rockets and satellites to obtain NO and OH concentrations in the mesosphere and ionosphere (Barth, 1964, 1966a, b; Anderson, 1971a, b; Rusch, 1973). Its selectivity and potential freedom from spectral interferences when excited with line sources now is well recognized. The advent of the laser as an intense excitation source sufficiently monochromatic to excite only a limited number of levels has fostered renewed interest and broadened the potential of fluorescence studies. The development of more intense atomic line sources primarily for atomic absorption and atomic fluorescence measurements also has played a contributary role in providing an increased number of intense, stable, electrodeless discharge and hollow cathode lamps. The ability to populate selectively has opened up new studies of the fundamental characteristics of individual states. A narrow line rarely excites more than one electronic, vibrational and rotational state. Consequently, fluorescence spectra are greatly simplified in comparison with continuum source excitation and most overlapping features are removed. This eliminates possible ambiguities in the spectral interpretations. Molecular constants, energy transfer processes, band intensity ratios, Franck-Condon factors, electric dipole and magnetic moments and various fine and hyperfine structure splittings, together with lifetime measurements and collisional quenching parameters are all being studied with renewed interest. Molecular level crossing and optical, radio, and microwave double-resonance experiments incorporating fluorescence techniques have introduced a precision into molecular spectroscopy approaching that of microwave and electron spin resonance studies.

Until recently, gas-phase fluorescence has been a minor area of molecular spectroscopy, whereas there has always been a vast accumulation of work with condensed phased systems. In fact, induced laser fluorescence from oil pollution on water using a He.Cd laser is being successfully used as an airborne monitor ("Nightime Detection of Pollutants," 1973). From the analytical point of view, the principal advantage of fluorescence techniques relates to the linear proportionality between the signal intensity and the species concentration. Accuracy depends solely upon how well the magnitude of the signal can be measured relative to the detector noise. In contrast, absorption methods rely on being able to accurately monitor the difference between two transmitted signals. At low concentrations this entails measuring a small difference between two large values and consequently is more demanding. Fluorescence can be a particularly sensitive analytical tool as illustrated by its ability to measure the vapor pressure of sodium at room temperature (Fairbank et al., 1973). This corresponds to about 4×10^5 atoms cm^{-3} and, since with the cw tunable dye laser system used, the signal to noise (S/N) ratio at this level was more than 10^3 it is expected that concentrations 3-4 orders of magnitude smaller could be monitored. The detection of only several atoms in an exciting beam appears not an unreasonable expectation for the near future with certain species. Similarly, an enterprising group at the Ford Scientific Research Laboratories (Wang, 1974; Wang and Davis, 1974) has reported successfully monitoring an atmospheric trace constituent using molecular fluorescence. Utilizing a tunable laser source, OH concentrations have been measured at ground level in ambient air to a detection limit of about 5×10^6 cm^{-3}, corresponding to 0.2 parts per trillion. Concentrations were found to range to a high value of 1.5×10^8 cm^{-3} in the early afternoon and drop below the detection limit if it was raining, overcast, or nighttime. That such a difficult measurement has been achieved at the present time lends tremendous impetus to the present quest of exploiting molecular fluorescence as a sensitive analytical technique for a wide range of simple molecular species.

STRATOSPHERIC COMPOSITION

The lower boundary of the stratosphere is defined by the temperature minimum that exists in the atmosphere. This altitude region, the so-called tropopause, is latitude dependent being at about 10 km at the poles and 15-16 km in the tropics. Above it and up to about 50 km is the stratosphere, a region owing its existence to its ozone content which absorbs most of the incoming ultraviolet solar radiation. This report will place emphasis on the 10 to 30 km region (33,000-98,000 ft). Although the major atmospheric constituents are well mixed up to these altitudes and even higher, as illustrated by the constancy of the mean atmospheric molecular weight, the minor components are affected by aeronomic reactions which result in their concentrations differing quite markedly through this region.

In these assessments of various fluorescing systems, a knowledge of the approximate composition of stratospheric air samples is required to calculate the extent of potential interferences or other background contributions to the fluorescent signal. Obviously, the extent of analytical sophistication is governed by the ultimate concentration levels to be measured. Sophistication beyond that necessary to accomplish the task is unnecessary. Consequently, a current list of stratospheric concentrations has been compiled in Table I to illustrate the required performance levels of suitable analyzers. The approximate range of values has been given for the 10 to 30 km region expressed both as a volume mixing ratio and as a molecular concentration. Some identification of the source of the data has also been listed. Atmospheric temperatures and number densities have been taken from Kantor and Cole (1973), (10 km, 223.1 K, 8.6×10^{18} cm^{-3}; 30 km, 226.6K, 3.7×10^{17} cm^{-3}). The data for H_2O, O_3, and CH_4 are in reasonably good shape. The water content of the stratosphere has been extensively studied during the past ten years. Mastenbrook (1974) has most recently reviewed the situation and quotes a median value of about 4 ppm, values falling in the range 1.6 to 6.4 ppm. Values for NO concentrations now are becoming much better established; Schiff (1974) has reviewed stratospheric measurements for NO, NO_2 and HNO_3. Although several balloon and plane measurements have provided some data for such species as H_2, N_2O, CO, HNO_3, and NO_2, these are very limited in most cases and more measurements are required to better establish their abundances and variabilities. The situation for NH_3, SO_2, H_2S, HCHO, O, HNO_2, and OH is such that hardly any experimental data exist at all for their stratospheric concentrations.

Table I. Range of Concentrations in the Stratosphere (10 to 30 km)

Major Stable Constituents (from Valley, 1965)

Species	Volume Mixing Ratio (ppm)	Concentration (molecule cm^{-3})
N_2	780,840	$(0.3-6.7) \times 10^{18}$
O_2	209,480	$(0.8-18) \times 10^{17}$
Ar	9,340	$(0.3-8.0) \times 10^{16}$
CO_2	320	$(0.1-2.7) \times 10^{15}$
Ne	18	$(0.7-16) \times 10^{13}$
He	5	$(0.2-4.5) \times 10^{13}$
Kr	1	$(0.4-9.8) \times 10^{12}$
Xe	0.09	$(0.3-7.4) \times 10^{11}$

Minor Constituents

Species	Volume Mixing Ratio (ppb)	Concentration (molecule cm^{-3})	Data Source	Reference
H_2O	2000–6000	$(0.1-5.0) \times 10^{13}$	Balloon, aircraft	McKinnon and Morewood, 1970; Mastenbrook, 1971, 1974; Harries and Burroughs, 1971; Sissenwine et al., 1972; Goldman et al., 1973b
O_3	150–4000	$(1-3) \times 10^{12}$	Extensively monitored	Banks and Kockarts, 1973.
CH_4	900–1400	$(0.3-12.0) \times 10^{12}$	Balloon, aircraft	Ackerman and Muller, 1972a; Lowe and McKinnon, 1972; *Ehhalt and Heidt, 1973a, b;* Cummings & *Lowe, 1973.*
H_2	500–750	$(0.3-4.3) \times 10^{12}$	Balloon	Ehhalt and Heidt, 1973a.
N_2O	<10–270	$(<0.04-23.0) \times 10^{11}$	Balloon, aircraft	Schutz et al., 1970; Harries, 1973; Goldman et al., 1973a; Ehhalt, 1974.
CO	30–120	$(0.01-1.0) \times 10^{12}$	Balloon, aircraft $\leqslant$ 15 km	Seiler and Warneck, 1972; Goldman et al., 1973c.
HNO_3	1–10	$(0.4-2.5) \times 10^{10}$	Balloon, aircraft	Williams et al., 1972; Harries, 1973; Murcray et al., 1973.
NH_3	< 10	$<(0.4-8.0) \times 10^{10}$	Ground level analyses	Junge, 1963; Pate et al., 1970.
NO_2	1–5	$(1.3-43.0) \times 10^{9}$	Balloon, aircraft	Ackerman and Muller, 1972b; Ackerman et al., 1974; Brewer et al., 1973.
SO_2	< 5	$<(0.2-4) \times 10^{10}$	Aircraft, ground level analyses	Kellogg et al., 1972; Harries, 1973.
NO	0.02–2.3	$(1.7-8.5) \times 10^{8}$	Balloon, aircraft	Ackerman et al., 1973, 1974; Toth et al., 1973; Ridley et al., 1973, 1974.
H_2S	< 1	$<(0.4-8.0) \times 10^{9}$	Ground level analyses	Lodge and Pate, 1966; Kellogg et al., 1972.
HCHO	$\leqslant$ 1–2	$\leqslant 2 \times 10^{10}$	Rain analyses, atmospheric models, aircraft	Wofsy et al., 1972; Levy, 1973a, b; Whitten et al., 1973; Farmer, 1974.
HCl	<0.18	$<1.5 \times 10^{9}$	Aircraft	Farmer, 1974.
O	$\leqslant$ 0.1	$\leqslant 4 \times 10^{7}$	Atmospheric models	Crutzen, 1971.
HNO_2	~0.01	$\sim 2 \times 10^{8}$	Tropospheric model	Levy, 1972.
OH	$\leqslant$ 0.01	$(1-5) \times 10^{6}$	Atmospheric Models	Leovy, 1969; McConnell et al., 1971.

Recently, Breeding et al. (1973) have monitored the levels of NH_3, NO_2, SO_2, H_2S, and total aldehydes (RCHO) at ground level in clean rural air. They obtained background levels for NH_3 in the range of 2-6 ppb, for NO_2 1-3 ppb, SO_2 1-2 ppb, $H_2S < 0.2$ ppb, and RCHO 1-2 ppb. Stratospheric concentrations are expected to be below these mixing ratios.

This report considers the feasibility of using molecular fluorescence techniques aboard aircraft flying through the stratosphere. Detection limits have been calculated for various possible systems for most of these minor species. Owing to an interest in the chlorine-based solid fuel (ammonium perchlorate) for the Space Shuttle engines, limits have also been calculated for such species as Cl, Cl_2, HCl, ClO, ClO_2, which may be exhausted in large quantities in the upper atmosphere.

LINE INDUCED ELECTRONIC FLUORESCENCE IN GASEOUS MOLECULES

Fluorescence studies of molecules have long been a useful and practical tool in elucidating molecular structure and the nature of radiative processes. However, excitation with monochromatic light sources, particularly laser lines, has renewed interest in the technique since this provides a convenient method for selectively producing nonequilibrium concentrations in specific electronic, vibrational and rotational states. Studies of the fundamental processes that lead to the re-establishment of equilibrium, such as rates of relaxation, energy transfer, and radiative lifetimes, provide a basic wealth of general information. At reduced pressures, in the absence of collisions, molecules emit a strikingly simple fluorescence spectrum in many cases, which consists solely of a line progression in υ'' and serves well to also accurately characterize the ground electronic state.

Line excitation of molecular fluorescence has its special difficulties and rewards. Owing to the specific selectivity of the pumping process, suitable coincidences between atomic and molecular lines are required. Generally, a degree of mismatch in the uv-visible region must be less than about 0.4 cm^{-1} if an adequate overlap between the lines is to occur, and even more exact in the infrared where linewidths at reduced pressures can be particularly narrow. This constitutes a major drawback to the general applicability of the technique since such coincidences are quite rare. By using tunable line sources or species with a quasi-continuum absorption spectrum, the problem is alleviated to a large extent. The magnitude of the fluorescence intensity is a consequence of a delicate balance between rates of absorption, radiation and quenching. For a fluorescent system to be highly sensitive, it is necessary to have an intense source located in a spectral region where the absorption cross-section is large, and with an excited state lifetime short so that collisional quenching will not reduce the fluorescence efficiency.

Fluorescence can be excited in a variety of ways. These include illumination with a resonance lamp or laser line, with continuum light, or radiation from radio-frequency or microwave discharges. The term 'fluorescence' is also applied to photo-dissociation processes that yield an excited fragment or to processes involving photo-sensitization with metastable excited atoms. Fluorescence has also been loosely applied to systems where excited states produced in the initial absorption undergo reactions that lead to excited molecular species which ultimately radiate. Such an example is that of mercury vapor where excitation by means of the 253.7 nm Hg line results in a 335 nm band of Hg_2. This is explained by the following sequence of reactions (Phaneuf et al., 1973),

$$
\begin{aligned}
&Hg + h\nu\ (253.7\ \mathrm{nm}) \rightarrow Hg\ (^3P_1)\\
&Hg\ (^3P_1) + N_2 \rightarrow Hg\ (^3P_0) + N_2\\
&Hg\ (^3P_0) + Hg + N_2 \rightarrow Hg_2\ (^31_u) + N_2\\
&Hg\ (^31_u) \rightarrow Hg + Hg + h\nu
\end{aligned}
$$

Since this exercise is to establish the feasibility of molecular fluorescence as a stratospheric monitor of species at the ppb concentration level, as free from spectral interferences as possible, only fluorescence directly excited by line sources or specific band systems such as CO, NO, or OH will be considered. Systems that require energy exchange processes are not feasible at such low ooncentrations.

In order to illustrate the extent of gas-phase fluorescence studies induced by line sources, a fairly complete survey of the literature has been made. All diatomic and triatomic molecular species have been included. Electronic fluorescence for larger polyatomic species (mainly organic in nature) is not of interest in this current work, but has been reviewed elsewhere by Parmenter (1972). Fluorescence studies excited by uv-visible line sources are listed according to the molecular species, in alphabetical order, in Table II. This illustrates, immediately, the extensive number of fundamental studies that have been reported, the majority within the last few years. The Table generally does not include investigations utilizing continuum light sources, but an exception has been made in one or two cases where quite narrow bandwidths were isolated. Likewise, emission band sources such as the NO ($A^2\Sigma^+ \rightarrow X^2\Pi$), CO (4th positive) or OH ($A^2\Sigma^+ \rightarrow X^2\Pi$) are not included. Such alternative exciting sources are discussed in detail later in the appropriate section dealing with these molecules. The spectral range of the fluorescence bands monitored is noted, occasionally with some indication of their intensity. The absorbing transitions are listed to indicate the states involved. These are quite often the original assignments. Some have been corrected in view of later work but no extensive effort has been made to check their current accuracy. Whereas some of them are quite well characterized, many are still uncertain and further analysis of the particular states involved is necessary. In the original analyses, transitions have often been identified either by a direct comparison under high resolution of the exciting line with the absorption spectra to note the overlapping feature or by using Franck-Condon factors and established molecular constants. The magnitude of the observed P, R branch doublet splittings observed in υ'' fluorescence progressions, in many cases can identify the particular J quantum numbers involved. From Table II it is possible, by noting the ground state vibrational level involved, to assess the extent of the absorption process as a function of temperature.

The ultimate in state selection in the uv-visible region is achieved using lasers oscillating in a single mode. The spectral resolution becomes so fine that individual isotopic components can be excited (Dworetsky and Hozack, 1973a). For a fluorescence analyzer, such resolution is not required and the narrowness of the exciting line is only important in the context of maximizing the overlap with an absorption feature or minimizing any overlap with a possible interfering absorption line.

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, λ_{vac}, nm		Fluorescence Reported, nm			Quantum States Involved in Absorption; υ', υ'', J', J''		Reference
AlO	465.789	(0.015W) Ar$^+$	465-564	(1,0 → 1,4)	s	B $^2\Sigma^+ \leftarrow X^2\Sigma^+$	(1,0; 17,18)	Johnson et al., 1972b.
	487.986	(1W) laser	485-564	(0,0→0,3; 1,1→1,4)	s	(0,0; 48, 49)	(1,1; 57,56)	
	447.0	Pulsed, tunable			s		(2,0)	
	465.0	N$_2$ dye			s		(1,0)	
	484.0	laser			s		(0,0)	
	514.532	(1W) Ar$^+$ laser			w	B $^2\Sigma^+ \leftarrow X^2\Sigma^+$		Johnson, 1971.
BaBr	520.831	(0.03W) Kr$^+$ laser	520-540	(0,0 → 0,1)	s	$C^2\Pi \leftarrow X^2\Sigma^+$	(0,0)	Capelle et al., 1973
	520.8	Pulsed, tunable, N$_2$ dye laser	520-540	(0,0 → 0,1)	s		(0,0)	
	514.532	(1W) Ar$^+$ laser	504-525	(11,8 → 11,12)			(11,10)	
BaCl	520.831	(0.03W) Kr$^+$ laser	513-532	(0,0 → 0,1)		$C^2\Pi \leftarrow X^2\Sigma^+$	(0,1)	Capelle et al., 1973
	524.3	Pulsed, tunable N$_2$ dye laser	513-532	(0,0 → 0,1)			(0,1)	
BaF	487.986 514.532	(1W) Ar$^+$ laser. (1W)	fluorescence reported			not identified		Capelle et al., 1973
BaO	450-650	Pulsed, tunable, N$_2$ dye laser	450-650 (U)		s	A $^1\Sigma \leftarrow X\ ^1\Sigma$	(υ'=0 to υ'=17)	Schultz et al., 1972
	454-598	(1-4 kW peak) Pulsed tunable, N$_2$ dye laser	(U)			A $^1\Sigma \leftarrow X\ ^1\Sigma$	(υ'=0 to υ'=11)	Johnson, 1972
	457.935	(0.12W) Ar$^+$	460 → (12, υ'')		vw	A $^1\Sigma \leftarrow X\ ^1\Sigma$	(12,1; 4 or 5, 3 or 4)	Sakurai et al., 1970; Johnson, 1971
	472.686	(0.09W) laser	473 → (12, υ'')		w		(12,2; 21 ± 1 or 14 ± 1, 20 ± 1 15 ± 1)	
	476.486	(0.22W)	476 → (9, υ'')		w		(9,0; 38,37)	
	487.986	(1W)	405-955	(8,0 → 8,16)	s		(8,0; 49,48)	
	496.507	(0.5W)	496-1060	(7,0 → 7,17)	s,s		(7,0; 3,2) (7,0; 7,6)	
	501.716	(0.22W)	496-1060	(7,0 → 7, 17)	w		(7,0; 52 ± 1, 53 ± 1)	
	514.532	(1W)	496-1060	(7,0 → 7,17)	m		(7,1; 19,20)	
	496.507	(0.2W) Ar$^+$ laser	513.5	(7,1)	s	A $^1\Sigma \leftarrow X\ ^1\Sigma$	(7,0; 2,1)	Field et al., 1972a,b
	568.188	(0.065) Kr$^+$ laser	560-1000	(2,0 → 2,12)	s	A $^1\Sigma \leftarrow X\ ^1\Sigma$	(2,0;41,40) (2,0;52,53)	Johnson, 1971
BeO	337.1	(100-200kW peak) N$_2$ pulsed laser		(R)	w			Capelle et al., 1972
	442.7	(2kW peak) Pulsed,		(R)	vw	B $^1\Sigma \leftarrow X\ ^1\Sigma$	(1,0)	
	471.0	tunable, N$_2$ dye	> 470	(R)	s		(0,0)	
	473.3	laser			vw		(1,1)	
BiBr	496.507	(0.5W) Ar$^+$ laser	481.5-528	(2,0 → 2,9)		A ← X	(2,3)	Capelle et al., 1973
BiCl	472.686	(0.1W) Ar$^+$	466-516	(0,0 → 0,8)		$AO^+ \leftarrow XO^+$	(0,2)	Capelle et al., 1973
	487.986	(1W) laser	446-556	(3,0 → 3,15)			(3,6)	
	514.532	(1W)	451-545	(2,0 → 2,13)			(2,9)	
Br$_2$	513.1	(1-4kW peak)	540-650 (U)			B $^3\Pi_{0_u^+} \leftarrow X^1\Sigma_g^+$	(υ'=31* or ~40)	Capelle et al., 1971
	522.1	Pulsed, tunable	540-650 (U)				(υ'=27* or ~31)	
	522.5	N$_2$ dye laser	570-650 (U)				(υ'=27* or ~31)	
	532.5		555-650 (U)				(υ'=23*, 27 or 30)	
	541.1		555 and 590-650 (U)				(υ'=20*, 23 or 27)	
	549.6		570-650 (U)				(υ'=17*, 20 or 23)	
	561.5		590-650 (U)				(υ'=14*, 17 or 19)	
	573.8		590-650 (U)				(υ'=11*, 13 or 16)	
	587.4		610-650 (U)				(υ'=9*, 11 or 13)	

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* Main excitation
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(U) spectrally unresolved; (R), resolved
bw bandwidth; EDL, electrodeless discharge lamp
kG kilogauss magnetic field required to Zeeman shift into coincidence

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, $\underline{\lambda_{vac}}$, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
Br_2 (Cont)	597.0 602.5 614.0 626.0		610-650 (U) 610-650 (U) 645-650 (U) 645-650 (U)		(υ'=6, 8 or 10*) (υ'=5*, 7 or 9) (υ'=3*, 6 or 7) (υ'=1*, 3 or 5)	* most probably excited
	576.960 579.066	Hg arc lamp	fluorescence reported			Plumley, 1933, 1934
	632.816	He-Ne laser	fluorescence reported		$B\,{}^3\Pi_{o_u^+} \leftarrow X\,{}^1\Sigma_g^+$	Manke (priv. comm.); Kiefer and Schrotter, 1970
	694.3	(0.2W) Ruby laser	694-759 (4 bands R)	w	$B\,{}^3\Pi_{o_u^+} \leftarrow X\,{}^1\Sigma_g^+$ ($\upsilon' \geqslant 5$)	Kiefer and Schrotter, 1970
$^{79,79}Br_2$	514.532	Ar^+ laser (single mode)	522.6-523.7 (R)		$B\,{}^3\Pi_{o_u^+} \leftarrow X\,{}^1\Sigma_g^+$($J'$=33 ±2, J''=32 ±2; J'=43 ± 2, J'' 42 ± 2	Dworetsky and Hozack, 1973a
	546.073	Hg arc lamp	556-760 (R)		$B\,{}^3\Pi_{o_u^+} \leftarrow X\,{}^1\Sigma_g^+$ (21, 0; 73, 74)	Plumley, 1933, 1934
$^{79,81}Br_2$	514.532	Ar^+ laser (single mode)	522.6-523.7 (R)		$B\,{}^3\Pi_{o_u^+} \leftarrow X\,{}^1\Sigma_g^+$ (J'=20± 2, J'' = 19± 2)	Dworetsky and Hozack, 1973a
	546.073	Hg arc lamp	556-760 (R)		(19, 0; 9, 8) (25, 1; 63, 64) 21, 0; 77, 76)	Plumley, 1933, 1934
$^{81,81}Br_2$	514.532	(1W) Ar^+ laser	515-685 (39, 1 → 39, 16)	s	$B\,{}^3\Pi_{o_u^+} \leftarrow X\,{}^1\Sigma_g^+$ (υ'~ 39, υ'=0, J=15)	Holzer et al., 1970a, b
	514.532	Ar^+ laser (single mode)	522.6-523.7 (R)		(J'=15± 2, J'' = 16 ± 2; J'= 38 ± 2, J''= 39± 2)	Dworetsky and Hozack, 1973a
	546.073	Hg arc lamp	556-760 (R)		(23, 1; 18, 17)	Plumley, 1933, 1934
C_2	501.716 514.532	Ar^+ laser (1.5W)	455-560 (R) 470-575 (R)	s s	$A\,{}^3\Pi_g \leftarrow X\,{}^3\Pi_u$ (υ' = 0,1) (υ' = 0,1)	Vear et al., 1972
CD_2O	308.2-353.5	(100kW peak) Pulsed, tunable laser (ruby + dye laser summed)	420 (20 nm bw) (U) 440 (20 nm bw) (U) 320-560 (U)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ (many levels populated)	Yeung and Moore, 1973
	313.9	(200 kW peak) Pulsed laser (ruby +573 nm dye laser summed)	422 (2 nm bw) (U)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ ($2^3_0\,4^1_0$ band)	Yeung and Moore, 1971
	347.2	(6 MW peak power) Doubled ruby laser	422 (2 nm bw) (U) 350-500 (R)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ (4^3_0 band)	Yeung and Moore, 1971, 1973
CH	425.0-435.0	Pulsed, tunable N_2 dye laser	425-435 (0, 0)	w	$A\,{}^2\Delta \leftarrow X\,{}^2\Pi$ (0, 0)	Barnes et al., 1973
CH_2O	326.2 329.6 353.2	(100 kW peak) Pulsed, tunable laser (ruby + dye laser summed)	420 (20 nm bw) (U) 440 (20 nm bw) (U) 420 (20 nm bw) (U)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ ($2^2_0 4^1_0$ band) ($2^1_0 4^3_0$ band) (4^1_0 band)	Yeung and Moore, 1973
	337.1	(100-200 kW peak) N_2 pulsed laser	420-500 (U)	s	$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ ($4^2_0 6^1_0$ band)	Sakurai et al., 1971b
	337.1	(200 kW peak) N_2 pulsed laser	350-700 (R) and (U)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ ($4^2_0 6^1_0$ band)	Aoki et al., 1973
CHDO	307.1-352.8	(100 kW peak) Pulsed, tunable laser (ruby + dye laser summed)	420 (20 nm bw) (U) 440 (20 nm bw) (U) 350-520 (U)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ (various levels populated)	Yeung and Moore, 1973
	337.1	(200 kW peak) N_2 pulsed laser	350-700 (R) and (U)		$\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ ($2^1_0 4^1_0$, $4^1_0 4^6_0$ levels)	Aoki et al., 1973

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, $\underline{\lambda_{vac}}$, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''		Reference
$^{35}Cl_2$	487.986	(1W) Ar^+ laser	500-550 (22,1→ 22,4)	w	$A\,^3\Pi_{0_u^+}\leftarrow X\,^1\Sigma_g^+$	(υ'=22, υ''=0; J=38 ± 1)	Holzer et al., 1970a,b
ClO_2	457.935	(0.032W) Ar^+	exciting line-700 (R)	s	$A\,^2A_2\leftarrow X\,^2B_1$	(1,2,0←0,1,0)*	Sakurai et al., 1971c;
	465.789	(0.025W) laser		s		(0,5,0←1,0,0)	Curl et al., 1973
	472.686	(0.08W)		s		(0,2,0←0,1,0)	
				w		(0,4,0←1,0,0)	
	476.486	(0.36W)		m,w		(0,0,0←0,0,0)	
	487.986	(0.8W)		m		(0,0,0←0,2,0)	$^*(\upsilon'_1, \upsilon'_2, \upsilon'_3\leftarrow\upsilon''_1,$
				m		(0,2,0←0,0,1)	
	496.507	(0.3W)		vw		(0,0,0←0,2,0)	$\upsilon''_2, \upsilon''_3)$
	501.716	(0.1W)		vw		(0,0,0←0,0,1)	
	476.486	(0.8W) Ar^+ laser, single and multi-mode	480-780 (R) (17 bands)	m	rotational states $23_{2,22}\leftarrow 24_{2,23}$; $38_{0,38}\leftarrow 37_{0,37}$)	(0,0,0←0,0,0;	Curl et al., 1973
CN	386.5-388.5	Pulsed dye laser	421.6 (10 nm bw) (U)	s	$B\,^2\Sigma^+\leftarrow X\,^2\Sigma^+$	(0,0)	Jackson, 1973
CO	$\underline{130.603}$	Oxygen atom line	228-280 (9,17→ 9,22)		$A\,^1\Pi\leftarrow X\,^1\Sigma^+$	(9,0;22,22)	Tilford et al., 1972
CO_2^+	$\underline{58.433}$	He microwave discharge	288-458 (R)		$A\,^2\Pi_u$, $B\,^2\Sigma_u^+$ $(CO_2^+)\leftarrow X\,^1\Sigma_g^+$ (CO_2)		Wauchop and Broida, 1971
CS	257.610	(0.1-0.5A) Mn^+ hollow cathode lamp	< 800 (U)		$A\,^1\Pi\leftarrow X\,^1\Sigma^+$	(0,0;8,7)	Silvers et al., 1970; Silvers and Chiu, 1972
	244.555	O^+ microwave discharge	< 650 (U)			(2,0;7,7)	
	244.58	CO^+ microwave discharge				(2,0)	
	244.618_2	(0.1A) Pd^+ hollow cathode lamp				(2,0;6,7)	
	244.618_8 257.726	(0.1A) Pb hollow cathode lamp				(2,0;6,7) (0.0;12,12)	
	257.610	(0.03A) Mn^+ hollow cathode lamp				(0,0;8,7)	
CS_2	280-350	(5 nm bandwidth) Xe lamp	350-612.5 (R) 430-650 (U)		Unassigned		Lambert and Kimbell, 1973
	337.1	(100 kW peak) N_2 pulsed laser	367.5-555 (U) 396,440,463,480,503,537, 570,614 (15 nm bw) (U)		Unassigned		Brus, 1971
Cs_2	457.935 472.686 476.486	Ar^+ laser	(U)		D or higher states		Baumgartner et al., 1970
	487.986	(1W)					
	487.986	(0.15W) Ar^+ laser	470-540,595-615,703-724		B or C States		McClintock and Balling, 1969
	632.816	He-Ne laser	703-724 (R)				
CuBr	487.986	Ar^+ laser	488-519.5 (0,0→ 0,4)		$A\leftarrow X\,^1\Sigma^+$	(0,0)	Capelle et al., 1973
CuCl	476.486	(0.25W) Ar^+ laser	476.5-506 (2,1→ 2,4)		$C\,^1\Sigma^+\leftarrow X\,^1\Sigma^+$	(2,1)	Capelle et al., 1973
D_2	$\underline{106.666}$	Ar microwave discharge	159-163 (4,14→4,15) (R) and (U)		$B\,^1\Sigma_u^+\leftarrow X\,^1\Sigma_g^+$	(4,0;6,5)	Akins et al., 1970; Becker and Fink, 1971; Fink et al., 1969,1972
H_2	$\underline{106.666}$	Ar microwave discharge (pressure broadened)	110-164 (3,1 →3,11) (R) and (U)	w	$B\,^1\Sigma_u^+\leftarrow X\,^1\Sigma_g^+$	(3,0;1,2)	Akins et al., 1970; Becker and Fink, 1971; Fink et al., 1969,1972

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, $\underline{\lambda_{vac}}$, nm		Fluorescence Reported, nm	Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
HD	$\underline{104.822}$	Ar microwave discharge	130-166 (5,6→5,15) (R) and (U) s	$B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ (5,0;2,3) H P. lamp	Akins et al., 1970; Becker and Fink 1971; Fink et al., 1969, 1972
			110-163 (6,1→6,15) (R) and (U) s	(6,0;5,6) L P. lamp	
			130-166 (5,6→5,15) (R) and (U) w	(5,0;5,4) press. broad. lamp	
	$\underline{106.666}$		110-165 (3,1→3,13) (R) and (U) s	(3,0;2,1)	
			151-163 (4,10→4,13) (R) and (U) w	(4,0;4,5) H P. lamp	
He_2	465.0	(1.5 MW peak) Pulsed, tunable dye laser	470.5 (J'=8, J''=9) (R)	$e^3\Pi_g \leftarrow a^3\Sigma_u^+$ (J'=8, J''=7)	Collins and Johnson, 1972
I_2	499.6-640	(1-5 kW peak) Pulsed, tunable, N_2 dye laser (95 wavelengths)	line - 650 (U)	$B^3\Pi_{0_u^+} \leftarrow X\ {}^1\Sigma_{0_g^+}$ (υ'~5 to ~70)	Capelle and Broida, 1973
	505-595.8	(1-5 kW peak) Pulsed, tunable, N_2 dye laser (17 wavelengths)	line - 650 (U)	(υ'=11-16,19,22,23,26, 38,45,55)	Capelle and Broida, 1972
	501.716 514.532	(0.05W) Ar^+ laser (1W)	507-650 (R) 520-650 (R)	(64,0;40,39) (62,0;27,26) (43,0;12,13) (43,0;16,15)	Holzer et al., 1970a; Yee and Miller, 1972
	501.716 514.532	Ar^+ laser	(R) 520-583 (43,1→43,11)	(?,0;27,26) (43,0;12,13) (43,0;16,15)	Menke, 1970; Halldorsson and Menke, 1970
	501.716	Ar^+ laser	507-629 (62,1 → 62,20)	(62,0;27,26)	Lobet et al., 1971; Yee and Miller, 1972
	501.716 514.532	Ar^+ laser	(R) (R)	(62,0;27,26) (43,0;12,13) (43,0;16,15)	Levenson and Schawlow, 1972
	508.582	Cd Osram lamp	(U)	(50,0;41,40) (49,0;8,9)	Chutjian et al., 1967; Yee and Miller, 1972
	508.582	Cd discharge lamp	510-650 (R)	(50,0;41,40) (49,0;8,9)	Steinfeld and Schweid, 1970; Yee and Miller, 1972
	514.532	Ar^+ laser	500-1300 (U)	(43,0;12,13) (43,0;16,15)	Ezekiel and Weiss, 1968; Yee and Miller, 1972; Reuben et al., 1973; Youmans et al., 1973
	514.532	Pulsed and cw Ar^+ laser	520-611 (43,1→ 43,15)	(43,0;11,12)* (43,0;15,14)* (45,0;63,64) (49,1;19,18) (50,1;38,39) (51,1;52,53)	Kurzel and Steinfeld, 1970; Kurzel et al., 1971
	514.532	Ar^+ laser (single mode)	520-858 (43,1→ 43,42)	(43,0;12,13) (43,0;16,15)	Dworetsky and Hozack, 1973b; Williams et al., 1974
	520.831 530.865 568.188 647.088	Kr^+ laser	(R)	(40,0;78,77)*(48,0;145,144) (50,0;152,151) (32,0;9,10)* (32,0;14,13)* (17,0;35,36)* (18,0;95,96)* (21,1;116,117) (21,1;122,121) (24,3;22,23) (26,3;111,112) (27,3;133,134) (11,7;99,98)* (12,7;137,138)*	Vigue and Lehmann, 1972
	520.831 530.865 568.188	Kr^+ laser	(R)	(40,0;79,78) (32,0;9,10) (21,1;116,117)?	Levenson and Schawlow, 1972
	528.689	Ar^+ laser	fluorescence reported	-	Dworetsky and Hozack, 1973c
	546.073	Hg low pressure arc	546-700 (25,0→25,19)	(25,0)	Arnot and McDowell, 1958
	546.073	(250W) Hg medium pressure arc	546-883 (25,0 → 25,37)	(25,0)	Polanyi, 1958
	546.073	(100W) Hg discharge lamp	(U)	(υ'=25,26,28)	Chutjian et al., 1967

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, λ_{vac}, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
I_2 (Con't)	546.073	Hg low pressure arc	552.5 - 691 (25, 1 → 25,19)		$B^3\Pi_{0_u}^+ \leftarrow X\,^1\Sigma_{0_g}^+$(25,0; 34,33)	Steinfield et al., 1965; Steinfield and Klemperer, 1965; Yee and Miller, 1972
	546.2 - 636.1	(1-5 kW peak) Pulsed, tunable, N_2 dye laser (17 wavelengths)	line - 650 (U)		(υ' = 0, 3-14, 17, 20, 24, 25, υ'' = 0)	Sakurai et al., 1971a
	568.188	Kr^+ laser (1W within cavity)	530 - 972 (R)	vs	(18,0;95,96) (17,0;36,37)	Sakurai and Broida, 1969a; Yee and Miller, 1972
	588.995 589.592	Na lamp	575-652.5 (15,0 → 15,9; 14,0 → 14,9; 16,0 → 16,9) 582-644 (14,0 → 14,9)		(15,2;44,43) (15,2;37,38) (14,1;106,107) (16,2;106,105) (14,1; 113,114)	Brown and Klemperer, 1964
	588.995 589.592	Na Osram lamp	(U)		(14,1;106,107) (14,1;113,114) (15,2;44,43) (15,2;37,38) (16,2; 106,105)	Chutjian et al., 1967
	632.816	He-Ne laser	601-806 (6,2 → 6,20; 11,1 → 11,11)		(6,3;32,33) (11,5;128,127)	Menke, 1970; Halldorsson and Menke, 1970
	632.816	He-Ne laser (intracavity cell)	593 → 695 (6,0 → 6,8; 11,0 → 11,12)	s	(6,3;32,33) (11,5;128,127)	Sakurai and Broida, 1970
	632.816	(0.080W) He-Ne laser	(R)		(6,3;32,33)* (11,5;128,127)	Kurzel et al., 1972
129 I_2	514.532	Ar^+ laser	(R)		$B^3\Pi_{0_u}^+ \leftarrow X^1\Sigma_{0_g}^+$ (51±1,0; 110,109) (53 ±1,1;68,67)	Levenson and Schawlow, 1972
	520.831 568.188	Kr^+ laser			(40, 0; 72, 71) (17,0; 19, 20)	
ICl	582-610	Pulsed, tunable dye laser	600-800 (U)	w	$A^3\Pi_1 \leftarrow X^1\Sigma^+$	Holleman and Steinfield, 1971
K_2	632.816	(0.050W) He-Ne laser	630-700 (7,0 → 7,17; 6, υ''; 8, υ'' progressions)	s, s, s	$B^1\Pi_u \leftarrow X^1\Sigma_g^+$ (7,0; 81,82) (6,0;17,18) (8,1;72,72)	*Tango et al., 1968*
	632.816	(0.001W) He - Ne laser	>640 (U)		(7,0;81,82) (6,0; 17,18) (8,1; 72,72)	Baumgartner et al., 1970
	694.3	(2MW peak) Pulsed ruby laser	620-900 (R) and (U)		(υ' ~ 11-16, υ'' ~ 20)	Abramov et al., 1968
KH	440-470 480-493	Pulsed, tunable N_2 dye laser	(R)		$A^1\Sigma^+ \leftarrow X^1\Sigma^+$($\upsilon'$=8-13, υ''=0)	Cruse and Zare, 1974
	487.986 496.507	cw Ar^+ laser	(7,0 → 7,4)	s vw	(7,0; 6,5)	Cruse and Zare, 1974

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, λ_{vac}, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
$^6Li_2$	476.486	Ar^+ laser	452-604 (9,2 → 9,19; 11,2 → 11,21)	s s	$B^1\Pi_u \leftarrow X^1\Sigma_g^+$ (9,3; 31,31) (11,5; 29,28)	Velasco et al., 1969; Ottinger et al., 1970; Ottinger and Poppe, 1971
	187.986		488-555 (1,0 → 1,7)	s	(1,0; 41,40)	
	514.532		478-555 (1,0 → 1,7; 3,0 → 3,8)	s, s	(1,3;41,40) (3,4;45,46)	
$^6Li\,^7Li$	476.486	Ar^+ laser	468.5-572 (5,1 → 5,13)	s	(5,2; 9,8)	
	496.507		496.5-544 (0,0 → 0,5)	s	(0,0; 45,45)	
$^7Li_2$	476.486	Ar^+ laser	469-571 (4,0 → 4,12)	s	(4,1; 24,24)	
	487.986		480-550 (2,0 → 2,8)	s		
	514.532		470-596 (3,0 → 3,8; 9,3 → 9,18; 7,0 → 7,18)	s, s s	(3,5;30,29) (9,9;30,37) (7,7;61,61)	
Na_2	457.935	(0.02 W) Ar^+ laser	470-560 (R)		$B^1\Pi_u \leftarrow X^1\Sigma_g^+$ (27, υ'';27, J'')	Demtroder et al., 1969;
	465.789	(0.02 W)		m	(17,4; 37,38)	
	472.686	(0.02 W)		s, w, w	(9,1;38,37) (19,7;50,50) (13,4; 10,9)	Bergmann and Demtroder, 1972
	476.486	(0.03 W)		vs, s, w	(10,3;12,13) (6,0;27,28) (10,1; 91,91)	
	487.986	(0.3 W)		vs, m, m, m, w	(6,3;43,43)(10,6;42,41) (7,2;99,99) (9,5;56,55) (15,7; 97,98)	
	496.507	(0.025W)		m, w	(7,6;43,44) (8,7;28,29)	
	501.716	(0.02 W)		m	(5,6;37,38)	
	514.532	(0.3 W)		m, m, m, w	(11,14;49,49) (2,6;84,85) (9,12;63,64) (9,11;96,97)	
	465.789 472.686 476.486 487.986 (1W)	Ar^+ laser	480-560 (U)		$B^1\Pi_u - X^1\Sigma_g^+$ (17,4;37,38) (9,1;38,37) (10,3;12,13) (6,3;43,43)	Baumgartner et al., 1970
	476.486	(0.15W) Ar^+ laser	534 (0.5 nm bw) (U)	vs	(10,3;12,13) (6,0;27,28) (10,1;91,91)	McClintock et al., 1969
	476.486	Ar^+ laser	512-535 (10,13 → 10,19; 6,10 → 6,15)	vs, s	(10,3;12,13) (6,0;27,28)	Sinha et al., 1973
	487.986	(1W) Ar^+ laser	528.8 (6,14) (R)		(6,3; 43,43)	Bergmann and Demtroder, 1971
	487.986	(0.4W) Ar^+ laser	477-560 (6,0 → 6,20) 525 ± 0.5 (U)		(6,3;43,43)	Drullinger and Zare, 1969, 1973
	632.816	(0.025W) He-Ne laser	590-850 (16,0 → 16,17; 14,0 → 14,19)	s s	$A^1\Sigma_u^+ - X^1\Sigma_g$ (14,2;44,45) (16,4;16,17)	Johnson et al., 1970
	640.107	(0.01W)	(11,0 → 11,23)	s w	(11,0;72,73) (20,8;52,51 or 46,47)	
NaK	487.986	(0.5W) Ar^+ laser	470-580 (R)		$D^1\Pi - X^1\Sigma$ (υ', υ'' = 7,1;10,3; 12,4;15,6;24,10;26,11; 28,12)	Alzetta et al., 1973
	496.507				(υ', υ'' = 4,2;7,4;10,6;13,8; 17,10;24,13)	
	501.716				(υ', υ'' = 3,3;6,5;9,7;15,11; 16,11)	
	514.532	(0.86W)	500-560 (R)		(υ', υ'' = 1,6;4,8;7,10; 10,12;13,14)	
	568.188	Kr^+ laser	565-770 (R)		$B^1\Sigma$, $C^1\Pi - X^1\Sigma$	

- · Main excitation
- s strong; m, medium; w, weak; vw, very weak intensities
- (U) spectrally unresolved; (R), resolved
- bw bandwidth; EDL, electrodeless discharge lamp
- kG kilogauss magnetic field required to Zeeman shift into coincidence

Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, $\underline{\lambda_{vac}}$, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
NaLi	496.507	Ar^+ laser	495-560 (R) (progression υ''=0-10)		$B^1\Pi - X^1\Sigma^+$ (υ',0;28,29)	Hessel, 1971; Vidal and Hessel, 1972
NO	$\underline{196.090}$	(3kG)(1000W) Se	196-365 $(3,0\rightarrow 3,14\ \gamma)$	m	$A^2\Sigma^+ - X^2\Pi$ (3,0;1,5/2)	Melton, 1971; Melton and Klemperer, 1973
	203.985	(13,17kG) 27 MHz EDL	205-355 $(2,0\rightarrow 2,12\gamma)$	w	(2,0;25,47/2)	
	206.279	(18kG)	210-500 $(3,0\rightarrow 3,17\beta)$	w	$B^2\Pi - X^2\Pi$ (3,0; 5,13/2) (3,0; 10,19/2)	
	202.551	(>20kG) (1000W) Zn^+	205-470 $(4,0\rightarrow 4,17\ \beta)$	m	(4,0;6,13/2) (4,0;11,23/2)	
	206.191	(20kG) 27 MHz EDL	210-500 $(3,0\rightarrow 3,17\beta)$	m	(3,0;3,9/2) (3,0;8,15/2)	
	204.169	(1000W) Ge	205-355 $(2,0\rightarrow 2,12\gamma)$	vw	$A^2\Sigma^+ - X^2\Pi$ (2,0; K',J'')	
	204.376	27 MHz EDL	205-355 $(2,0\rightarrow 2,12\ \gamma)$	vw	(2,0; K', J'')	
	225.600	(2kG)	226-320 $(0,0\rightarrow 0,7\ \gamma)$	m	(0,0; 16,31/2)	
	205.293	(19kG) (1000W) Hg^+	205-355 $(2,0\rightarrow 2,12\ \gamma)$	w	(2,0;10,23/2) (2,0;11,25/2)	
	226.223	(16,20kG) 27 MHz EDL	226-320 $(0,0\rightarrow 0,7\ \gamma)$	w	(0,0;1,5/2) (0,0;14,31/2)	
	213.856	Zn (90W) 2450 MHz EDL	215-387 $(1,0\rightarrow 1,12\gamma)$		(1,0;19,35/2) (1,0;23,45/2) (1,0;29,59/2)	Broida and Carrington 1963; Poland and Broida 1971a,b
	214.438	Cd^+ 2450 MHz EDL	215-387 $(1,0\rightarrow 1,12\ \gamma)$		(1,0;13,25/2)	
	213.856	(18kG) (1000W) Zn 27 MHz EDL	215-345 $(1,0\rightarrow 1,10\ \gamma)$	m	(1,0; 29, 59/2)	Melton, 1971; Melton and Klemperer, 1973
	214.281	(12,21kG) (1000W) Te	215-345 $(1,0\rightarrow 1,10\ \gamma)$	m	(1,0;22,45/2)	
	214.725	(2kG) 27 MHz EDL	215-345 $(1,0\rightarrow 1,10\ \gamma)$	m	(1,0;10,21/2)	
	225.903	(13,18kG)	226-320 $(0,0\rightarrow 0,7\ \gamma)$	m	(0,0; 7,11/2) (0,0;10,19/2)	
	226.553	(18kG)	226-320 $(0,0\rightarrow 0,7\ \gamma)$	m	(0,0;10,19/2)	
	214.438	(11,21kG) (1000W) Cd^+	215-345 $(1,0\rightarrow 1,10\gamma)$	s	(1,0; 13,25/2)	
	226.502	(17kG) 27 MHz EDL	226-320 $(0,0\rightarrow 0,7\ \gamma)$	s	(0,0; 11,21/2)	
	214.438	Cd^+ discharge lamp	214-300 $(1,0\rightarrow 1,7\gamma)$		(1,0; 13, 25/2)	Gouedard and Lehmann, 1970
	214.438	Cd^+ 2450 MHz EDL	215-330 $(1,0\rightarrow 1,9\gamma)$		(1,0; 13,25/2)	German et al., 1971
	214.725	Te 2450 MHz EDL	226-268 $(1,5\ \gamma)$ 230-420 (U)		(1,0; 10,21/2)	Weinstock et al., 1972
	226.345 226.909 226.921	(1000W) Al 27 MHz EDL	226-320 $(0,0\rightarrow 0,7\ \gamma)$	w	(0,0)	Melton, 1971; Melton and Klemperer, 1973
$^{15}N^{16}O$	$\underline{191.379}$	(1-2kG) (1000W) Se	192-250 $(0,0\rightarrow 0,7\ \delta)$	w	$C^2\Pi - X^2\Pi$(0,0)	Melton, 1971; Melton and Klemperer, 1973
	$\underline{191.919}$	(1-2kG) 27 MHz EDL	192-250 $(0,0\rightarrow 0,7\delta)$	w	(0,0)	
	$\underline{196.090}$	(4kG)	196-365 $(3,0\rightarrow 3,14\gamma)$	m	$A^2\Sigma^+ - X^2\Pi$ (3,0;2,5/2) (3,0;3,7/2)	
	225.903	(1000W) Te 27 MHz EDL	226-320 $(0,0\rightarrow 0,7\gamma)$	m	(0,0,17,31/2)	
	226.502	(17kG) (1000W) Cd^+ 27 MHz EDL	226-320 $(0,0\rightarrow 0,7\gamma)$	s	(0,0;12,23/2)	

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(U) spectrally unresolved; (R), resolved
bw bandwidth; EDL, electrodeless discharge lamp
kG kilogauss magnetic field required to Zeeman shift into coincidence

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, $\underline{\lambda_{vac}}$, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ", J', J"	Reference
NO_2	404.656 407.783	(500W)Hg high pressure lamp	462-700(U), 436-785 (5-7.5 nm bw) (U)	s	-	Myers et al., 1966; Keyser et al., 1971
	435.833		462-700 (R) and (U), 470-785 (5-7.5 nm bw) (U)	s	-	
	546.073		570-700(R) and (U), 599-785 (5-7.5 nm bw) (U)	m	-	
	576.960 579.066		594-700 (U), 635-785 (5-7.5 nm bw) (U)	m	-	
	404.656 407.783 435.833 546.073 576.960 579.066	Hg high pressure lamp	470-785 (10 wavelengths with 5-10 nm bw) (U)		-	Keyser et al., 1968
	422.0	(10kW peak) Pulsed, tunable, N_2 dye laser	430-700 (U)		Unassigned	Sakurai and Capelle, 1970
	451.0		490-700 (U)			
	484.0		500-700 (U)			
	520.0		-	vw		
	604.0		-	vw		
	436.5	Frequency doubled, Raman shifted, ruby laser	475 (20 nm bw), > 480, > 630 (U)		$^2B_1 \leftarrow \tilde{X}\ ^2A_1$	Sidebottom et al., 1972
	440-490	Pulsed, tunable, dye laser	520-750, 610-750 (U)		-	Sackett and Yardley, 1970
	451.5-460.5	Pulsed, tunable, dye laser	520-750, 610-750, 660-750 (U)		-	Sackett and Yardley, 1972
	454.4-455.0	Pulsed, tunable, dye laser	520-750 (U)		-	Sackett and Yardley, 1971
	457.935 465.789 472.686 476.486 487.986 496.507 501.716 514.532	Ar^+ laser (0.15W) (5W within cavity)	line-750 (bands and continuum) (R)		Continuous and discrete spectral features over whole range	Sakurai and Broida, 1969b
	461.915 476.243 520.831	Kr^+ laser	line-750 (bands and continuum) (R)			Sakurai and Broida, 1969b
	487.986	(0.25W) Ar^+ laser	505-550 (R)	s	$^2B_2 \leftarrow \tilde{X}\ ^2A_1$ (N' = 9, K' = 4 ν_2 bending mode excited)	Abe et al., 1971
	514,532	(0.25W)	535-585 (R)	s		
	487.986	(0.25W) Ar^+ laser	700-830 (U)			Tucker et al., 1973
	514.532	Ar^+ laser	495-496, 534-536.5 (R)	s	$^2B_2 \leftarrow \tilde{X}\ ^2A_1$ (Difficult to assign, one transition to $^2B_1$ state from 000 ground state)	Abe, 1973
	632.816	He-Ne laser	-	w		
	532.4	(1MW peak) Frequency doubled, pulsed Nd laser	570 (40 nm bw), > 570, > 600 (U)		$^2B_1 \leftarrow \tilde{X}\ ^2A_1$	Sidebottom et al., 1972
	593.4-594	Pulsed dye laser	594-733 (R) 610-650 (U)		$^2B_2 \leftarrow \tilde{X}\ ^2A_1$ (Weak fluorescence also from $^2B_1$, no continuum observed)	Stevens et al., 1973
	593.6	(0.05W) cw tunable, dye laser	~ 620 (U) (band to $\upsilon_2'' = 1$)		$^2B_2 \leftarrow \tilde{X}\ ^2A_1$ (N'=9, K'=0, J'=17/2, 19/2; $10_{0,10}$, J"=19/2, 21/2) (N'=8, K'=1, J'=15/2, 17/2; $9_{1,9}$, J"=17/2, 19/2)	Tanaka et al., 1973

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bw bandwidth; EDL, electrodeless discharge lamp
kG kilogauss magnetic field required to Zeeman shift into coincidence

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, λ_{vac}, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ", J', J"	Reference
NO_2(Cont)	647.088	(0.6W) Kr^+ laser	647-855(R)	s	$^2B_2 \leftarrow \tilde{X}\,^2A_1$ $(\nu'_1, \nu'_2, \nu'_3; \nu''_1, \nu''_2, \nu''_3$ 0, 5, 0; 0, 0, 0)	Brand et al., 1973a
	694.3	Pulsed ruby laser	> 720 (U)		$^2B_1 \leftarrow \tilde{X}\,^2A_1$	Sidebottom et al., 1972
NS	230.424	Ba^+ discharge lamp	fluorescence from various K'levels		$C^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ (0,0)	Silvers and Chiu, 1973
OD	307.158	Ba 2450 MHz flowing EDL	230-420 (U)		$A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0;1,3/2,1,3/2) (υ'υ";K'J', K"J")	German et al., 1973; Weinstock and Zare, 1973
OH	282.17 282.58	Pulsed, frequency double, ruby-dye laser	303-315 (0,0) (R)		$A^2\Sigma^+ \leftarrow X^2\Pi$ (υ',υ";K', J', K", J"; 1,0;0,1/2,1,3/2) (1,0;1,3/2, 2, 5/2)	Baardsen and Terhune, 1972; Wang, 1974; Wang and Davis, 1974
	306.766 306.767 306.775 306.776	Bi 2450 MHz EDL	(R)		(0,0;11, 21/2, 10, 19/2) (0,0; 10,19/2, 9, 17/2)	Carrington, 1959, 1960
	306.772	(15mA, 3W) Bi hollow cathode lamp	310 ± 10 (U)		(0,0;11, 21/2, 10, 19/2) (0,0,10, 19/2, 9, 17/2)	Hooymayers and Alkemade, 1967
	300-320	Frequency doubled, pulsed, tunable, dye laser	(0,0) (R)		(0,0)	Becker et al., 1972, 1974
	307.206	Zn 2450 MHz, heated EDL	308 ± 5, 230-420 (U)		(0,0;2,3/2,1,3/2)	German and Zare, 1969a, b; German et al., 1973; Weinstock and Zare, 1973
Pb_2	496.507	(0.5W) Ar^+ single	496.5-520 (4,0 → 4,8)	s	B ← X (4,0)	Johnson, 1971;
	514.532	(1W) mode laser	490-520 (3,0→3,7; 5,0 → 5,9)	s	(3,5) (5,8)	Johnson et al., 1972a
	647.088	(0.3W) Kr^+ laser	630-670 (6,0 → 6,4; 8,0 → 8,7)	s	A ← X (6,0) (8,3)	
	Excited by most lines of Ar^+ and Kr^+ lasers					
PbBr	476.486	(0.25W) Ar^+ laser	462-532 (5,0 → 5,22)	w	$A \leftarrow X^2\Pi_{1/2}$ (5,3)	Capelle et al., 1973
	514.532	(1W)	496-540 (0,2 → 0,14)	w	(0,7)	
PbCl	461.915	(0.01W) Kr^+ laser	449-540 (2,0 → 2,13)	w	$A \leftarrow X^2\Pi_{1/2}$ (2,2)	Capelle et al., 1973
	487.986	(1W) Ar^+ laser	449-540 (2,0 → 2,13)	w	(2,6)	
	496.507	(0.5W)	444-534 (3,0 → 3,13)	w	(3,8)	
	514.532	(1W)	464-546 (0,1 → 0,12)	w	(0,8)	
PbO	420-455	Pulsed, tunable, N_2 dye laser	440-550 (R)	s	$B1 \leftarrow X^1\Sigma^+$ (0,0) (1,1) (3,0)	Johnson, 1971
Rb_2	457.935	Ar^+ laser	(U)		$C \leftarrow X^1\Sigma_g^+$	Baumgartner et al., 1970
	465.789				$B^1\Pi_u$, $C \leftarrow X^1\Sigma_g^+$	
	472.686				$B^1\Pi_u \leftarrow X^1\Sigma_g^+$	
	487.986	(1W)			$B^1\Pi_u \leftarrow X^1\Sigma_g^+$	

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, λ_{vac}, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
Rb_2(Cont)	487.986	(0.15W) Ar^+ laser	593-608 (3 bands resolved)		$B^1\Pi_u \leftarrow X^1\Sigma_g^+$	McClintock and Balling, 1969
	694.3	Pulsed ruby laser	680-725 (R), 720-900 (U)		$B^1\Pi_u \leftarrow X^1\Sigma_g^+$ (υ' ~2-6, υ'' ~6-10)	Kostin et al., 1972
S_2	292.863 293.651	Mg^+ spark source	286-375 (8,0 → 8,2) (R) and (U)		$B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ (8,1; K'=37,41)	Durand, 1940
	307.590 326.106	Zn discharge lamps Cd	300-586 (4,0 → 4,25) 303-562 (3,0 → 3,23)		(4,1; K', J', 40, 41, K'', J'', 41, 42) (3,3; 42, 43, 43, 44)	Meyer and Crosley, 1973a,b,c; Yee et al., 1972
	312.567 313.155 313.184 334.148 365.015	Hg lamp	?		(5,1; 70, 69 or 70; 69, 68 or 69) (5,1; 68, 67 or 68; 69, 68 or 69) (4,2; 14, 13, 13, 12) (1,3; 30, 29, 29, 28) (0,6; 30, 30, 29, 29)	Meyer and Crosley, 1974
	514.532	Ar^+ laser	306-531 (4,1 → 4,22)	w	(4,21; 42, 41, 39, 40)	
$^{78}Se_2$	476.486	Ar^+ laser	(R)	w	$B^3\Sigma_u^-(0_u^+) \leftarrow X^3\Sigma_g^-(0_g^+)$ (1,13; ~155, ~156)	Yee and Barrow, 1972a
	487.986		(R)	s	$(1_u) \leftarrow (1_g)$ (2,13; 67, 66)	
				m	$(0_u^+) \leftarrow (0_g^+)$ (1,15; 55, 56)	
				m	$(1_u) \leftarrow (1_g)$ (2,14; ~115, ~114)	
	514.532		483.5-586.5 (0,4 → 0,16)	w	n ← a (0,8; ~54, ~55)	
$^{80}Se_2$	476.486	(0.1W) Ar^+ laser	417.5-502 (0,4 → 0,15)	s	$B^3\Sigma_u^-(1_u) \leftarrow X^3\Sigma_g^-(1_g)$ (0,12; 16, 15)	Beattie et al., 1970; Barrow et al., 1971
	487.986	(0.5W)	407.0-588 (1,3 → 1,24)	s	$(1_u) \leftarrow (1_g)$ (1,14; 39, 38)	
	487.986	Ar^+ laser	460.5-656 (2,2 → 2,24)	w	n ← a (2,6; ~30, ~29)	Yee and Barrow, 1972a
	496.507		(R)	s	$B^3\Sigma_u^-(0_u^+) \leftarrow X^3\Sigma_g^-(0_g^+)$ (0,15; 131, 130)	
				w	$(1_u) \leftarrow (1_g)$ (0,13; ~176, ~175)	
	501.716		(R)	w	$(0_u^+) \leftarrow (0_g^+)$ (1,16; ~149, ~148)	
				w	$(1_u) \leftarrow (1_g)$ (0,14; ~153, ~154)	
	514.532		(R)	w	$(0_u^+) \leftarrow (0_g^+)$ (5,21; 59, 58)	
				s, w	$(1_u) \leftarrow (1_g)$ (0,16; 95, 94) (4,19; 41, 40)	
SO_2	209.986	Zn^+ high voltage	212-245 (R)	s	$B_2 \leftarrow \tilde{X}\,^1A_1$ $(J_{K_{-1}K_1}\ 11_{1,10} \leftarrow 12_{1,11})$	Brand et al., 1973b
	210.221	AC discharge lamp	215-239 (R)	w	$(17_{5,12} \leftarrow 16_{5,11})$	
	213.856	Zn	214-245 (R)	s	$B_2 \leftarrow \tilde{X}\,^1A_1$	
	213.856	Zn (15W) Osram	290-400 (U)			Okabe et al., 1973
	228.802	Cd discharge lamp	290-400 (U), 230-420 (R)			
	215.24	D_2 flash lamp (0.081 nm bw)	(U)	vw	$\tilde{D} \leftarrow \tilde{X}\,^1A_1$ $\nu_1', \nu_2', \nu_3'; \nu_1'', \nu_2'', \nu_3''$; 0,6,0; 0,0,0)	Hui and Rice, 1972
	216.93			vw	(0,5,0; 0,0,0)	
	218.78			vw	(0,4,0; 0,0,0)	
	220.63			m	(0,3,0; 0,0,0)	
	222.41			m	(0,2,0; 0,0,0)	
	224.3			s	(0,1,0; 0,0,0)	

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Table II. Line-Induced Electronic Fluorescence of Molecules in the Gaseous Phase

Species	Exciting Line λ_{air}, $\underline{\lambda_{vac}}$, nm		Fluorescence Reported, nm		Quantum States Involved in Absorption; υ', υ'', J', J''	Reference
SO_2(Cont)	225.8			s	$\tilde{C}-\tilde{X}\,^1A_1$ (1,3,0; 0,0,0)	
	226.09			s	$\tilde{D}-\tilde{X}\,^1A_1$ (0,0,0; 0,0,0)	
	227.71			s	$\tilde{C}-\tilde{X}\,^1A_1$ (1,2,0; 0,0,0)	
	229.75			s	(1,1,0; 0,0,0)	
	230-320	Frequency doubled, pulsed, tunable dye laser	311	s		Morey and Penney, 1973
	260-320	Frequency doubled, pulsed, tunable, doubled Nd. Yag dye laser	310-450 (U)		$\tilde{A}\,^1B_1 \leftarrow \tilde{X}\,^1A_1$	Brus and McDonald, 1973
	265 275 285 296 302 313	(1000W) Hg. Xe lamp	line-470 (R)		$\tilde{A}\,^1B_1 - \tilde{X}\,^1A_1$	Mettee, 1968
	266.2	4th harmonic, pulsed Nd laser	295-345, 295-395, 365-395 (U)		$\tilde{A}\,^1B_1 \leftarrow \tilde{X}\,^1A_1$	Sidebottom et al., 1972
	289.36 296.73 302.15 312.57-313.18	(1000W) Hg discharge lamp	300-525 (R)		$\tilde{A}\,^1B_1 - \tilde{X}\,^1A_1$	Strickler and Howell, 1968
$^{128}Te_2$	476.486	Ar^+ laser	(R)	s	B $0_u^+ \leftarrow$ X 0_g^+ (2,6;77,76)	Yee and Barrow, 1972b
	487.986		(R)	s	A $0_u^+ \leftarrow$ X 0_g^+ (10,1; 79, 78)	
			(R)	w	B $0_u^+ \leftarrow$ X 0_g^+ (0,6; ~177, ~176)	
	496.507		(R)	w	A $0_u^+ \leftarrow$ X 0_g^+ (9,1; ~163, ~164)	
	501.716		(R)	m	A $0_u^+ \leftarrow$ X 0_g^+ (11,4; 31,32)	
			468-590 (3,5 → 3,24)	s	B $0_u^+ \leftarrow$ X 0_g^+ (3,11;97,96) (3,11; 85,86)	
	514.532		457.5-576.5 (0,1 → 0,20)	s	B $0_u^+ \leftarrow$ X 0_g^+ (0,11;91,92)	
			535-641 (0,5 → 0,18)	w	B $0_u^+ \leftarrow$ X 1g (υ' = 0)	
$^{130}Te_2$	441.563	(0.05W) He. Cd^+ laser	437-670.5 (5,0 → 5,35)		B $0_u^+ \leftarrow$ X 0_g^+ (5,1;103,102)	Degenkolb et al., 1971
	487.986	Ar^+ laser	(R) ($B0_u^+ \rightarrow X0_g^+$) 549-604 (0,7 → 0,14 $B0_u^+ \rightarrow X1_g$)		B $0_u^+ \leftarrow$ X 0_g^+ (0,6;~177,~176)	Yee and Barrow, 1972b

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* Main excitation
s strong; m, medium; w, weak; vw, very weak intensities
(U) spectrally unresolved; (R), resolved
bw bandwidth; EDL, electrodeless discharge lamp
kG kilogauss magnetic field required to Zeeman shift into coincidence

INFRARED FLUORESCENCE EXCITED BY MONOCHROMATIC SPECTRAL LINE SOURCES

In principle, three possible techniques may be invoked using infrared fluorescence. The most straight-forward and obvious entails absorption in for example one part of the fundamental band with subsequent detection of radiation from another. In various instances P branch laser lines have been used as the exciting source with detection in part of the R branch, which is isolated with an interference filter. Polyatomic systems offer the possibility that the initially produced state may either be partially relaxed to an intermediate state, which then fluoresces, or have an additional allowed radiative transition. The third possibility invokes energy transfer from the vibrationally excited state, initially produced, to another species which then radiates. Such processes as

$$HCl\ (\upsilon=1) + HCl\ (\upsilon=1) \rightarrow HCl\ (\upsilon=2) + HCl\ (\upsilon=0)$$

$$CO\ (1) + CO\ (1) \rightarrow CO\ (2) + CO\ (0)$$

cannot be exploited at the very low concentrations being considered here. However, at higher concentrations such energy level climbing mechanisms are frequently observed and can produce fluorescence at much shorter wavelengths than that of the excitor. For a polyatomic species such as CH_3F or CH_3Cl, such mechanisms are so fast that a rapid equilibration occurs amongst all of the vibrational modes, somewhat contracting the benefits of single-mode excitation. Only the direct approach of excitation followed by the normal fluorescence process would appear feasible for the current application.

The first laser excited vibrational relaxation studies were reported eight years ago (Hocker and Kovacs, 1966; Yardley and Moore, 1966), from which time the field has become increasingly active, interest centering particularly on energy exchange processes. Table III has been compiled to illustrate the extent of the work that has already been accomplished with line excited infrared fluorescence. This is a fairly complete and up-to-date listing of the various reported investigations and illustrates among other things the potential line sources that have been most used.

For many such systems, owing to the long radiative lifetimes of the vibrational levels in the ground electronic state, the fluorescence efficiency is much reduced and intensities generally are quite weak. This coupled to the fact that opto-electronic radiation detectors in the infrared do not have the sensitivity of uv-visible photomultipliers, makes it appear unlikely that infrared fluorescence is exploitable as a sensitive detection technique particularly for sub ppm concentration levels. Another factor to be considered concerns the more demanding requirements for spectral coincidences in this region. Doppler broadened linewidths in the infrared are very narrow at room temperatures, for example, lines in the fundamental NO band at around 5.3 μm have a Doppler width of about 0.004 cm^{-1}. Pressure broadening is more important in this spectral region and at atmospheric pressure can be an order of magnitude larger (Ludwig et al., 1973). However, at stratospheric pressures of 10 to 100 torr, pressure broadening is much reduced, although still evident to some extent, and the requirements for a coincidence between exciting and absorbing lines can be quite severe. In order to predict spectral coincidences, it is of course necessary to have sufficiently accurate spectroscopic data. In this instance it has to be characterized to better than a few hundredths of a wavenumber and refer to vacuum conditions. For example, the frequency doubled CO_2 laser line ($00^01 \rightarrow 10^00$ band, P(8)) at 1909.092 cm^{-1} appears to be in better coincidence with the $NO\ {}^2\Pi_{1/2}$ (1, 0) R(19/2) line if the wavelength for this is taken from James and Thibault's (1964) analysis (1909.139), rather than that of Shaw (1956) (1909.16). Although this coincidence has been used by Stephenson (1973a) to study vibrational relaxation in NO, the coincidence may not be sufficiently close, or limited only to the wings of the absorption line at low pressures. It is not unreasonable therefore, to expect that the fluorescence intensity may be strongly pressure dependent.

Generally, laser line wavelengths have been taken from the tabulations of Willett (1971) or the CRC Handbook of Lasers (Pressley, 1971). In many instances through more accurate values now are available, particularly for various CO_2 (Chang, 1970; Schiffner, 1972), CO (Mantz et al., 1970; Yardley, 1970b; Eng et al., 1974; Roh and Rao, 1974), and N_2O (Sokoloff and Javan, 1972) laser lines. As an illustration of the rapidity of growth of the laser field, 200 additional CO infrared lasing lines already can be added to the 1971 CRC Handbook of Lasers compilation.

Table III. Infrared Fluorescence Excited by Monochromatic Spectral Line Sources

Species	Exciting Source $\lambda_{vac\,\mu m}$, $(1/\lambda_{vac} cm^{-1})$	Fluorescence Monitored $\lambda_{\mu m}$, $(1/\lambda\ cm^{-1})$	Quantum States Involved in Absorption	Reference
CH_3Cl	9.603573 (1041.2791) P(26) CO_2 Q-switched laser	$\sim$ 13 ($\sim$770) ν_3 band $\sim$ 3* ($\sim$ 3300) ν_1, ν_4 bands - weak	$\tilde{X}\,^1A_1$ (coincidences in ν_6 band)	Lee and Ronn, 1973; Knudtson and Flynn, 1973b
	9.603573 (1041.2791) P(26) CO_2 Q-switched laser	$\sim$7.4* ($\sim$1350) ν_2 band $\sim$3* ($\sim$3300) ν_1, ν_4 bands	$\tilde{X}\,^1A_1$ (coincidences in ν_6 band)	Grabiner and Flynn, 1974
CH_3F	9.552428 (1046.8542) P(20) CO_2 TEA laser (CO_2-N_2-He mixture)	$\sim$ 3.4* ($\sim$2940) ν_1, ν_4 bands	$\tilde{X}\,^1A_1$ (coincidences in ν_3 band)	Karny et al., 1972
	9.552428 (1046.8542) P(20) CO_2 Q-switched laser	$\sim$3.4* ($\sim$2940) ν_1,ν_4 bands	$\tilde{X}\,^1A_1$ (coincidences in ν_3 band)	Weitz et al., 1972; Weitz and Flynn, 1973a; Grabiner et al., 1973
	9.50-9.67 (1033-1052) P(14)-P(34)	No fluorescence except with P(20) line		
	9.552428 (1046.8542) P(20) 3.5W CO_2 Q-switched laser	$\sim$ 3.3* ($\sim$ 3030) ν_1, ν_4 bands $\sim$ 6.7* ($\sim$ 1495) ν_2, ν_5 bands $\sim$ 8.6* ($\sim$ 1160) ν_6, band $\sim$ 4.8* ($\sim$ 2080) $2\nu_3$ overtone $\sim$ 4.5* ($\sim$ 2220) $\nu_3 + \nu_6$ combination	$\tilde{X}\,^1A_1$ (coincidences in ν_3 band)	Weitz and Flynn, 1973b
$^{13}CH_3F$	9.657416 (1035.4736) P(32) CO_2 Q-switched laser	$\sim$ 3.4* ($\sim$2940) ν_1, ν_4 bands	$\tilde{X}\,^1A_1$ (coincidences in ν_3 band)	Weitz et al., 1972
CH_4	1.6451 (6078) Er: Yag laser	Absorption noted	$\tilde{X}\,^1A_1$ (coincidence with R(6) $2\nu_3$ overtone band)	White and Schleusener, 1972; Fox, 1974
	3.3922 (2947.90) 10 mW He-Ne laser	$\sim$ 7.7 ($\sim$ 1300) (U) ν_4 band 3.12-3.38 (2960-3200) ν_3 band	$\tilde{X}\,^1A_1$ (coincidence with P(7) ν_3 band)	Yardley and Moore, 1966, 1968 a,b; Yardley et al., 1970
C_2H_4	10.233167 (977.2146) R(22) CO_2 laser 10.532080 (949.4800) P(14) 10.653156 (938.6890) P(26)	Strong absorption noted	$\tilde{X}\,^1A_g$ (coincidences in ν_7 band)	Hanst, 1971
	10.513114 (951.1930) P(12) cw CO_2 laser 10.532080 (949.4800) P(14) 10.551387 (947.7427) P(16) 10.571037 (945.9810) P(18) 10.591035 (944.1948) P(20) 10.611385 (942.3841) P(22) 10.632090 (940.5488) P(24) 10.653156 (938.6890) P(26) 10.674586 (936.8045) P(28) 10.696386 (934.8952) P(30) 10.718560 (932.9611) P(32) 10.741113 (931.0022) P(34)	$\sim$ 3* ($\sim$ 3330) ν_9,ν_{11} bands $\sim$5* ($\sim$2000) $\nu_7+\nu_8$, $\nu_6+\nu_{10}$ combinations	$\tilde{X}\,^1A_g$ (coincidences in ν_7 band)	Robinson and Dake, 1973a,b
	10.571037 (945.9810) P(18) 50W CO_2 laser (CO_2-N_2-He mixture) 10.591035 (944.1948) P(20)	9.9-11.2 (890-1010) (R) ν_7 band	$\tilde{X}\,^1A_g$ (coincidences in ν_7 band)	Ronn, 1968
	10.6 (940) cw CO_2 laser	$\sim$ 10.5 (950) ν_7 band $\sim$ 6.9* (1440) ν_{12} band $\sim$ 3.3* (2990) ν_{11} band $\sim$ 3.2* (3105) ν_9 band	$\tilde{X}\,^1A_g$ (coincidences in ν_7 band)	Bailey et al., 1971

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* Involves multiphoton absorption or, more generally, energy transfer collisions to populate these higher energy levels.

s,m,w. strong, medium, weak fluorescence.

(U), (R) unresolved, resolved.

FWHM filter characteristic, full width at half maximum transmission.

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Table III. Infrared Fluorescence Excited by Monochromatic Spectral Line Sources

Species	Exciting Source $\lambda_{vac\,\mu m}$, $(1/\lambda_{vac}\,cm^{-1})$	Fluorescence Monitored $\lambda_{\mu m}$, $(1/\lambda\ cm^{-1})$	Quantum States Involved in Absorption	Reference
C_2H_4 (Cont)	10.653156 (938.6890) P(26) CO_2 cw and Q-switched laser	~ 5* (1890) $\nu_7+\nu_8$, $\nu_6+\nu_{10}$ combination (U) 3.22* (3105) ν_9 band (U) 3.34* (2990) ν_{11} band (U) 4.99* (2000) $\nu_6+\nu_{10}$ combination (R) 5.25* (1905) $\nu_7+\nu_8$ combination (R)	$\tilde{X}\ ^1A_g$ (coincidences in ν_7 band)	Yuan and Flynn 1972, 1973
	10.84101 (922.423) P(19) N_2O Q-switched laser	Absorption noted	$\tilde{X}\ ^1A_g$ (coincidences in ν_7 band)	Brunet and Voignier, 1969; Sokoloff and Javan, 1972
CO	2.33372 (4285.00) (100W peak) Opt. 2.33555 (4281.65) Parametric Oscill., Nd. Yag laser	~ 4.7 (~2130) 2,1 band (U)	$X\ ^1\Sigma^+$(υ'υ"; J'J") (2,0;7.6) (2,0;6,5)	Sackett et al., 1973
	4.609845 (2169.270) R(30) Frequency doubled (Te crystal) CO_2 pulsed TEA laser	$(2,1)^*$ (1,0) (U)	$X\ ^1\Sigma^+$ (1,0;7,6 at 2169.198 cm^{-1})	Green and Hancock, 1973b; Stephenson, 1973b
	4.641222 (2154.605) R(18)		(1,0;3,2 at 2154.598 cm^{-1})	
	4.793113 (2086.323) P(24)		(1,0;13,14 at 2086.328 cm^{-1})	
	5.05-6.20 (1610-1980) P lines CO_2 flowing Q-switched laser	2.3-2.7 (3700-4350) (U) (13,11) to (2,0) overtone bands	$X\ ^1\Sigma^+$ (5,4) to (19,18)	Yardley, 1970a
CO_2	10.6 (940) CO_2 Q-switched laser (CO_2-N_2-He mixture)	~ 4.3 (~ 2325) (U) ($00^01 \rightarrow 00^00$)	$X\ ^1\Sigma_g^+$ ($00^01 \leftarrow 10^00$)	Hocker et al., 1966; Moore et al., 1967; Yardley and Moore, 1967; Alexander et al., 1968; Kovacs et al., 1968; Stephenson et al., 1968, 1971, 1972a,b; Kovacs and Javan, 1969; Rosser et al., 1969, 1971; Rosser and Gerry 1969, 1971; Heller and Moore, 1970; Stephenson and Moore, 1970, 1972; Margottin-Maclou et al., 1971; Christophe and Offenberger, 1972; Rao et al., 1972; Cramp and Lambert, 1973; Rosenberg and Lowenstein, 1973
	10.6 (940) 50W cw CO_2laser	~ 4.3 (2325) ($00^01 \rightarrow 00^00$) (U) ~ 9.4 (1060) ($00^01 \rightarrow 02^00$) (U) ~ 10.6 (940) ($00^01 \rightarrow 10^00$) (U) (0.5 FWHM filter)	$\tilde{X}\ ^1\Sigma_g^+$ ($00^01 \leftarrow 10^00$) (U)	Offenberger et al., 1972
DCl	~ 4.9-5.2 (~ 1925-2040) DCl pulsed laser (Cl_2-DI mixture)	(1,0) (U)	$X\ ^1\Sigma^+$ (1,0)	Zittel and Moore, 1973a,b

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* Involves multiphoton absorption or, more generally, energy transfer collisions to populate these higher energy levels.

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(U), (R) unresolved, resolved.

FWHM filter characteristic, full width at half maximum transmission.

Table III. Infrared Fluorescence Excited by Monochromatic Spectral Line Sources

Species	Exciting Source $\bar{\lambda}_{vac\,\mu m}$, ($1/\lambda_{vac}$ cm^{-1})	Fluorescence Monitored $\lambda_{\mu m}$, ($1/\lambda$ cm^{-1})	Quantum States Involved in Absorption	Reference
DF	3.5811 (2792.4) P(5) 0.5W, cw DF transverse flow laser, (He-SF_6-D_2 mixture)	3.23-3.42 (2920-3095) 1,0 band (U).	$X\,^1\Sigma^+$ (1,0;4,5)	Stephens and Cool, 1971, 1972
	3.6128 (2767.9) P(6)		(1,0;5,6)	
	3.6456 (2743.0) P(7)		(1,0;6,7)	
	3.6983 (2703.98) P(5)		(2,1;4,5)	
	3.7310 (2680.28) P(6)		(2,1;5,6)	
	3.7651 (2655.97) P(7)		(2,1;6,7)	
	3.5811 (2792.4) P(5) DF helical pin laser	(1,0) (2,1)*	$X\,^1\Sigma^+$ (1,0;4,5)	Ernst et al., 1973
	3.6128 (2767.9) P(6) DF laser, pulsed pin, transverse excited (SF_6-D_2-He mixture)	3.25-3.39 (2950-3075) 1,0 band (U)	$X\,^1\Sigma^+$ (1,0;5,6)	Hinchen, 1973a,b
	~3.7 (~2700) P_{1-0} lines DF, pulsed, TEA laser (SF_6-D_2)	(1,0) (2,1)*	$X\,^1\Sigma^+$ (1,0)	Bott, 1973, 1974; Bott and Cohen, 1973b
HBr	4.017 (2489) P(4) HBr pulsed, TEA laser (flowing H_2-Br_2 mixture)	(1,0) (2,1)*	$X\,^1\Sigma^+$ (1,0; 3,4)	Burak et al., 1972a
	4.047 (2471) P(5)		(1,0; 4,5)	
	4.078 (2452) P(6)		(1,0; 5,6)	
	4.111 (2432) P(7)		(1,0; 6,7)	
	4.078 (2452) P(6) HBr pulsed laser (flowing Br_2-HI mixture)	(1,0) (2,1)*	$X\,^1\Sigma^+$ (1,0; 5,6)	Chen, 1971a,b; Chen and Chen, 1972; Hopkins and Chen, 1972a, 1973; Zittel and Moore, 1973c
	4.111 (2432) P(7)		(1,0; 6,7)	
	4.144 (2413) P(8)		(1,0; 7,8)	
	4.180 (2392) P(9)		(1,0; 8,9)	
HCHO	3.4883 (2866.7) Kr laser 3.4895 (2865.7)	Absorption noted	$\tilde{X}\,^1A_1$ (coincidence in ν_4 band)	Hanst, 1971
	3.5080 (2850.6) Xe laser (He-Xe mixture)	Absorption noted	$\tilde{X}\,^1A_1$ (absorption line mis-matched by 190 MHz)	Sakurai et al., 1967
	5.85519 (1707.887) $P_{16-15}(13)$ CO laser	Absorption noted	$\tilde{X}\,^1A_1$ (coincidence in $\nu_2$band)	Johns and McKellar, 1973; Nielsen, 1934
HCl	1.7472 (5723.3) Pulsed, tunable parametric oscillator (frequency doubled Nd. Yag)	(2,1) (1,0) (U)	$X\,^1\Sigma^+$ (2,0; 3,2)	Leone and Moore, 1973
	3.3957 (2944.9)	(2,1)* (1,0) (U)	(1,0; 3,2)	
	~ 3.37-3.70 (~2700-2960) HCl P(1)-P(8), R(0)-R(3) Q-switched laser (flowing H_2-NOCl mixture)	(1,0)	$X\,^1\Sigma^+$ (1,0)	Margottin-Maclou et al., 1971
	3.57-3.89 (2570-2800) P(4)-P(13) HCl pulsed laser (Cl_2-HBr mixture)	(2,1)*	$X\,^1\Sigma^+$ (1,0)	Hopkins and Chen, 1972b
	3.63-3.81 (2625-2750) P(6)-P(11) HCl pulsed, TEA laser (H_2-Cl_2 mixture)	(2,1)*	$X\,^1\Sigma^+$ (1,0)	Burak et al., 1972b; Noter et al., 1973

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(U),(R) unresolved, resolved.

FWHM filter characteristic, full width at half maximum transmission.

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Table III. Infrared Fluorescence Excited by Monochromatic Spectral Line Sources

Species	Exciting Source $\lambda_{vac}\ \mu m$, $(1/\lambda_{vac}\ cm^{-1})$	Fluorescence Monitored $\lambda_{\mu m}$, $(1/\lambda\ cm^{-1})$		Quantum States Involved in Absorption	Reference
HCl (Cont)	3.7345 (2677.7) P(9) HCl pulsed laser (flowing Cl_2-HI)	3.33-3.52 (2840-3000) 1,0 band (U)		$X\ ^1\Sigma^+$ (1,0; 8,9)	Chen et al., 1968; Chen and Moore, 1971a,b; Hopkins et al., 1973; Zittel and Moore, 1973a,c
	3.7708 (2652.0) P(10)			(1,0; 9,10)	
	3.8085 (2625.7) P(11)			(1,0; 10,11)	
HF	1.3404 (7460.4) Nd. $YAlO_3$ pulsed laser, temperature tuned	2.7 (3700) (2,1) (1,0)		$X\ ^1\Sigma^+$ (2,0; 5,6)	Bina and Jones, 1973
	2.608 (3834) P(3) HF pulsed, pin laser (flowing SF_6-H_2)	2.27-2.50 (4000-4400) 1,0; 2,1* band		$X\ ^1\Sigma^+$ (1,0;2,3)	Bott, 1972; Bott and Cohen, 1973a; Blair et al., 1973
	2.640 (3788) P(4)	1.25-1.8 (5550-8000) 2,0*band 0.8-1.2 (8330-12,500) 3,0*band		(1,0; 3,4)	
	2.7075 (3693.5) P(6)	0.62-0.8 (12,500-16,000) 4,0*band 0.55-0.6 (16,600-18,200) 5,0*band		(1,0; 5,6)	
	2.640 (3788) P(4) 1W, cw HF transverse flow laser (He-SF_6-H_2 mixture)	2.27-2.64 (3790-4405) 1,0 band		$X\ ^1\Sigma^+$ (1,0; 3,4)	Stephens and Cool, 1971, 1972; Ahl andCool, 1973
	2.673 (3741) P(5)			(1,0; 4,5)	
	2.7075 (3693.5) P(6)			(1,0; 5,6)	
	2.7604 (3622.7) P(4) 0.8 W			(2,1; 3,4)	
	2.7953 (3577.5) P(5)			(2,1; 4,5)	
	2.8318 (3531.3) P(6)			(2,1; 5,6)	
	2.640 (3788) P(4) HF pulsed, helical pin laser (H_2-SF_6 mixture)	(1,0) (2,1)* (R) and (U)		$X\ ^1\Sigma^+$ (1,0; 3,4)	Osgood et al., 1972, 1973
	2.7275 (3666.38) P(3)	(2,1) (1,0) (3,2)*		(2,1; 2,3)	
	2.640 (3788) P(4) HF pulsed, pin, transverse excited laser (SF_6-H_2-He mixture)	2.27-2.47 (4050-4405) 1,0 band		$X\ ^1\Sigma^+$ (1,0; 3,4)	Hinchen, 1973a,b
	2.7075 (3693.5) P(6)			(1,0; 5,6)	
	2.7075 (3693.5) P(6) HF pulsed laser (F_2O-HCl mixture)	2.27-2.50 (4000-4400) 1,0band		$X\ ^1\Sigma^+$ (1,0; 5,6)	Airey and Fried, 1971
	2.7441 (3644.16) P(7) HF pulsed TEA laser (SF_6-CH_4, C_2H_6, C_3H_6-He mixture)	2.4 (4170) 1,0 band (U)		$X\ ^1\Sigma^+$ (1,0; 6,7)	Hancock and Green, 1972a,b, 1973; Green and Hancock, 1973a
NH_3	10.233167 (977.2146) R(22) CO_2 laser	Absorption noted	m	$\tilde{X}\ ^1A_1$ (coincidences in $\nu_2$band)	Hanst, 1971
	10.718560 (932.9611) P(32)		s		
	10.741113 (931.0022) P(34)		w		
	10.764052 (929.0182) P(36)		w		
	10.571037 (945.9810) P(18) 50W cw CO_2 laser (CO_2-N_2-He mixture)	Fluorescence reported		$\tilde{X}\ ^1A_1$ (coincidences in ν_2 band)	Borde et al., 1966 Ronn, 1968
	10.591035 (944.1948) P(20)				
	10.611385 (942.3841) P(22)				
	10.632090 (940.5488) P(24)				
	10.718560 (932.9611) P(32) CO_2 laser	Absorption noted		$\tilde{X}\ ^1A_1$ (Q (5,3) line, ν_2 band)	Letokhov, 1973
	10.77885 (927.7425) P(13) N_2O laser	Absorption noted		$\tilde{X}\ ^1A_1$ (^qQ (8,7) line, ν_2 band, mismatch 7.4 MHz)	Shimizu, 1970a,b; Shimizu and Oka, 1970a,b Freund et al., 1973; Jones and Eyer, 1973; Kreiner et al., 1973; Kreiner and Rudolph, 1973

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Table III. Infrared Fluorescence Excited by Monochromatic Spectral Line Sources

Species	Exciting Source $\lambda_{vac}\,\mu m$, $(1/\lambda_{vac}\,cm^{-1})$	Fluorescence Monitored $\lambda_{\mu m}$, $(1/\lambda\ cm^{-1})$	Quantum States Involved in Absorption	Reference
$^{15}NH_3$	10.551387 (947.7427) P(16) CO_2 laser	Absorption noted	$\tilde{X}\,^1A_1$ (R(0,0) line, ν_2 band)	Letokhov, 1973
	10.114826 (988.6477) R(42) CO_2 laser	Absorption noted	$\tilde{X}\,^1A_1$ (R(2,0) line, ν_2 band)	Shimizu, 1970b
NO	2.70752 (3693.42) P_{1-0}(6) HF pulsed laser (SF_6-H_2 mixture)	Absorption noted	X $^2\Pi_{1/2}$(2,0; 15/2, 17/2 at 3693.504 cm^{-1})	Nachshon and Coleman, 1973
	5.16667 (1935.484) P_{7-6}(13) CO laser	Absorption noted	X $^2\Pi_{3/2}$(1,0; 39/2, 37/2 at 1935.493 cm^{-1})	Menzies, 1971; Mantz et al., 1970; James and Thibault, 1964
	5.18865 (1927.282) P_{7-6} (15)		$^2\Pi_{3/2}$(1,0; 33/2, 31/2 at 1927.273)	
	5.26304 (1900.043) P_{9-8} (9)		$^2\Pi_{1/2}$(1,0; 15/2, 13/2 at 1900.082)	
	5.30682 (1884.369) P_{9-8} (13)		$^2\Pi_{3/2}$(1,0; 5/2, 3/2 at 1884.316)	
	5.42646 (1842.82) P_{9-8} (23) 5.42646 (1842.821) P_{10-9} (17)		$^2\Pi_{1/2}$(1,0; 17/2, 19/2 at 1842.933)	
	5.21163 (1918.785) P(2) CO_2 frequency doubled, helical, pulsed TEA laser	~5.3 (~1890) (1,0) (2,1)*	X$^2\Pi_{3/2}$(1,0; 27/2, 25/2 at 1918.69 cm^{-1})	Stephenson, 1973a; James and Thibault, 1964
	5.28809 (1909.092) P(8)		$^2\Pi_{1/2}$(1,0; 21/2, 19/2 at 1909.14)	
	5.31604 (1881.098) P(24)		$^2\Pi_{1/2}$(1,0; 3/2, 1/2 at 1881.04)	
	5.42988 (1841.660) P(44)		$^2\Pi_{3/2}$(1,0; 17/2, 19/2 at 1841.78	
	5.4048 (1850.21) Ne laser	Absorption noted	X $^2\Pi_{1/2}$ (1,0; 13/2, 15/2 at 1850.164 cm^{-1})	Hanst, 1971; James and Thibault, 1964; Shaw, 1956
	5.4987 (1818.6) I atom laser		$^2\Pi_{3/2}$ (1,0; 29/2, 31/2 at 1818.74)	
	5.4987 (1818.6) I atom laser	Absorption noted	X $^2\Pi_{3/2}$ (1,0; 29/2, 31/2 at 1818.74 cm^{-1})	Menzies et al., 1970; Shaw, 1956
	5.60436 (1784.33) P_{12-11}(19) CO laser		$^2\Pi_{1/2}$ (1,0; 47/2, 49/2 at 1784.40)	
NO_2	6.03059 (1658.212) P_{18-17}(13) CO laser	Absorption noted	$\tilde{X}\,^2A_1$ ν_3 band coincidences at 1658.228 cm^{-1})	Menzies et al., 1970; Menzies, 1971; Mantz et al., 1970; Hurlock, 1970; Hurlock et al., 1974; Roh and Rao, 1974
	6.05582 (1651.303) P_{19-18} (8)		1651.304	
	6.12250 (1633.320) P_{20-19} (6)		1633.301	
	6.17449 (1619.568) P_{20-19}(10)		1619.561	
	6.36799 (1570.355) P_{22-21} (10)		1570.365	
	6.44076 (1552.611) P_{23-22}(8)		1552.614	
	6.48314 (1542.462) P_{23-22}(11)		1542.461	
N_2O	10.6 (940.0) 0.5 kW N_2O Q-switched laser (flowing N_2O-He-N_2 mixture)	4.5 (2220) (U) (100→000)	$\tilde{X}\,^1\Sigma^+$ [100 (2224 cm^{-1}) - 001 (1285 cm^{-1})]	Bates et al., 1968; Yardley, 1968; Margottin-Maclou et al., 1971; Shimanouchi, 1972

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* Involves multiphoton absorption or, more generally, energy transfer collisions to populate these higher energy levels.

s, m, w. *strong, medium, weak fluorescence.*

(U), (R) unresolved, resolved.

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Table III. Infrared Fluorescence Excited by Monochromatic Spectral Line Sources

Species	Exciting Source $\lambda_{vac}\,\mu m$, $(1/\lambda_{vac}\,cm^{-1})$	Fluorescence Monitored $\lambda_{\mu m}$, $(1/\lambda\ cm^{-1})$		Quantum States Involved in Absorption	Reference
O_3	9.473060 (1055.6251) P(10) CO_2 tunable laser	9.6 (1040) (U) 9.2-10 (1000-1087) (R)	w	$\tilde{X}\,{}^1A_1$(coincidences in ν_3 band)	Robinson and Guagliardo, 1973
	9.488355 (1053.9235) P(12)		m		
	9.503937 (1052.1956) P(14)		s		
	9.519808 (1050.4413) P(16)		s		
	9.535972 (1048.6608) P(18)		s		
	9.552428 (1046.8542) P(20)		m		
	9.569179 (1045.0217) P(22)		m		
	9.586227 (1043.1633) P(24)		w		
	9.603573 (1041.2791) P(26)		m		
	9.621219 (1039.3693) P(28)		m		
	9.639166 (1037.4341) P(30)		w		
	9.488355 (1053.9235) P(12) 200W peak, CO_2 Q-switched laser	Absorption noted		$\tilde{X}\,{}^1A_1$(coincidence in $\nu_3$band)	Gordon and Lin, 1973
	9.488355 (1053.9235) P(12) CO_2 pulsed, TEA laser (CO_2-He mixture) 9.503937 (1052.1956) P(14) 9.639166 (1037.4341) P(30)	4.76* (2100) 0.2 μm FWHM filter (101 → 000)	w	$\tilde{X}\,{}^1A_1$(coincidences in ν_3 band)	Rosen and Cool, 1973
	9.694831 (1031.4775) P(36) CO_2 stabilized laser 9.713998 (1029.4423) P(38) 9.733473 (1027.3825) P(40)	Absorption noted		$\tilde{X}\,{}^1A_1$ (ν_3 band coincidences at 1031.4618 cm^{-1}) 1029.4450 1027.3825	Young and Bunner, 1974; Chang, 1970
SO_2	7.26430(1376.596) $P_{30-29}(10)$ CO laser	Absorption noted		$\tilde{X}\,{}^1A_1$ (ν_3 band coincidences at 1376.57 cm^{-1})	Menzies, 1971; Shelton et al., 1953; Yardley, 1970b; Roh and Rao, 1974
	7.37583 (1355.779) P_{31-30} (9)			1355.83	
	7.40988 (1349.55) P_{31-30} (11)			1349.49	
	7.44136 (1343.84) P_{32-31} (5)			1343.87	
	7.45781 (1340.877) P_{32-31} (6)			1340.93	
	7.52561 (1328.796) P_{32-31} (10)			1328.79	
	7.4237 (1347.03) Ne laser	Absorption noted		$\tilde{X}\,{}^1A_1$ (ν_3 band coincidences at 1346.83, 1347.55 cm^{-1})	Hanst, 1971; Shelton et al., 1953
SF_6	10.571037 (945.9810) P(18) 10 kW peak, CO_2 Q-switched laser	~10.5 (~952) ν_3 band (U)		$\tilde{X}\,{}^1A_{1g}$ (coincidences in $\nu_3, 2\nu_3, \nu_3+\nu_6$ bands)	Wood and Schwarz, 1970
	10.591035 (944.1948) P(20)				
	10.611385 (942.3841) P(22)				
	10.571037 (945.9810) P(18) CO_2 Q-switched laser	16 (625) ν_4 band		$\tilde{X}\,{}^1A_{1g}$ (coincidences in ν_3, $2\nu_3$, $\nu_3+\nu_6$ bands)	Knudtson and Flynn, 1973a
	10.591035 (944.1948) P(20) CO_2 laser	~ 10.6 (~ 943) ν_3 band 16 (625) ν_4 band		$\tilde{X}\,{}^1A_{1g}$ (coincidences in ν_3, $2\nu_3$, $\nu_3+\nu_6$ bands)	Brunet, 1967
	~ 10.6 (~ 943) CO_2 Q-switched laser (CO_2-He-N_2 mixture)	~ 10.6 (~943) ν_3 band 16 (625) ν_4 band		$\tilde{X}\,{}^1A_{1g}$ (coincidences in ν_3, $2\nu_3$, $\nu_3+\nu_6$ bands)	Bates et al., 1970, 1971, 1972; Bailey et al., 1971; Garbuny and Feichtner, 1972

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* Involves multiphoton absorption or, more generally, energy transfer collisions to populate these higher energy levels.

s, m, w. strong, medium, weak fluorescence.

(U), (R) unresolved, resolved.

FWHM filter characteristic, full width at half maximum transmission.

PRINCIPLES INVOLVED IN ESTABLISHING THE MOLECULAR FLUORESCENCE DETECTION LIMITS

FLUORESCENCE SIGNALS

Atomic fluorescence, emission, and absorption techniques have become invaluable aids for the analytical chemist and often complement rather than compete against each other in resolving analyses problems. Their relative sensitivities have been well documented for the various elements of the periodic table. Through their importance in this role, many studies have been made determining the optimum operating conditions and establishing the factors that control the recorded signal to noise ratios (McCarthy et al., 1967; Winefordner et al., 1967 a,b; Jenkins, 1967; Parsons et al., 1967; DeGalan et al., 1967; Omenetto et al., 1973b; Svobada et al., 1973). The principles invoked describing atomic fluorescence apply equally well to molecular systems. However, the latter become more involved owing to the multitude of available rotational and vibrational levels which may be involved in either the absorption or re-emission of radiation. Consequently, a molecular fluorescence spectrum excited with a broadband continuum source generally will become complex as a result of the many levels that are populated. Recent renewed interest in the technique is a result of being able to selectively excite particular rotational and vibrational states using atomic line or laser sources. The resulting fluorescence in many cases then consists of rather simply analyzed line progressions in υ''. Dependent upon the radiative lifetime of the excited state, a molecule suffers many collisions with other gaseous constituents before fluorescing, and there is a certain probability that it will be quenched, either completely or partially, during this period. The fluorescence efficiency is completely controlled by the relative rates of the various radiative and quenching processes. Its spectral dependence is determined by the relative Franck-Condon factors for an electronic transition or a consequence of the appropriate selection rules for rotation-vibration transitions.

The kinetics of molecular fluorescence can be simply illustrated by the following scheme:

Absorption $NO_2 \xrightarrow{I_a} NO_2^*$

Fluorescence $NO_2^* \xrightarrow{k_f} NO_2 + h\nu$

Dissociation $NO_2^* \xrightarrow{k_d} NO + O$

Quenching $\mathrm{NO_2}^{*} + \mathrm{M} \xrightarrow{k_q} \mathrm{NO_2} + \mathrm{M}$

For such a system, assuming a steady state $\mathrm{NO_2}^{*}$ concentration, the total fluorescence intensity, I_f, may be expressed as:

$$I_f = \frac{k_f I_a}{k_f + k_d + k_q [M]}$$

where I_a represents the absorbed intensity. k_f has the value of τ^{-1} where τ is the natural radiative lifetime of the excited state involved. Any evaluation of a process involving absorption must entail a consideration of the line shapes of the exciting source and the absorbing line. This has been discussed already in the literature for atomic absorption and fluorescence cases, approximate limiting case solutions being derived for systems involving continuum or line sources, broad or narrow absorbing lines and conditions of high and low concentration levels. In the present study line sources are to be considered. The absorbing gas pressure (10 to 100 torr) is sufficiently low that an assumption of a Doppler shaped absorption line is a satisfactory approximation. Concentrations will be low and Beers absorption Law applicable:

$$I_\nu / I_\nu^o = \exp(-n \sigma_\nu \ell)$$

$$I_a^\nu = I_\nu^o - I_\nu = I_\nu^o \left[1 - \exp(-n \sigma_\nu \ell) \right]$$

where I_ν^o = intensity of the incident radiation at frequency ν

I_ν = intensity of the transmitted radiation at frequency ν

I_a^ν = intensity of the radiation absorbed at frequency ν

n = number density of absorbing species, cm^{-3}

σ_ν = absorption cross-section, cm^2, at the frequency ν

ℓ = absorbing path length in the field of view, cm.

Quite often, absorptions are described by means of an absorption coefficient, k_ν cm^{-1} NTP^{-1} (base e). This is a function of temperature, T K, and pressure, p atm, and is related to the absorption cross-section by the expression (see next page):

$$n\sigma_\nu = p\,\frac{273}{T}\,k_\nu$$

or $$\sigma_\nu = 3.72 \times 10^{-20}\,k_\nu$$

Two limiting cases will require consideration, those resulting from a source linewidth being broader or narrower than the absorption line. Consider a source of radiant intensity I_s, watts cm^{-2} ster^{-1}, of area a_s. Using a lens of area a_F to collimate the radiation falling within a solid angle Ω_s, then the exciting radiancy is given by $I_s\,a_s\,\Omega_s/a_F$ watts cm^{-2}. For a laser beam of energy I_L watts cm^{-2} and cross-sectional area a_L the corresponding exciting radiancy will be $I_L\,a_L/a_F$ watts cm^{-2} if the beam is modified to have a cross-sectional area of a_F.

For a continuum source, the total energy absorbed, I_a, by a spectral line can be described by the expression:

$$I_a = I_{\text{continuum}}\,\frac{a_s\,\Omega_s}{a_F}\,A_T\,,\ \text{watts cm}^{-2}$$

where $I^o_{\text{continuum}}$ = amplitude of the continuum radiant intensity, watts-sec cm^{-2} ster^{-1}

A_T = total absorption factor, sec^{-1}. The fraction of the incident radiation that is absorbed in the frequency bandwidth considered.

When the exciting radiation is a line source $I^o_{\text{continuum}}$ can be replaced by:

$$I_s\ 2(\ln 2)^{1/2} \Big/ (\pi^{1/2}\,\Delta\nu_s)$$

which represents the peak amplitude of the source intensity and $\Delta\nu_s$ its line half-width (FWHM) in sec^{-1} for a line with Gaussian contour. The $2(\ln 2)^{1/2}/\pi^{1/2}$ factor is necessary to convert the Gaussian half-width to a triangular half-width which simplifies the calculation of line areas. Its value is close to unity. Consequently, for a line source

$$I_a = \frac{2(\ln 2)^{1/2}}{\pi^{1/2}}\,\frac{I_s\,a_s\,\Omega_s}{a_F\,\Delta\nu_s}\,A_T,\ \text{watts cm}^{-2}$$

The total absorption factor, A_T, is evaluated from the following expression:

$$A_T = \int_0^\infty \frac{I_\nu^o - I_\nu}{I_\nu^o} d\nu$$

$$= \int_0^\infty [1 - \exp(-n\sigma_\nu \ell)] d\nu$$

$$= \int_0^\infty n\sigma_\nu \ell \, d\nu, \text{ sec}^{-1}$$

this latter approximation holds for the small values of $n\sigma_\nu \ell$ encountered in this study. Evaluation of this integral is the crux of the problem and will be derived for the two limiting cases of specific interest here.

(i) Absorption linewidth much narrower than the source linewidth

It has been shown by Winefordner et al. (1967 a) that the integral in the expression for A_T under these conditions reduces to:

$$A_T = \frac{\pi^{1/2}}{2(\ln 2)^{1/2}} n\sigma_o \ell \Delta\nu_D ; \text{ sec}^{-1}$$

where σ_o is the absorption cross-section at the absorption line center, and $\Delta\nu_D$ the Doppler half-width of the absorption line, sec^{-1}. For this case the absorbed intensity per unit area will be given by:

$$I_a = \frac{I_s a_s \Omega_s}{a_F} n\sigma_o \ell \frac{\Delta\nu_D}{\Delta\nu_s}, \text{ watts cm}^{-2}$$

(ii) Absorption linewidth large compared to the source linewidth

In this case the integration for A_T is taken over the source line rather than the absorption line.

$$A_T = \frac{\pi^{1/2}}{2(\ln 2)^{1/2}} n\sigma_s \ell \Delta\nu_s, \text{ sec}^{-1}$$

$$I_a = \frac{I_s a_s \Omega_s}{a_F} n\sigma_s \ell, \text{watts cm}^{-2}$$

A third case that may also be included at this point, owing to its simple form, concerns the case where source and absorbing lines are of identical shape and are superimposed. In such a situation, the above expression reduces to:

$$I_a = \frac{I_s a_s \Omega_s}{a_F} \; \frac{n \sigma_o \ell}{(2)^{1/2}}, \text{ watts cm}^{-2}$$

In order to estimate the fluorescence signal, various additional factors need to be considered. These include the fluorescing volume, $a_F \ell$ cm^{-3}, in the field of view, the detector solid angle, Ω_F steradians, the fraction, f, of the total fluorescence that lies within the detector bandpass, and the transmission factor, θ, for the detector wavelength discriminant. Taking these into account for a system as in case (ii) the total fluorescence signal incident on the photodetector can be described by the expression:

$$I_f = \frac{\Omega_F}{4\pi} f \, \theta \cdot \frac{k_f}{k_f + k_d + k_q [M]} \cdot I_s a_s \Omega_s n \sigma \ell, \text{ watts}$$

The first factor represents the detection efficiency, the second the fluorescence efficiency, and the last the exciting source energy absorbed. Factors accounting for any decrease in the intensity of the exciting radiation between the source and the field of view, and similar attenuation of the fluorescence enroute to the detector are considered to be negligible and have not been included. The expression illustrates the linear relationship between the intensity of the fluorescence and the absorbing species number density which is observed at low concentrations.

For a photomultiplier with a photocathode radiant sensitivity of C amps/watt at the detection wavelength, and with a gain of G, the fluorescence will produce an anode current, i_s, given by:

$$i_s = I_f \, C \, G, \text{ amps}$$

THE NOISE LEVEL

The rms noise recorded by the detector can arise from various sources. It can be a result of the contributions from the electronic circuits, from the photodetector, or from the random fluctuations in the intensity of the exciting source. Background dc levels arising from scattered light or other species are regarded as interferences and do not contribute to any fluctuations. In detection systems utilizing photomultiplier tubes at very low light levels, the limit of detection is generally controlled by the tubes dark current noise level. This is the case for the NO chemiluminescent detector now in use as a stratospheric NO monitor, (Ridley et al., 1972a, b, 1974). In this analysis it has been assumed that the noise level in the exciting source can be made negligibly small or can be so controlled that detection will likewise be dark current limited. The rms anode dark current noise, i_{an}, measured with a bandwidth of Δf for a cathode dark current of i_{cd} amps is given by the expression:

$$i_{an} = (2 e i_{cd} \Delta f)^{1/2} \, Ga \, , \text{ amps}$$

where e is the electron charge, 1.6×10^{-19} coulombs, and 'a' is a factor which accounts for random variations in the interdynode amplification. 'a' decreases with increasing gain of the first dynode stage. Operating the tube with a high first-stage gain gives a minimum 'a' value which closely approximates to unity. With pulse counting electronics $a = 1$ because the contribution of every photoelectron to the recorded signal is made equal by pulse shaping. Manufacturers generally quote the tubes anode or cathode dark current, or occasionally give the equivalent noise input of the tube. The latter represents a value of the radiant flux or the incident luminosity that would produce a signal equal to that of the dark current noise level.

Tubes of high sensitivity and low dark current noise level are required in the detection of very low light levels. Cooling to -20°C generally will be necessary to reduce the noise level to as low a value as possible. Dependent upon the photocathode material, this can decrease the tube's noise level by several orders of magnitude and is one way of producing a significant improvement in detection performance.

In this analysis, the limit of detection will be defined as the concentration level at which the mean fluorescence signal is equal to the rms variations of any dc background signal. The latter variation will be assumed to approximate to that of the tube's dark current noise level.

OPTIMUM CONDITIONS

A comparison of the equations representing the fluorescence signal and the dark current noise illustrate the various requirements for optimum sensitivity. These may be summarized as:

(i) A source with as high an intensity as possible, concentrated in a narrow linewidth, and efficiently coupled to the fluorescence cell.

(ii) A system with a high photon absorption cross-section.

(iii) Dissociation and collisional quenching rates of the excited state should be small compared to the rate of fluorescence.

(iv) A light collection system of high efficiency with as long a fluorescing path length as possible in its field of view.

(v) Fluorescence bands of high transition probability require to be monitored.

(vi) A photomultiplier tube of high cathode radiant sensitivity at the fluorescing wavelength region and low cathode dark current. Tube gain is not a S/N controlling factor.

(vii) The fluorescent detector bandpass should be spectrally removed as far as possible from the exciting wavelength so that scattered light can be efficiently discriminated against by choosing appropriate filter and photomultiplier characteristics.

For the low level concentrations to be considered in these present analyses, gas sample flow rates through the fluorescence cell will not be a controlling factor. In the NO chemiluminescent reactor, radiation resulting from the NO + O_3 chemical reaction is monitored and the detection system is optimum for high flow rates. This results from the requirement to maintain NO and O_3 concentrations as large as possible in the field of view. In fluorescence studies, although the effective lifetime of the excited state is very short, reversion to the initial ground level state will not occur directly but via a chain of vibrational relaxation steps. At the low concentration levels and the low absorption rates being considered here, only in cases where a very intense source is used in a system with a relatively large absorption cross-section, will a substantial fraction of the absorbing species be excited. Even so, at the pressures in the cell, rotational relaxation will rapidly equilibrate the absorbing state and no saturation effects are to be expected. Consequently, there would appear to be little reason to invoke high flow rates through the cell in the majority of cases.

EXPERIMENTAL PARAMETERS

EQUIPMENT DIMENSIONS

In a general discussion, experimental parameters are always difficult to tie down to specific values if many options are available for the individual systems of interest. For instance, in the present case, sources may consist of a laser beam, a hollow cathode line source or an RF excited molecular source. The latter two would require a certain degree of collimation using a lens or, possible, a concave reflecting mirror and lens assembly for greater collection efficiency of the radiating light. In such cases it has been assumed that an f/2 system can be designed to couple the source energy into the fluorescing cell. That is the source has an effective aperture of $4\pi/64$ steradians. Similarly, the detector arrangement might be one of several. Three possible approaches are illustrated in Figure 1. The photomultiplier tube, fitted with an appropriate interference filter may be placed close to the beam to maximize a collection solid angle with auxiliary mirrors on the opposite side of the beam to increase the efficiency. Another approach might utilize an inverse cassagrain (convex/torroidal concave) mirror system (West and Cresser, 1973) or an elliptical reflector. An f/2 collection efficiency should be attainable with such systems and will be the assumed solid angle in these assessments. The calculated detection limits can be scaled accordingly if superior or inferior systems are designed. Observed beam length will be assumed equal to the size of the photomultiplier photocathode. These vary in dimensions and improvement realized in a lower dark current noise level from a smaller photocathode will have to be offset against the reduced light collection solid angle of the detector unless some focusing system is incorporated.

The transmission characteristics of an interference filter depend on the angle of incidence of light falling on the filter face. Its peak transmission is shifted to shorter wavelengths for off-normal incident light. With filters in the ultraviolet through near infrared regions the magnitude of this shift can be predicted by the equation:

$$\lambda_\varphi = \lambda_N (1 - \sin^2\varphi/b^2)^{1/2}$$

where φ = angle of incidence, measured from the normal

λ_φ = wavelength of peak transmission at an angle φ

λ_N = wavelength of peak transmission at normal incidence

b = effective refractive index of the filter material, typically ~1.7.

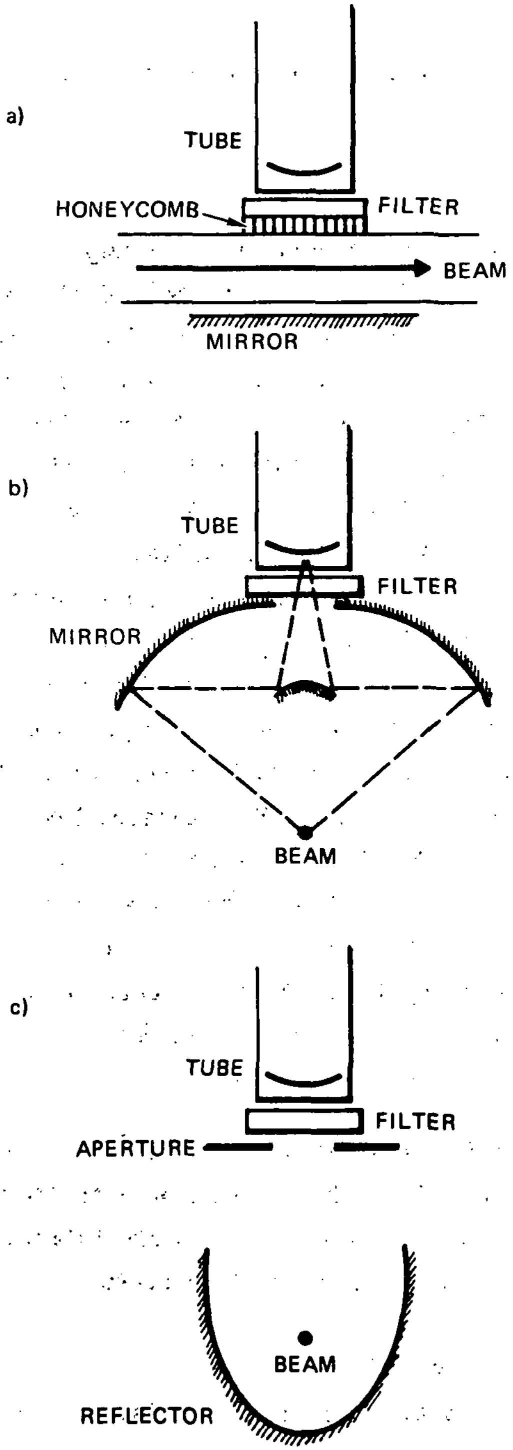

Figure 1. Various Possible Fluorescence Detector Systems

This has to be considered in assessing the actual filter transmission bandpass, and it generally imposes a certain restriction on the accepted angles of incidence. The latter can be controlled by placing a honeycomb grid in front of the filter face. The magnitude of the shift in the peak transmission for light at several wavelengths and at various angles of incidence is illustrated in Table IV. It is to be noted that at larger angles these shifts are quite significant. Restriction of the field of view, although undesirable from the S/N point of view will be necessary to maintain a desired wavelength bandpass.

TABLE IV. Wavelength Shift (nm) of the Peak Transmission of an Interference Filter with Angle of Incidence φ

λ_N, nm	5°	10°	20°	30°	40°	50°
300	0.39	1.57	6.13	13.3	22.3	32.2
500	0.66	2.61	10.2	22.1	37.1	53.6
700	0.92	3.66	14.3	31.0	52.0	75.1
900	1.18	4.71	18.4	39.8	66.8	96.5

Measurements will be made on flowing atmospheric samples brought into the aircraft by ram flow lines. These samples will flow directly through the fluorescence cell and will be at slightly higher pressure than the ambient static pressure at the particular altitude due to this sampling technique. A pressurized system can be invoked if the sensitivity for a particular system is pressure dependent and there is a requirement to maximize the response. Although this is undesirable, if it can be avoided, calculations for atmospheric pressure samples have been included in this report for comparison.

SOURCE INTENSITIES

Fluorescence studies require intense light sources, free of self-absorption, with relatively narrow lines and possessing minimum drift and intensity fluctuation characteristics. Such sources are of prime importance particularly for atomic absorption and atomic fluorescence analytical studies. As a result of extensive development efforts, spurred by the wide-scale general acceptance of these techniques, a multitude of hollow cathode and RF or microwave excited electrodeless discharge lamps have become available. In assessing the feasibility of any experiment incorporating such sources a problem arises owing to the limited documentation available concerning the absolute lamp intensities and line shape characteristics. Manufacturers of hollow cathode and electrodeless discharge lamps tend to provide only the relative intensities of the various lines emitted by a particular lamp together with the analytical detection sensitivity measured on a particular atomic absorption spectrophotometer. Consequently, comparison of lamps of one manufacturer with another is rather difficult since this sensitivity is a function of the entire instrumentation system employed and depends for example on the particular flame burner efficiency, fuel mixture, light geometry and detection electronics.

For specificity, fluorescence studies require the isolation of a single exciting line from others emitted by the source. This is generally achieved with a selective filter which may be either an interference or glass filter, a chemical filter (Muel and Malpiece, 1969), an absorption cell or a combination of these.

The suitability of four types of line sources, namely, metal vapor, hollow cathode, electrodeless discharge lamps, and lasers, will now be described in some detail.

Metal Vapor Discharge Lamps

Osram and Philips gas discharge spectral lamps have been commercially available for many years. Although available for only a limited number of elements, these have become a convenient standard laboratory light source. Lamps are available for Zn, Cd, Hg; He, Ne, Ar, Kr, Xe; Na, K, Rb, Cs; Ga, In, Tl. Generally more intense than hollow cathode lamps, these can be subject to strong line-broadening and self-absorption effects. However, the Zn, Cd and Tl sources have been used quite extensively in analysis work (Winefordner and Mansfield, 1967). The Hg and alkali metal lamps are highly self-reversed; other metal vapor lamps such as In and Ga are very weak. The lamps generally show a continuum background radiation. To illustrate the magnitude of the intensity to be expected for some of the strongest lines emitted, together with the corresponding background at these wavelengths, Table V has been compiled from some literature supplied for the various Osram lamps. In cases where the background radiation cannot be ignored, steps have to be taken to discriminate against it by selectively isolating the particular line of interest with a narrow bandpass filter.

Where coincidence with a narrow absorption line is important, some consideration is necessary of the isotopic splitting of the source lines in lamps containing a natural isotopic mixture of the element. Zn, Cd, and Tl all have two or more major stable isotopes. Herzberg (1944), for example, quotes the separation between the ^{64}Zn and ^{68}Zn atomic ion lines at about 0.2 cm^{-1} in the vicinity of 620 nm which is an order of magnitude larger than the corresponding Doppler

Table V.
The Strongest Lines and Corresponding Background Intensities for Various Osram Spectral Lamps

Type	λ, nm	Line Intensity, W cm^{-2} $ster^{-1}$ (x 10^4)	Continuum Intensity W cm^{-2} $ster^{-1}\mu m^{-1}$ (x 10^4)
Cd	326.1	31	1.5
	480.0	22	1.4
	508.6	25	1.3
Cs	455.5 459.3	1.2	4.0
	658.6	1.2	13
	697.3	1.5	13
He	587.6	44	2.7
	667.8	12	1.9
	706.5	7	2.7
Hg	253.6	520	4×10^{-5}
	312.6 313.2	1200	1×10^{-5}
	365.0 366.3	1330	1×10^{-5}
	404.6 407.8	500	5×10^{-6}
	435.8	700	$<5 \times 10^{-6}$
	546.1	800	$<5 \times 10^{-6}$
	577.0 579.0	660	$<5 \times 10^{-6}$
K	404.4 404.7	0.55	0.4
	691.1 693.9	0.45	0.7
	766.5 769.9	114	1.1
Rb	420.2 421.5	0.9	1.5
	620.6 629.8	1.1	1.0
	775.8 775.9 780.0	138	45
Tl	377.6	14	0.6
	535.0	24	0.8
Zn	330.3	7.5	1.0
	334.5	6.5	1.1
	468.0 472.2	20	1.3
	481.0	21	1.3

width of a line at room temperature. Hyperfine splitting for those isotopes having nuclear spin also has to be considered in such cases. Bismuth, for example, has no isotopes but four hyperfine components in its 412.2 nm line resulting from a nuclear spin, I = 9/2. The resulting total splitting is of the order of 2.6 cm^{-1} (Herzberg, 1944). Consequently, these two effects which are relevant to any type of atomic line source, may severely impair the amount of energy in the source that overlaps the absorption feature. A lamp consisting of only the pertinent isotope would then increase its useful output. The consequences of hyperfine nuclear splitting cannot be avoided and necessarily imply a reduced coupling efficiency with a narrow absorption line.

Hollow Cathode Lamps

These lamps are available for more than 65 elements, the major suppliers being - Perkin-Elmer, Varian, Beckman, Westinghouse, and EMI. Several years ago, for a limited period, lamps were manufactured incorporating two discharges, one to produce the cathodic sputtering and the second to excite the atomic vapor. At the time, intensity enhancements of one to two orders of magnitude were achieved over the conventional design (West and Cresser 1973). These are no longer available. Improvements in design and a recognition that the brightness was a strong function of the filler gas made the conventional lamp sufficiently intense for its major application in atomic absorption spectrophotometers. Hollow cathode lamps are not a particularly intense source of line radiation and comparison of the various manufacturers' lamps is difficult through a lack of absolute spectral radiancy data. Prugger (1969) has reported their absolute intensities and compared them with other radiation sources. His data is reproduced in Figures 2 and 3. If operated in the usual continuous current mode the intensities are generally less than an available metal discharge lamp. However, the lamps do provide excellent stability with low noise. Neon or argon gases are used as fillers and their presence has to be borne in mind. The resulting neon emission will offer most interference in the 330 to 370 and 500 to 650 nm regions, argon in the 400 to 500 nm region. The temperature of the discharge is moderate so that Doppler widths of the spectral lines are reasonably small. Wagenaar and DeGalan (1973) measured the shape for various lines emitted for nine elements (Al, Ca, Cr, Ga, In, K, Mn, Mo, and Ti) operating at a low current level. Their data, reproduced in Table VI gives Doppler temperatures ranging from 400 to 700 K. Increasing the lamp current as a means of increasing the emission causes a broadening of the linewidth beyond that generally desired and self-absorption becomes increasing severe. These workers also indicated that, except for a few elements (Ca, Si), hyperfine structure is the most

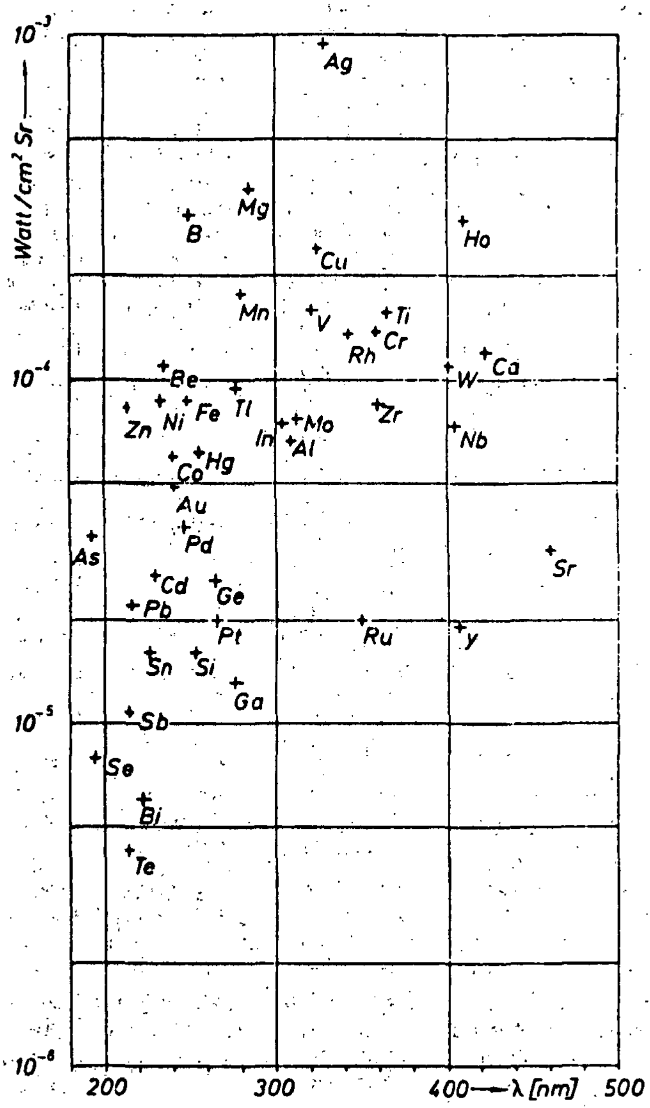

Figure 2. Radiation of the Sensitive Resonance Lines of Commercially Available Hollow Cathode Lamps (from Prugger, 1969)

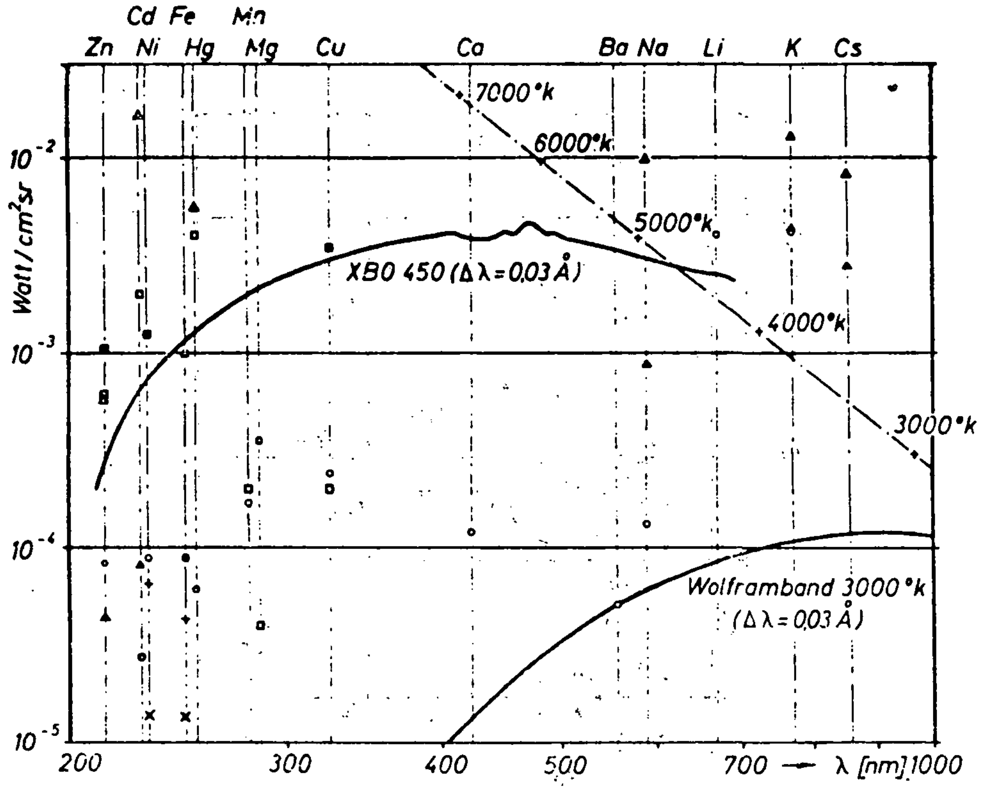

Figure 3. Comparison of the radiation from several hollow cathode lamps (o-o), high intensity lamps, with (+ - +) and without (x - x) additional arc, respectively, metal vapor lamps with the specified current (△ - △) or reduced current (▲ - ▲) of 0.8 amps for Cd, Cs, K, Na, and 1.3 amps for Zn. Concentrated glow discharge (■ - ■) from Grimm (1968) and electrodeless high-frequency lamp data from Mansfield et al. (1968). By way of comparison, the intensities of a continuum, 0.003 nm bandwidth are illustrated: black body Xe arc XBO 450 (+ - - - +) at its maximum, W ribbon at 3000 K (from Prugger, 1969).

Table VI. Linewidths and Doppler Temperatures of Various Hollow Cathode Lamps (from Wagenaar and DeGalan, 1973)

Transition (λ in nm)	Make[a]	Current (mA)	Experimental Profile Width (10^{-3} cm^{-1})	Doppler Temp. (K)
Al 394.4	PEI	7	142 ± 0.5	440 ± 10
Al 396.1	PEI	7	86 ± 1	480 ± 20
CaI 422.7	PEI	6	65 ± 1	590 ± 20[g]
CaII 393.3	PEI	8	65 ± 1.5	510 ± 25
CaII 396.8	PEI	8	64 ± 2	500 ± 30
Cr 425.4	PEI	10	61 ± 1	(680 ± 20)[b]
Ga 403.3	VT	6	223 ± 1	550 ± 10
Ga 417.2	VT	6	101 ± 0.5	570 ± 20
In 410.2	ASL	6	44.4 ± 1[d]	630 ± 40
K 404.4	PE	7	62 ± 1	430 ± 10
K 404.7	PE	7	60 ± 1.5	410 ± 15
K 404.4	O[f]	1200	119 ± 1	1200 ± 100
K 404.7	O[f]	1200	109 ± 0.5	1000 ± 100
Mn 403.1	ASL	7	---	720 ± 10
Mn 403.3	ASL	7	---	625 ± 10
Mn 403.4	ASL	7	---	630 ± 10
Mo 390.3	ASL	9	75 ± 2	(1600 ± 100)[b]
Ti 398.2	PE	15	80 ± 2	(945 ± 30)[b]
Ti 399.0	PE	15	74 ± 2	(815 ± 30)[b]
Ti 399.8	PE	15	74 ± 2	(815 ± 30)[b]

(a) Hollow-cathode lamps: PE(I) is Perkin-Elmer (Intensitron), VT is Varian Techtron, ASL is Atomic Spectral Lamps.
Vapour discharge lamp: O is Osram (lamp was air cooled to reduce self-absorption).

(b) effective values calculated from overall profiles without spectrum simulation.

(d) single component line width not corrected for instrument broadening.

(f) red shift relative to hollow-cathode line in 10^{-3} cm^{-1} is 6 ± 2: profile analysis shows $\Delta\sigma_D$ 0.090 cm^{-1}, $\Delta\sigma^c$ 0.032 cm^{-1}, a-value 0.3 ± 0.1.

(g) Doppler temperature after correction for self-absorption 510 K.

important factor in determining the profile of atomic transitions. Bruce and Hannaford (1971) have extensively studied the line profiles for a calcium hollow cathode lamp and report linewidths predominantly controlled by the Doppler component.

Improvements in lamp design since Prugger's experiments undoubtedly have taken place and it may not be unrealistic to assume that such lamps may now be available with slightly higher intensities than those illustrated in Figure 2.

Dawson and Ellis (1967), Weide and Parsons (1972) and Omenetto et al. (1973a) have assessed hollow cathode line sources utilized in a pulsed mode in atomic absorption and atomic fluorescence spectrometry. It has been noted that lamps that normally are operated continuously at some arbitrary current will provide much higher peak radiancies if pulsed at greater current levels. In the normal mode, in order to maintain a satisfactory heat dissipation in the lamp, the current flow has to be limited. Pulsing at much higher current levels enhances the intensity output by at least one to two orders of magnitude without sacrificing the desired line shape characteristics. In addition there is no corresponding increase in the intensity of the spectrum of the filler gas. The enhancement obtained is greatest with the metals of lower melting points. For others, a supplementary low constant current through the lamp is necessary. Results obtained for detection limits using hollow cathode lamps operating in such modes compared well with those obtained with intense electrodeless discharge lamps. In this pulsed mode, lamps generally are operated with a low dc current component upon which are superimposed short pulses (15-100 μsec) of up to at least ten times the normal current rating at frequencies up to a kilohertz. Linewidths appear unchanged (Dawson and Ellis, 1967; Katskov et al., 1969). For the copper hollow cathode lamp, for example, optimum operating conditions were found to be: dc component 0.4 mA, pulse current 300 mA, pulse width 15 μsec, pulse frequency 400 Hz. These conditions produced a 200-fold gain in light output over dc operation at the same mean current.

Electrodeless Discharge Lamps - Atomic

Analytical work has stimulated the development of radio-frequency and the more commonly used microwave powered discharge tubes as intense and economical sources for more than 50 elements (Mansfield et al., 1968; Zacha et al., 1968). Excited by suitable coils, antennas, or resonant microwave cavities, such lamps produce stable, narrow resonance lines with little if any self-reversal (Bazhov and Zherebenko, 1971; Browner and Winefordner, 1973). This is due to the nature of the discharge which maintains an intense relatively thin layer of excited material near the lamp wall. Their preparation, operation and performance has been reviewed most recently by Haarsma et al. (1974). Although Headridge and Richardson (1970) did report comparable detection limits for several electrodeless discharge lamps and hollow cathode tubes, the superiority of the former, in the majority of cases by several orders of magnitude is now well established. Smith (1971a) has illustrated their performance for various elements relative to other light sources; his data is reproduced in Table VII. Typical intensities for several such lamps are illustrated in Tables VIII and IX for 2450 MHz and radio-frequency (17-120 MHz) excitations. The latter also lists some measured line half-widths. Jansen et al. (1974) have compared electrodeless discharge lamps (EDL) and hollow cathode lamps (HCL) for strontium. Whereas the EDL gave a half-width (FWHM) of about (7-10) x 10^{-4} nm independent of microwave power the dc HCL half-width increased from about (7-20) x 10^{-4} with increasing current and up to 25 x 10^{-4} nm at its maximum rating at which it was heavily self-reversed.

Generally home-made, such tubes are available commercially from Ophthos Instruments, and EMI. Perkin-Elmer now are introducing a line of radio-frequency (27.5 MHz) excited discharge lamps (As, Cd, Sb, Se, Sn, Te) having very similar dimensions to their Intensitron hollow cathode lamps and equally easy to use. Intensities reportedly are 5 to 10 times better than the hollow cathode sources. Vacuum uv line sources for H, O, N, S, C, F, Cl, Br, I, Xe and Kr also have been developed with intensities greater than at least 10^{14} quanta sec^{-1} (Davis and Braun, 1968; Clyne and Cruse, 1971, 1972; Bemand and Clyne, 1973).

Intensities are a function of the exciting frequency and can be several orders of magnitude more intense in microwave than in radio-frequency discharges. Also, the process that gradually discolors the walls of the tube and shortens the lamp life, referred to as 'clean-up' proceeds more slowly at higher frequencies. Electronic modulation of such lamps often improves the lamp's noise level and drift, besides also prolonging lamp lifetime (Haarsma et al., 1974). When thermostated and operated at the correct temperature, the 2450 MHz excited source appears to be the most intense, stable and long-lived source presently used in atomic absorption or fluorescence work (Browner and Winefordner, 1973).

Electrodeless Discharge Lamps - Molecular

Such lamps have been used in molecular absorption studies particularly for OH, NO and CO and have been excited with radio or microwave frequency discharges. Carrington and Broida (1958) compared 150 MHz, 2450 MHz and 9000 MHz excitation of OH in a flowing

Table VII. Detection Limits ($\mu g\ cm^{-3}$) in Atomic Fluorescence Obtained By Using Different Excitation Light Sources[a] (from Smith, 1971a)

Element line, Å	150-Watt Xe arc (b)	"Intensitron" hollow cathode (b)	High-intensity hollow cathode (c)	Electrodeless discharge tube (d)
Ag 3281	0.2	0.003	0.002[e]	0.02
As 1937	...	...	1.0	0.4
Bi 3068	200	10	...	0.1
Cd 2288	2.0	0.1	...	0.0001
Cr 3579	10	20	...	0.05
Co 2407	2.0	0.2	0.04	0.04
Cu 3247	0.3	0.01	0.001	0.03
Fe 2483	1.0	0.4	0.1	0.008
Ga 4172	5.0	0.5	...	0.3
In 4105	2.0	0.2	...	1.0
Mg 2852	0.1	0.01	0.001[f]	...
Mn 2795	0.5	0.05	...	0.01
Ni 2320	3.0	0.1	0.003	0.006
Pb 4058	3.0	1.0	0.02	0.06
Zn 2138	20	0.05	...	0.0002

[a] The results given have been obtained on modified, commercially available, atomic absorption instruments, namely, Perkin-Elmer PE 303 (b , c), Hilger AA2 (d), and Techtron AA4 (e, f) . Although not the best detection limits appearing in the literature, these results have been chosen because they represent the fairest comparison of the several light sources used.

Table VIII. Spectral Characteristics of 2450 MHz Frequency, Electrodeless Discharge Lamps* (from Mansfield et al., 1968)

Element-line (Å)	Output power microwave supply (percent)	Source intensity (W/cm² sterad)	Source r.m.s. Noise† (W/cm² sterad⁻¹/(Δf))	Source drift‡ (W/cm² sterad/min)	Self-reversal§
Hg 2537	10	4×10^{-3}	3×10^{-7}	4×10^{-7}(B)	S
Hg 2537**	10	3×10^{-3}	3×10^{-6}	1×10^{-4}(L)	S
Ga 4172	90	3×10^{-3}	3×10^{-5}	3×10^{-3}(O)	G
Cd 2288	100	2×10^{-3}	4×10^{-6}	2×10^{-5}(O)	S
In 4105	90	1×10^{-3}	$<1 \times 10^{-6}$	$<3 \times 10^{-9}$	S
In 4105††	100	1×10^{-5}	2×10^{-6}	4×10^{-3}(O)	G
Zn 2139	100	6×10^{-4}	2×10^{-5}	1×10^{-4}(O)	S
Tl 3776‡‡,***	100	5×10^{-4}	1×10^{-6}	2×10^{-4}(O)	S
Tl 3776§§,***	100	4×10^{-4}	3×10^{-6}	4×10^{-5}(O)	S
Te 2143	100	4×10^{-4}	3×10^{-6}	2×10^{-5}(L)	—
Mn 2794	90	2×10^{-4}	8×10^{-6}	3×10^{-9}(L)	S
Mn 2794††	100	2×10^{-4}	—	—	G
Cu 3248	60	2×10^{-4}	8×10^{-7}	2×10^{-6}(O)	S
Cu 3248	60	2×10^{-4}	1×10^{-6}	1×10^{-5}(O)	S
Cu 3248††	100	7×10^{-5}	6×10^{-6}	2×10^{-7}(L)	S
Sn 2863	70	1×10^{-4}	8×10^{-7}	8×10^{-6}(O)	G
Bi 3068††	100	5×10^{-5}	1×10^{-6}	2×10^{-6}(L)	S
Bi 3068	90	5×10^{-5}	5×10^{-7}	1×10^{-6}(L)	S
Mg 2852	100	4×10^{-5}	8×10^{-7}	5×10^{-6}(O)	G
Pb 4057	100	1×10^{-5}	3×10^{-7}	2×10^{-6}(O)	S
Pb 2833	100	4×10^{-6}	3×10^{-7}	8×10^{-7}(O)	S
Ag 3281	100	7×10^{-6}	1×10^{-7}	4×10^{-7}(B)	S
Au 2676	100	1×10^{-6}	1×10^{-8}	3×10^{-8}(L)	S
Co 2407	100	5×10^{-7}	—	1×10^{-7}(B)	S

* Elements are listed in order of decreasing source intensities. Lamps of Se and As were not measured because their resonance lines were outside the spectral response of the detector. Lamps of Sb, Fe, Ni, Ba, and Ca emitted resonance lines too weak to be detected. All lamps were 9 mm i.d., had 2 mm argon pressure, and were made from the metal iodide except for the following: the commercial Hg lamp (see footnote §); the Zn, Cd, Te, and Hg lamps were made from the metals; the amalgam lamps (see footnote **) were made from the metals and were 11 mm i.d.; the second copper lamp in the table is 5 mm i.d.; the Mn and Bi lamps have 10 mm argon pressure and 9 mm i.d. An intensity of 10^{-3} W/cm² sterad for a 9 mm i.d. lamp corresponds to a total output radiant power of about 0.15 W.

† Source r.m.s. noise and source drift are relative to the source intensity for the specified metal and line. The frequency response bandwidth of the electrometer–amplifier–readout system is 1 Hz.

‡ *O, slow oscillatory drift. L, long term drift. B, slow oscillatory drift superimposed on long term drift.*

§ S, no measurable self-reversal. G, measurable self-reversal.

** Commercial lamp (Ophthos Instrument Co., Rockville, Md.)

†† Amalgam lamps (lamps contain a small quantity of mercury and 2 mm argon pressure as well as a small amount of metal).

‡‡ Tl lamp operated with *no* central arc column.

§§ Tl lamp operated with a central arc column.

*** A heated nichrome wire was wrapped around the bulb of the Tl lamp.

Table IX. Basic Characteristics of Electrodeless Discharge Lamps at 17-120 MHz Excitation Frequencies (from Baronov et al., 1969)

Style *	Element	Line, nm	Max. striking current (mA)	Working current, mA			Line output at opt. current (mW/ster-cm^2)	Half-width, nm at opt. current	Working life (h) at opt. current	Main lines emitted, nm
				min.	opt.	max.				
II	Na	589,0	140	90	170	180	2,1	0,01	1000	589,6; 589,0;
I					50					818,3; 819,4
II	Rb	780,0	120	70	86	130	9,3	0,02	1000	420,0; 421,5;
I					40					780,0; 794,7
II	Cs	852,0	200	75	80	110	5,8	0,08	1000	455,5; 459,3; 807,9; 852,0;
I					40					894,3; 1002,4; 1012,4
II	K	769,9	140	90	120	140	6,1	0,02	1000	404,4; 404,7;
I					50					466,4; 769,9;
II	Cd	508,6	180	100	150	160	5,0	0,006	1000	228,8; 298,0; 346,6;
I					60					508,6; 643,8; 734,6; 738,5
II	Zn	481,0	200	140	175	175	1,2	0,003	1000	213,8; 328,2; 330,2; 334,5;
I					60					468,0; 472,2; 481,0; 636,2
II	Te	535,0	180	175	260	275	1,3	0,0024	100	322,9; 315,9; 276, 8;
I					110					377,5; 535,0
II	Hg	435,8	260	125	155	220	0,8	0,003	300	365,0; 404,7; 435,8; 546,1;
										579,0; 253,6; 296,7; 312,6;
										334,0
II	Bi	306,8	250	260	260	260	5	0,003	200	289,8; 222,8; 223,1; 306, 8
II	Sb	231,1	250	200	240	260	2,5	0,003	200	252,8; 206,8; 217,5; 231,1
II	In	303,9	250	160	160	240	0,75	0,006	50	451,1; 410,2; 325,8; 303,9
II	Pb	283,3	250	200	260	260	0,75	0,0013	200	405,8; 217,0; 283,3
II	Sn	286,3	250	80	100	100	0,27	0,002	200	452,5; 317,5; 286,3; 224,6
II	Cn	324,7	250	120	140	180	4	0,003	50	521,8; 578,2; 324,7; 327,4
II	Se	203,9	250	80	100	100	—	—	200	473,1; 207,5; 206,3; 203,9

* I 1 cm diameter lamp

II 2 cm diameter lamp

Filled with xenon, 1-3 torr

stream containing a trace of H_2O in argon at low pressure. The highest frequency discharge produced only weak emission. Spectral intensities from sources utilizing the other frequencies were not particularly different, although their overall rotational distributions did vary significantly. The radiation was concentrated in the $A^2\Sigma^+ \rightarrow X^2\Pi$ (0, 0) vibrational band. Houghton and Jachimowski (1970) have used a 28 MHz excitation frequency. As normally operated, such lamps emit narrow lines of Doppler shape very suitable for analytical studies (Kaufman and DelGreco, 1963). Intense CO (4th positive) bands (140-200 nm) radiate from discharge lamps containing traces of CO or CO_2 (Slanger and Black, 1969; Comes and Fink, 1972). Felder et al. (1970) indicate combined output of about 10^{15} quanta sec^{-1}. Kurzeg et al. (1957) and Young also have investigated discharges in N_2/O_2 mixtures as a source of the NO band systems. A high voltage discharge between electrodes in flowing water vapor/argon or nitrogen, oxygen, argon mixtures at low pressure in a capillary tube has been used for OH and NO absorption studies, respectively (McGregor et al., 1972). Urani et al. (1973, 1974) have excited NO emission by applying a 27 MHz radio-frequency discharge between parallel plates in a cell.

Laser Line Sources

Lasers surpass the limitations of incoherent sources in many ways; they can radiate more energy, produce short pulses, have narrower spectral lines and be better collimated and focused. Table X has been compiled from a "Laser Selection Guide" (1973) and the Laser Focus Buyers Guide (1974) to illustrate which lasers are currently available on the commercial market and give an indication of their power levels and operating wavelengths. The models, cw or pulsed, can be categorized into one of four types, gas, solid state, liquid dye, or semiconductor.

Gas lasers, in most common use for practical applications, utilize either an electric discharge, a chemical reaction, or gas-dynamic flow to produce the population inversion. Their dimensions generally are not small since power output depends primarily on length, which can be a meter or more. Available power levels are constantly increasing. Alferov et al. (1973), for example, now have reported the initial development of the 500 W cw argon ion laser. The natural lifetimes of the excited levels involved in a laser transition are relatively short, 10^{-8} sec is typical for an atomic transition, so that the natural linewidth

$$\Delta\nu_N = (2\pi\tau)^{-1}, \ sec^{-1}$$

Table X. Commercially Available Lasers

	CW			Pulsed				
	Wavelength, nm	Type	Power, W	Wavelength, nm	Type	Pulse Energy, J	Rep Rate, Hz	Max Average Power output, W
Ultraviolet	226	Quad Nd. Yag	0.1	265	Quad Nd. Glass	0.0025-0.0750	0.02-50	1.0
	325	He. Cd	0.001-0.015	266	Quad Nd. Yag	$(1-10) \times 10^{-5}$	0.5-24,000	0.2
	350/356	Kr^+	0.040-0.500	337	N_2	$3 \times 10^{-6} - 0.3$	1-1000	3.0
	351/364	Ar^+	0.020-0.740	347	Doubled ruby	0.020-0.150	1-50	1.0
				350/356	Kr^+	10^{-8}	20×10^{6}	0.2
				351/364	Ar^+	2×10^{-8}	20×10^{6}	0.4
						5×10^{-5}	50-3000	0.15
				354	Tripled Nd. Glass	0.020	1-50	1.0
				364	Xe^+	50×10^{-6}	10	0.5mW
Visible	442	He. Cd	0.005-0.050	442	He. Cd	$(5.0-7.5) \times 10^{-9}$	10^{6}	0.015
	454/514	Ar^+	0.025-20	454/514	Ar^+	$(0.008-1.0) \times 10^{-3}$	60-3000	3.0
	462/676	Kr^+	0.025-4.0			0.5×10^{-6}	20×10^{6}	10.0
				462/676	Kr^+	$(20-60) \times 10^{-6}$	60	4.0mW
	460/627	Xe^+	?			0.5×10^{-6}	20×10^{6}	10.0
	532	Doubled Nd. Yag	0.010-2	495/596	Xe^+	$(30-150) \times 10^{-6}$	10-60	0.010
	633	He. Ne	0.0001-0.0500	473/679	Doubled Nd. Yag	$(0.2-1.0) \times 10^{-3}$	30-75	0.075
	670	Doubled Nd. Yag	1.0	511	Cu	$(0.4-1.0) \times 10^{-3}$	1000	1.0
	525-700	Tunable dye	0.050-1.50	532	Doubled Nd. Yag	0.0002-0.50	0.5-24,000	4.8
				530	Doubled Nd. Glass	0.35-2.0	0.03-0.06	4.0
				540	Ne	30×10^{-6}	1-500	0.015
				633	He. Ne	10^{-9}	10^{6}	0.001
				694	Ruby	0.005-400	$0.01-10^{5}$	100.0
				220-980	Tunable dye	$5 \times 10^{-6} - 10.0$	0.02-2000	10.0
				415-3400	Parametric oscillator	$(5-70) \times 10^{-6}$	1-2000	0.1
Red-Near IR	752/799	Kr^+	0.030-0.150	850	GaAlAs diode	$(0.3-27.0) \times 10^{-6}$	1000-5000	0.027
	1064	Nd. Yag	0.100-1000	852	GaAs diode	$(0.050-3.0) \times 10^{-3}$	10,000	30.0
	1340	Nd. Yag	0.100-12.0	1060	Nd. Glass	$1 \times 10^{-9} - 1000$	0.002-50	225
	1152	He. Ne	0.0007-0.0500	1064	Nd. Yag	0.0001-100.0	0.03-50,000	100
						1.5×10^{-9}	$(100-200) \times 10^{6}$	0.3
				946/1358	Nd. Yag	$70 \times 10^{-6} - 0.001$	30-75	0.07
				1340	Nd. Yag	0.040-0.050	0.5-10	0.5
				1817	Ar	0.002	10	0.02
Infrared	3.391μm	He. Ne	$50 \times 10^{-6} - 0.020$	2.0/3.6μm	Xe	0.0001-0.0020	10-50	0.02
	5.0/5.5μm	CO	2.0	2.2/7.3μm	Ar	0.0001-0.0020	10-50	0.02
	9.2/10.8μm	CO_2	1-10	2.6/3.0μm	HF	0.015-1.0	0.5-3.0	2.0
	10.6μm	CO_2	1-2000	3.4μm	Ne	0.002	10	0.02
	10.8μm	N_2O	5	3.5/4.1μm	DF	0.2-0.7	1-3	1.2
	28/220μm	H_2O	0.001-0.010	5.1/5.6μm	CO	0.001-0.100	0.5-50	5.0
	311/337μm	HCN	0.001-10	9.1/11.0μm	CO_2	0.04-15.0	1-50	50
				10.6μm	CO_2	0.004-1000	0.01-3000	700
				8/12μm	N_2O	0.100-1.0	1-50	5.0
				28/118μm	H_2O	$(10-100) \times 10^{-6}$	1-30	0.001
				126/372μm	HCN	$10^{-5} - 10^{-3}$	1-30	0.020

is about 16 MHz. Other factors, Doppler, isotopic, or Zeeman broadening are more significant and overall linewidths of 5 GHz (0.2 cm^{-1}) are not uncommon in the visible spectral region for gas laser systems. However, the laser output is not continuous over the broadened line but occurs only at discreet frequencies. A laser cavity is resonant only for frequencies whose corresponding wavelengths are integral multiples of twice the cavity length. These frequencies or longitudinal cavity modes are separated by c/2L where L is the cavity length. Consequently, for a laser one meter in length, c/2L = 150 MHz, so that about 30 modes can oscillate within the gain curve of the laser line. At any instant, several of these modes will be oscillating simultaneously. As a result the effective laser radiation has a characteristic spectral distribution given by the Doppler gain curve. In fluorescence, to enhance the probability of a coincidence between laser frequencies and molecular absorptions and to eliminate intensity fluctuations, it may be preferable to use a laser in such multimode operation. Situations can arise where fluorescence is very weak or may not be observed at all if a small gas laser oscillating in a single frequency mode is used, but can become quite intense for a long cavity laser having many axial modes. The competition between oscillations at the various mode frequencies may result in large amplitude fluctuations at the individual frequencies on a short time scale. However, the total power output will remain the same since when one mode goes up another tends to come down. In cases where the absorption line is only partially overlapped by a multi-mode laser amplitude stability may not be satisfactory for these reasons unless integrated over a finite time period. When a very sharp line is required, this can be produced with single mode operation using for example a tilted etalon as a frequency selector.

The Doppler linewidth is proportional to frequency. Consequently, the cavity frequency spacing, c/2L is larger in the infrared spectral region than the Doppler widths and in such cases the laser can operate only at a single frequency. In fact, in the very far infrared the cavity length has to be tuned to the laser transition. Typical gas laser overall linewidths (FWHM) are He. Ne, 633 nm, 1500 MHz; He.Cd, 442 nm, 1800 MHz (single isotope), 4000 MHz (natural mixture); Ar^+, 488, 514 nm, 2000 to 7000 MHz; CO_2, 10.6 μm, 100 MHz (Arecchi and Schulz-Dubois, 1972).

Although many gas lasing transitions have been reported (Pressley, 1971) few have yet been exploited commercially. Rapidly advancing E-beam technology undoubtedly will increase the number of available gas lasers in the near future.

Solid state lasers consist of a rod which is a transparent matrix doped with the active material. They are pumped with flashlamps or other intense light sources. Ruby and neodymium are the best known examples and are available in small portable sizes. By incorporating various non-linear optical crystals, frequency doubled ruby, and up to quadrupoled neodymium lasers are available. Linewidths for these lasers are quite broad, typically being of the order of 6000 MHz for ruby and 6000 to 30,000 MHz for Nd.Yag lasers (Arecchi and Schulz-Dubois, 1972).

Dye or liquid lasers constitute the best characterized class of tunable laser frequencies. Efficiently pumped by flashlamps or other lasers, a particular dye provides tunability over several decades of nanometers for a particular dye. A summary of the various dyes used and their wavelength ranges is available in the Handbook of Lasers (Pressley, 1971). By using a highly frequency selective optical resonator (grating, etalon and mirror combination) the spectral linewidth can be narrowed to about 10^{-3} nm. Without this sophistication, linewidths are much broader being typically 0.05 to 0.5 nm for grating/mirror cavities. Their overall dimensions generally are large owing to their more complex nature. However, this has not prevented their incorporation into laser radar equipment aboard aircraft (Fox et al., 1973).

Other tunable devices, cw or pulsed, are the semi-conductor lasers and systems utilizing non-linear interactions such as the spin-flip Raman laser, optical parametric oscillators and optical mixers. A multitude of semi-conductor laser materials in the 1 to 30 μm region are in various stages of advanced development. Wavelength ranges which can be covered with such alloyed materials are illustrated in Figure 4 taken from Hinkley (1972b). Operating best at cryogenic temperatures these low power lasers can be tuned by changing their temperature, pressure, magnetic field or the diode current. They can be of very small dimensions. Also, linewidths are particularly narrow, that of a $Pb_{0.88}Sn_{0.12}Te$ diode laser at 10.6 μm was measured as 54kHz (1.8×10^{-6} cm^{-1}) (Schlossberg and Kelley, 1972). Spin-flip Raman lasers use a fixed frequency CO or CO_2 gas laser to pump a semi-conductor crystal in a magnetic field. In general, they may be particularly useful in the 5.2 to 6.4 μm range at low magnetic fields. Other important non-linear optical devices such as optical mixers and parametric oscillators rely on the properties of non-linear crystals. Parametric oscillators extend into the infrared to about 4 μm and require laser pump sources.

The important contribution that lasers can make to the analytical field is rapidly gaining recognition, particularly for atmospheric environmental monitoring. Power levels, amplitude and frequency stabilization now are sufficient for most applications.

LINE SHAPES

In low pressure systems, absorption lines are predominantly Doppler broadened and at low temperatures linewidths are quite narrow. Typical magnitudes at 250 K for various molecular weights are illustrated in Table XI as a function of wavelength. To fall within this linewidth, coincidences have to be quite exact calling for wavenumber agreements between the source and absorption line to within a few hundredths or thousandths of a wavenumber. The prediction of coincidental overlap can in fact be hampered occasionally by the inaccuracy of available spectroscopic data particularly in the infrared where lines are very narrow. For systems at higher pressures, collisional or Lorentz pressure broadening begins to make a significant contribution as can be seen from Table XII, particularly at atmospheric pressure or above. For such cases, a good approximation to the total Voight linewidth is given by the expression (Whiting, 1968)

$$\Delta\nu_{\text{Voight}} = \frac{\Delta\nu_L + \Delta\nu_N}{2} + \left\{ \left(\frac{\Delta\nu_L + \Delta\nu_N}{2} \right)^2 + \Delta\nu_D^{\,2} \right\}^{1/2}$$

Collisional and natural broadening halfwidths are due to a damping type of broadening and add linearly whereas Doppler broadening is of a Gaussian type. These two different types add quadratically (Svobada et al., 1972, 1973).

Consequently, in assessing previous fluorescence studies, the operating pressure must be taken into account. At a lower pressure, fluorescence may no longer occur if the region of overlap depends heavily on the collisional broadening factor. Similarly, attempts to promote fluorescence by increasing the systems operating pressure may be thwarted by other factors such as enhanced rates of collisional quenching. As previously mentioned, considerations of fluorescing systems introduce the problems normally encountered in high resolution spectroscopic studies. Wavelengths must be carefully identified and refer to vacuum conditions, and the spectral positions of isotopic and nuclear hyperfine components noted. Zeeman, Stark, or absorption pressure effect studies are particularly useful in many instances in accurately establishing the closeness of spectral coincidences. Examples are to be found in the work of Melton and Klemperer (1973) who investigated NO fluorescence from the $A^2\Sigma^+$ and $B^2\Pi$ states excited by a

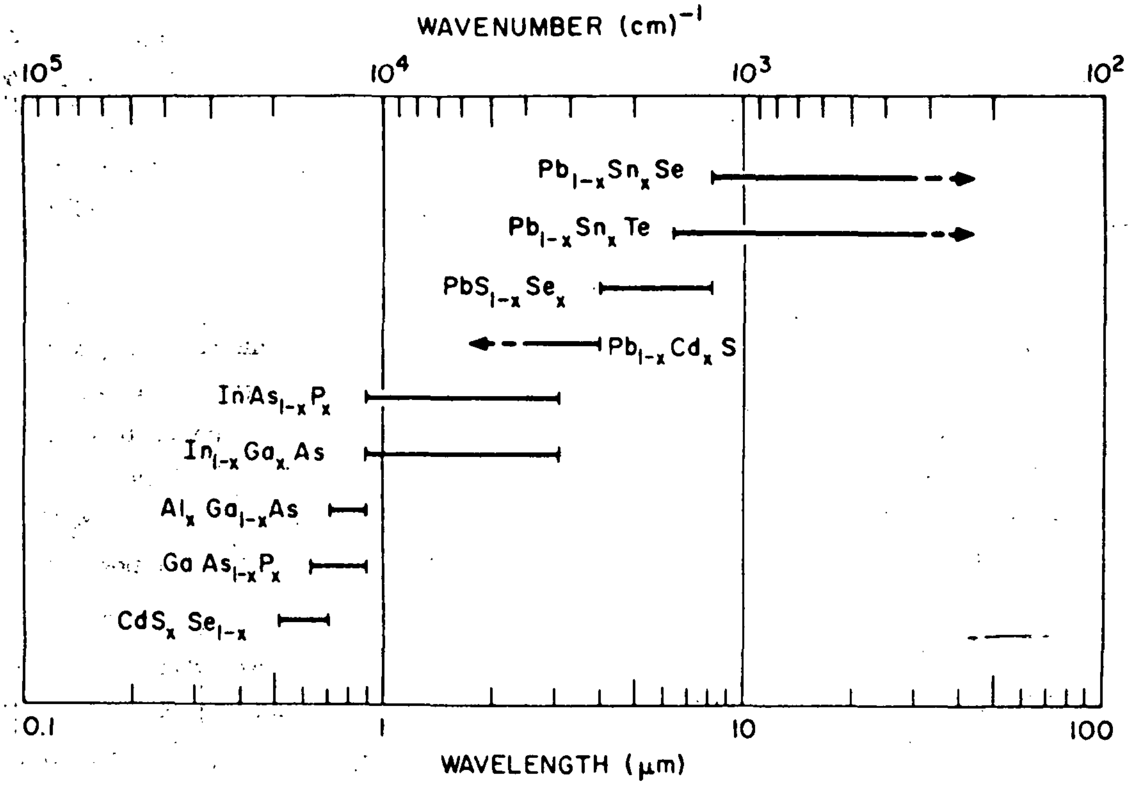

Figure 4. Wavelength Ranges for Semiconductor Lasers Made from Different Alloys and Compositions (from Hinkley, 1972b)

Table XI. Doppler Linewidths* (250 K; MHz, cm^{-1})

Species	Molecular Weight	200	400	600	800	1000	2500	5000	10,000	
		Wavelength, nm								
H_2	2.0	11,955	5977	3985	2989	2391	956	478	239	
H_2S	34.0	2910	1455	970	727	582	233	116	58.2	MHz
Cl_2	70.9	2016	1008	672	504	403	161	80.6	40.3	
H_2	2.0	0.399	0.199	0.133	0.099_7	0.079_7	0.031_9	0.015_9	0.008_0	
H_2S	34.0	0.097_1	0.048_5	0.032_3	0.024_3	0.019_4	0.007_8	0.003_9	0.001_9	cm^{-1}
Cl_2	70.9	0.067_2	0.033_6	0.022_4	0.016_8	0.013_4	0.005_4	0.002_7	0.001_3	

* $\Delta\nu_D = \frac{2}{\lambda}\left(\frac{2\,RT\ln 2}{M}\right)^{1/2} \doteq c\Delta(1/\lambda)_D$

Table XII. Lorentz Pressure Broadening Linewidths* (250K; MHz, cm^{-1})

Species	Pressure 10 torr ($1.333 \times 10^2\ Nm^{-2}$)	100 torr ($1.333 \times 10^3\ Nm^{-2}$)	760 torr ($1.013 \times 10^5\ Nm^{-2}$)	
H_2 in Air	62.21	622.1	4728	
H_2S in Air	24.47	244.7	1880	MHz
Cl_2 in Air	25.40	254.0	1930	
H_2 in Air	0.0020_7	0.0207	0.1577	
H_2S in Air	0.0008_2	0.0081_6	0.0620	cm^{-1}
Cl_2 in Air	0.0008_5	0.0084_7	0.0644	

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* Collision diameters: Air, 0.36; H_2, 0.26; H_2S, 0.30; Cl_2, 0.36 nm

$$\Delta\nu_L = \frac{2}{\pi} d^2 n \left(\frac{2\pi RT}{\mu}\right)^{1/2} = c\Delta(1/\lambda)_L$$

where d = collision diameter
n = number density, cm^{-3}, of perturber
μ = reduced mass, molecular weight (gms), of colliding species

variety of Zeeman shifted line sources. Similarly, Shimizu (1970a) has measured the electric field strengths necessary for about 100 coincidences between NH_3 and laser lines of CO_2 and N_2O. Sakurai et al. (1967) and Johns and McKellar (1973) have examined laser coincidences in HCHO and the deuterated compound at 3.5 and 5.8 μm, respectively. Studies of the absorption as a function of pressure of the HF $P_{1,0}(6)$ laser line by a line of NO at 3693.5 cm^{-1} have accurately located their relative positions (Nachshon and Coleman, 1973).

From the point of view of designing a simple analytical technique suitable as flight hardware, the possibility of invoking such Zeeman or Stark effects to shift one of the components of a source or absorption line into exact coincidence is not attractive. Shifts of the order of 1 cm^{-1} can require magnetic fields as high as 20,000 gauss (2T), and electric field strengths of the order of 200 esu (60kV/cm). Such high intensity fields automatically introduce a variety of experimental difficulties. However, as a more general analyzer such considerations may be justifiable. This appears to be the case for the extensive efforts that have been directed into producing an NO monitor by Zeeman shifting one of its absorption lines into coincidence with the CO laser line at 1884.37 cm^{-1} (Kaldor et al., 1972; Bonczyk and Ultee, 1972).

For the species of current interest, vibrational frequencies are of the order 500 to 4000 cm^{-1}. In systems at temperatures in the vicinity of 250 K this implies that at least 95% of the species will be in the $\upsilon = 0$ level of the ground state. Consequently, only fluorescence resulting from absorptions from this lowest level are relevant to this study.

SPECTRAL CONSIDERATIONS

Fluorescent emissions have been induced in a wide spectral region ranging from the vacuum ultra-violet through to the infrared. However, in systems which contain air, water vapor, and only a trace of the species that is to be optically pumped, spectral considerations alone may rule out the appropriateness of various regions. For example, in the 0.74 to 25 μm region extensive band systems of CO_2 and H_2O eliminate all but various narrow window regions at about 1.06, 1.27, 1.55 to 1.75, 2.04 to 2.35, 3.50 to 4.18, and 8.6 to 13.1 μm (Pressley, 1971; McClatchey and Selby, 1974). Similarly, at the other end of the spectral range, absorption bands of the Schumann-Runge system of O_2 $(B^3\Sigma_u^- - X^3\Sigma_g^-)$ lie below 200 nm and merge into a strong dissociative continuum between 175 and 125 nm, with complex absorption bands in the 100-125 nm region.

Consequently, most of the vacuum uv spectral region is automatically eliminated from our considerations. For example, a path length of 1 cm of air at 100 torr absorbs at least 98% of the incident radiation at wavelengths between 135 and 160 nm ($\sigma \geq 5 \times 10^{-18} cm^2$). A 10 cm pathlength will absorb about 46% of the radiation between 120 and 135 nm ($\sigma \geq 10^{-19} cm^2$) and at least 20% between 160 and 175 nm ($\sigma \geq 2 \times 10^{-19} cm^2$; Hudson, 1971). The Schumann-Runge band system ($B^3\Sigma_u^- - X^3\Sigma_g^-$) lies between 175 and 200 nm. At low temperatures contributions from the $\upsilon'' = 1$ bands are small and the region then consists of a band progression from $\upsilon' = 0$ to $\upsilon' = 21$. Cross-sections increase from a value of about $2 \times 10^{-23} cm^2$ for the (0, 0) band at 202.5 nm, to $2.5 \times 10^{-19} cm^2$ for the (21, 0) band at 175 nm (Ackerman et al., 1970). Such absorption, besides drastically reducing the intensity of the incident beam also constitutes a potential interference since fluorescence to high lying υ'' values occurs in the uv and blue spectral regions. In well characterized systems, if an absorption line is known to lie within a window of this region, such that at least portions of the line are not overlapped by O_2 absorbing lines, the fluorescence technique may still be feasible. By passing the source line first through a cell containing O_2 it can be effectively reshaped so that it becomes completely transparent to oxygen and absorption in a test cell then would only occur with the desired species. However, for wavelengths shorter than the (4, 0) band at 192 nm, the absorption lines are quite densely populated and it is unlikely that such an approach can be invoked here.

It would therefore appear from the outset that the most profitable spectral region for sensitive fluorimetry, most free from potential interference effects will lie in the uv and visible regions between 200 and 700 nm.

SCATTERED RADIATION

Incident radiation is scattered by various mechanisms in a fluorescence cell. Resonance fluorescence re-emits at the same wavelength as the emitting source and its magnitude relative to other fluorescent emissions at various wavelengths is controlled by the relative Franck-Condon factors. Rayleigh and Raman scattering effects also arise through interactions with the various gaseous components of the mixture. The intensity of the scattered light in these cases is inversely proportional to the fourth power of the wavelength. Mie scattering from potential stratospheric particulates can also arise and is much less wavelength dependent being more important in the visible and infrared regions.

Rayleigh scattered light is of the same frequency as that of the incident beam. However, if viewed perpendicular to the direction of the exciting beam, it is almost completely plane polarized with the plane of vibration perpendicular to the common plane of the incident and scattered beams. If necessary, this feature offers one well-recognized method for its partial discrimination. However, large aperture polarizers with a high rejection ratio are very expensive if available at all. If the incident beam is plane polarized, for example, using a polarized laser source, a matching of its vibrational plane with that of the incident and scattered beams will effectively attenuate the Rayleigh scattering to a certain extent. Complete rejection is not possible owing to the finite angular size of the detector. Raman scattering for completely symmetrical vibrations also results in highly polarized lines, whereas fluorescence is completely unpolarized if excited with non-polarized radiation. A polarized light source will produce partially de-polarized fluorescence dependent upon the collisional history of the excited state. Rayleigh, Raman and Mie scattering occur in approximately 10^{-14} sec, whereas fluorescence lifetimes fall in the range 10^{-6} - 10^{-9} sec. In the present case Raman scattering will be predominantly from molecules in $\upsilon = 0$ and, therefore, will consist of one Stokes rotation - vibration band separated from the exciting wavelength by the $\upsilon'' = 1 - \upsilon'' = 0$ energy ($\omega_e - 2\omega_e x_e$ cm^{-1}). Overtone Stokes lines ($\Delta \upsilon \geq 2$) are very weak and can be neglected.

An estimate of the Rayleigh, Raman, and Mie scattering effects is necessary in these assessments. Although it is well known that they are extremely weak and their cross-sections are many orders of magnitude below those for fluorescence, this may be more than compensated for by the correspondingly large discrepancy between the concentrations of nitrogen and oxygen and the ppb levels of the species of interest. Consequently, estimates will be necessary for the combined Rayleigh, Mie and resonance fluorescence scattering of the incident wavelength in order to insure sufficient blocking in the interference filter of the detection system at this wavelength and prevent leakage of light through the filter at any but the designated bandpass. Similarly by noting the location of the various Stokes lines, any such interfering radiation can be discriminated against by prudent choice of the exciting wavelength and detector bandpass. The Raman shift in cm^{-1} for the molecules of interest are: CO_2 1285.4, 1388.1, O_2 1556.2 and N_2 2329.7. It is not mandatory to eliminate these scattering effects since they will produce a constant background signal which can be removed by calibration. However, too large a contribution to the signal will increase the photomultiplier noise and degrade the sensitivity. Consequently, steps are recommended to minimize their effects.

Rayleigh cross-sections for a dry air mixture as a function of wavelength are given in Table XIII. Penndorf (1957) has calculated the total scattering cross-sections and their angular dependence. Taking the value for the direction perpendicular to the incident beam and integrating over an f/2 detector aperture the required cross-sections for scattering into the detector optics have been obtained. Raman cross-sections are typically about three orders of magnitude smaller. Cooney (1968) obtained:

$$\sigma_{\text{Raman}} / \sigma_{\text{Rayleigh}} = 1.88 \times 10^{-3}$$

for N_2 at 694.3 nm. In the current assessments, this value is assumed to be valid for all wavelengths. Cross-sections for O_2 and the two Raman-active vibrations for CO_2 (1285, 1388 cm^{-1}) are about 1.3, 0.9 and 1.5 times larger, respectively, than for N_2 (Penney et al., 1972; Lidholt, 1972; Fenner et al., 1973).

Scattered intensities, I_{scatt}, are related to the incident intensity, I^o, by the expression:

$$I_{scatt} = I^o n \sigma \ell$$

where n = number density of the scattering species, cm^{-3}
σ = scattering cross-section, cm^2

As measurements are to be made directly on stratospheric samples brought into the aircraft by Ram flow lines, particulates may be present in the system to various extents particularly at those altitudes where aerosol layers are known to be concentrated (20 km in the Tropics). Elterman (1968) and McClatchey et al. (1971) have developed atmospheric attenuation models for various spectral wavelengths based on absorption and scattering. Values for the relative importance of Mie to Rayleigh scattering as a function of altitude and wavelength in the atmosphere can be derived from their tabulated data. Values from the two sources are in reasonable agreement. Elterman's data are listed in Table XIV and illustrated in Figure 5. It is seen that at wavelengths up to 500 nm, Mie scattering is less or equal to the Rayleigh component of the scattered intensity. However, at longer wavelengths particle scattering becomes more important and must be included in any assessment of the total scattered light. The extent of the sum of Mie and Rayleigh scattering are calculated later for stratospheric samples at 10 torr (30 km) and 100 torr (15km).

Table XIII. Rayleigh Scattering Cross-Sections for Standard Air (from Penndorf, 1957)

λ, um	Total Cross-Section, cm^2	Cross-Section/Steradian at 90°	Approxims to Cross-Section for f/2 Detector at 90°
0.20	3.551×10^{-25}	2.196×10^{-26}	4.312×10^{-27}
0.21	2.802	1.733	3.402
0.22	2.244	1.388	2.725
0.23	1.836	1.135	2.229
0.24	1.511	9.344×10^{-27}	1.835
0.25	1.258	7.780	1.527
0.26	1.057	6.537	1.283
0.27	8.959×10^{-26}	5.540	1.088
0.28	7.645	4.728	9.283×10^{-28}
0.29	6.568	4.062	7.975
0.30	5.676	3.510	6.892
0.31	4.933	3.051	5.990
0.32	4.309	2.665	5.232
0.33	3.782	2.339	4.592
0.34	3.334	2.062	4.048
0.35	2.951	1.825	3.583
0.36	2.622	1.621	3.184
0.37	2.337	1.445	2.838
0.38	2.091	1.293	2.539
0.39	1.877	1.161	2.279
0.40	1.689	1.045	2.051
0.41	1.525	9.431×10^{-28}	1.852
0.42	1.380	8.534	1.676
0.43	1.252	7.743	1.520
0.44	1.139	7.044	1.383
0.45	1.038	6.419	1.260
0.46	9.482×10^{-27}	5.864	1.151
0.47	8.680	5.368	1.054
0.48	7.961	4.923	9.667×10^{-29}
0.49	7.316	4.524	8.884
0.50	6.735	4.165	8.178
0.51	6.211	3.841	7.542
0.52	5.736	3.547	6.965
0.53	5.307	3.282	6.444
0.54	4.917	3.041	5.971
0.55	4.563	2.822	5.541
0.56	4.239	2.622	5.147
0.57	3.945	2.440	4.790
0.58	3.675	2.273	4.462
0.59	3.428	2.120	4.163
0.60	3.202	1.980	3.888
0.61	2.994	1.852	3.636
0.62	2.802	1.733	3.402
0.63	2.626	1.624	3.189
0.64	2.464	1.524	2.992
0.65	2.313	1.430	2.809
0.66	2.175	1.345	2.641
0.67	2.046	1.265	2.484
0.68	1.927	1.192	2.340
0.69	1.816	1.123	2.205
0.70	1.713	1.059	2.080
0.71	1.618	1.001	1.965
0.72	1.529	9.456×10^{-29}	1.857
0.73	1.446	8.942	1.756
0.74	1.369	8.466	1.662
0.75	1.296	8.015	1.574
0.76	1.229	7.600	1.492
0.77	1.166	7.211	1.416
0.78	1.106	6.840	1.343
0.79	1.051	6.500	1.276
0.80	9.989×10^{-28}	6.177	1.213
0.90	6.212	3.842	7.543×10^{-30}
1.00	4.065	2.514	4.936
1.10	2.771	1.714	3.365
1.20	1.954	1.208	2.373
1.30	1.417	8.763×10^{-30}	1.721
1.40	1.052	6.506	1.277
1.50	7.979×10^{-29}	4.934	9.689×10^{-31}
1.60	6.160	3.809	7.480
1.70	4.831	2.988	5.866
1.80	3.842	2.376	4.665
1.90	3.094	1.913	3.757
2.0	2.519	1.558	3.059
2.5	1.031	6.376×10^{-31}	1.252
3.0	4.968×10^{-30}	3.072	6.033×10^{-32}
3.5	2.681	1.658	3.255
4.0	1.571	9.716×10^{-32}	1.908
4.5	9.807×10^{-31}	6.065	1.191
5.0	6.434	3.979	7.813×10^{-33}
5.5	4.394	2.717	5.336
6.0	3.102	1.918	3.767
6.5	2.252	1.393	2.734
7.0	1.582	9.784×10^{-33}	1.921
7.5	1.271	7.860	1.543
8.0	9.815×10^{-32}	6.070	1.192
8.5	7.701	4.762	9.351×10^{-34}
9.0	6.127	3.789	7.440
9.5	4.935	3.052	5.992
10.0	4.020	2.486	4.881
11.0	2.746	1.698	3.334
12.0	1.938	1.198	2.353
13.0	1.407	8.701×10^{-34}	1.708
14.0	1.046	6.469	1.270
15.0	7.940×10^{-33}	4.910	9.641×10^{-35}
16.0	6.133	3.793	7.447
17.0	4.813	2.976	5.844
18.0	3.829	2.368	4.649
19.0	3.084	1.907	3.745
20.0	2.512	1.553	3.050

Table XIV. Ratio of the Intensities of Mie to Rayleigh Scattering (from Elterman, 1968)

λ, um	Altitude, km 10	15	20	25	30
0.27	0.075_5	0.133_9	0.164_8	0.102_0	0.066_8
0.36	0.213_8	0.379_5	0.466_3	0.288_3	0.189_2
0.50	0.578_5	1.026	1.261	0.782_0	0.512_0
0.65	1.433	2.540	3.133	1.935	1.265
0.90	4.511	7.989	9.835	6.083	3.991
1.26	15.71	27.83	34.35	21.21	13.89
1.67	44.15	78.06	96.32	59.42	40.03
2.17	109.5	194.3	238.8	147.2	96.61
3.50	607.4	1077	1311	823.0	540.0

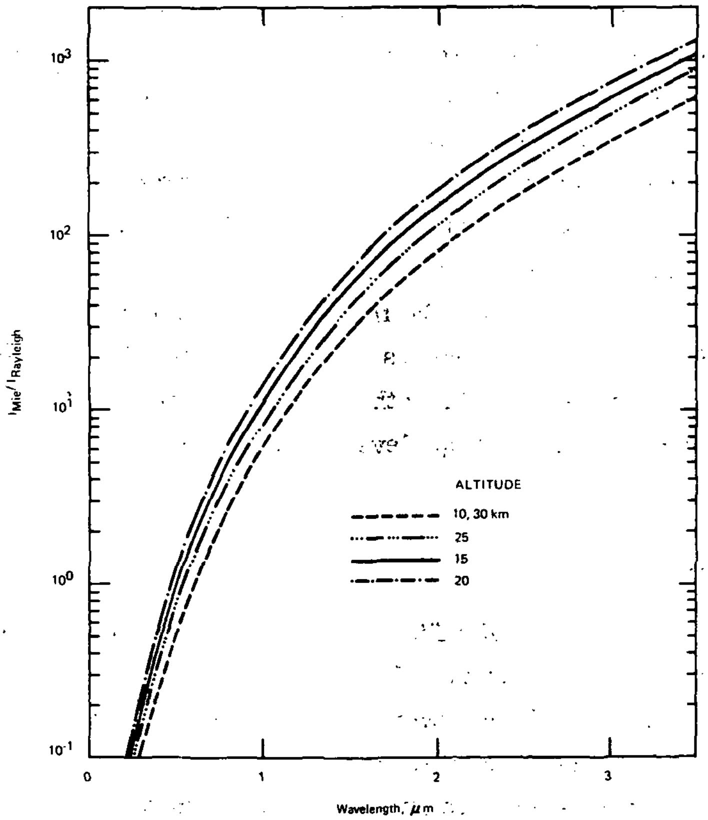

Figure 5: Relative Magnitude of Mie to Rayleigh Scattering in the Atmosphere as a Function of Wavelength (Elterman, 1968)

For a sample pressurized to atmospheric pressure it is assumed that all particulates will be removed and only the Rayleigh component is therefore evaluated in this particular case.

Actual aerosol or particulate concentrations in the troposphere are variable but generally have a magnitude measured in thousands cm^{-3} at ground level. Their concentration falls off exponentially to 5 to 10km and at the tropopause are of the order of several particles cm^{-3}. McClatchey et al. (1971) have taken an atmospheric model based on particle concentrations in the range 2 to 57 cm^{-3} in the 30 to 10km region. However, measurements in the Southern hemisphere have reported densities of 0.1 to 1.5 particles cm^{-3} (Clemesha and Rodrigues, 1971). It would appear safe to conclude that the ratio of stratospheric to ground level concentrations is of the order of at least 10^{-2} to 10^{-3}.

Gelbwachs and Birnbaum (1973) have noted an unusual interference in their ground level monitoring of NO_2 concentrations at El Segundo, California. They report observing broadband fluorescence in the visible region from aerosol particles. For heavy aerosol loadings this interference was equivalent to NO_2 concentrations as high as 1ppm. The nature of the fluorescence, whether it arises from an organic component of the aerosol has not been determined. However, the fact that the interference was removed by filtering through a 5μm pore size glass frit indicates that the effect is produced predominantly by large particles. Mean particle size estimates for stratospheric aerosols have been made by Bigg et al. (1970), who find values in the range 0.2 to 0.8 μm and that most consist of H_2SO_4 with varying degrees of ammoniation. This coupled with the very low particulate densities makes it unlikely that such an effect will constitute an interference even at concentrations in the ppb level for stratospheric fluorescence measurements.

DETECTION SYSTEMS

The detection system will consist of a filter, a photomultiplier and the necessary electronic and recording components. Preliminary discussion has already been presented of the possible need to restrict the field of view to limit the angles of incidence of fluorescent radiation falling on the face of an interference filter (q.v. equipment dimensions). Such filters are readily available and can be custom made to almost any desired specifications. Accuracy is now such that filters can be centered to within 0.1 nm in the visible region with required half-widths tailored to very close tolerances. Peak transmission is usually about 20% to 60%. Leakage through the filter outside of the bandpass is a critical factor and filters are normally supplied with blockage (rejection factor) to better than 10^{-5} in the uv, 10^{-3} to 10^{-5} in the visible, and 10^{-5} to 10^{-4} in the infrared. They are usually completely blocked on the short wavelength side and at longer wavelengths may be complete or to the detector sensitivity limit. It is known that most filter glasses fluoresce particularly when irradiated with uv light. Interference filters are no exception since fluorescent glasses are commonly used as a substrate layer (Turner, 1973). However, for the intensity levels in the detection system, this hopefully will not be a problem. The use of chemical filters in certain cases should also be considered since prudent choice may provide the desired characteristic with an overall higher transmission.

For optimum detection sensitivity using pulse-counting techniques a photomultiplier is required with high quantum efficiency at the fluorescing wavelength and with a large cathode area but low refrigerated cathode dark current noise (Morton, 1968). In general, the larger the factor: cathode sensitivity x cathode area/equivalent noise input, the better will be the tube for this application. This consideration is necessary since dark noise is a function of cathode size. Characteristics are listed in Table XV for the most suitable tubes, 2" diameter or less, manufactured by RCA, EMI, and EMR. When cooled to -20°C most of these have particularly low equivalent noise inputs (ENI) or dark current count rates. Wide variations in dark current readings for a particular tube often arise and it is desirable that a required tube be individually selected for the desired property (Rodman and Smith, 1963). In the development of the NO chemiluminescent detector for stratospheric measurements Ridley et al. (1972a, b; 1974) have used the dry-ice cooled EMI 9558, 9659, and RCA C31034A tubes. The first two of these produced NO detection limits of the order of 0.03 ppb. Slight improvement to about 0.02 ppb was obtained with the latter RCA tube. This is compatible with the approximate manufacturer's specifications listed in the table. However, for detection in the 300 to 500 nm region, owing to its large cathode size, a tube such as the EMI 9813 may be superior. For the detection of fluorescence over a narrow bandwidth, wide spectral response tubes are not necessary and may aggravate detection problems. An optimum situation is one where the tube discriminates against the spectral region of the exciting and scattered radiation.

Infrared detectors do not have the sensitivity of photomultipliers as is evidenced by the fact that Bott (1972) while monitoring the fundamental band of HF at 2.7 μm could also detect up to the $\Delta \upsilon = 5$ overtone band of HF in the vicinity of 600 nm in spite of its much lower intensity. The noise equivalent power (ENI) of these detectors is given by the reciprocal of the detectivity value (D*), which figure is usually quoted for a particular material:

$$\mathrm{ENI} = D^{*-1}, \ \mathrm{W\ cm^{-1}\ sec^{1/2}}$$

For a detector of area A, with a bandpass of Δf,

$$\mathrm{ENI} = D^{*-1}\ A^{1/2}\ \Delta f^{1/2}, \ \text{watts.}$$

In the 1 to 15 μm spectral region, values of D* are of the order of 5×10^{12} to 5×10^{10} $\mathrm{W^{-1}\ cm\ sec^{-1/2}}$ so that with a bandpass $\Delta f = 1$ and 0.1 $\mathrm{cm^2}$ area, equivalent noise inputs are of the order of 6×10^{-12} to 6×10^{-14} W, many orders of magnitude larger than the corresponding values for uv - visible photomultiplier tubes. Infrared photocathode areas generally are much smaller than the 0.1 $\mathrm{cm^2}$ figure assumed here. However, to maximize the collection solid angle in fluorescence studies, as large an area as possible is required.

Table XV. Characteristics of Some of the Most Suitable Photomultiplier Tubes

Tube	Cathode Material	Spectral Response, nm	Stages	Useful* Range, nm	Quantum* efficiency, %	Peak Cathode Sensitivity Luminous :	Radiant	Cathode dimensions, cm	Cathode equivalent noise input, W	
						µA/lm	mA/W		20°C	-20°C
RCA C31034A†	GaAs	200-920	11	280-880	15-48	1000	155	0.4x1.0	6×10^{-16} (10,000 cps)	1×10^{-18} (12 cps)
EMR 681B-01-13	GaAs	260-900	13	290-870	7-22	600	73	0.76x0.51	3.5×10^{-16} (8000 cps)	1×10^{-18} (10 cps)
EMI 9658 R	Trialkali	300-950	11	300-600	14-33	350	95	4.4 dia	5×10^{-16}	6×10^{-17}
EMI 9558†	Trialkali	300-840	11	340-570	9-22	180	64	4.4 dia	3.5×10^{-16}	4×10^{-17}
EMI 9659†	Trialkali	340-930	11	340-600	9-20	250	76	4.4 dia	4×10^{-16}	5×10^{-17}
EMR 543E-01-14	Trialkali	270-850	14	300-600	10-22	150	74	4.3 dia	1×10^{-16} (1600 cps)	2×10^{-17} (50 cps)
EMI 9789 B QB	Bialkali	310-650 170-650	13	320-480 170-480	14-20 14-20	50	-	1.0 dia	1.5×10^{-17} (50 cps)	5×10^{-18} (10 cps)
EMI 9813 B QB	Bialkali	300-650 170-650	14	325-500 290-500	15-27 15-27	-	86	4.6 dia	8×10^{-17}	1×10^{-17}
EMR 543N-01-14	Bialkali	270-700	14	270-480	12-18	55	60	4.3 dia	4×10^{-17} (125 cps)	1.5×10^{-17} (35 cps)
RCA C31005	CsTe	180-350	12	190-280	3- 5	-	9.2	1.3 dia	1×10^{-17}	-
EMI G26H315	CsTe	110-360	15	130-260	9-13	-	-	1.6 dia	5×10^{-18} (1 cps)	-
EMR 542F-08-18	CsTe	105-350	18	200-280	5- 7	-	14	2.8 dia	2×10^{-16}	-

* Sensitivity ≥ 70% peak value: corresponding quantum efficiencies

† Used by Ridley et al. (1972a,b; 1974) in the NO chemiluminescent detector

CALCULATED FLUORESCENCE DETECTION LIMITS FOR INDIVIDUAL SPECIES

It is required to calculate the concentration of a particular species that will produce fluorescent signals leading to a S/N detection ratio of unity. Fluorescent intensities have been calculated from the previously derived expression:

$$I_f = \underbrace{\frac{\Omega_F f\theta}{4\pi}}_{\substack{\text{Detector}\\ \text{factor}}} \cdot \underbrace{\frac{k_f}{k_f + k_d + k_q\,[M]}}_{\substack{\text{Fluorescence}\\ \text{efficiency}}} \cdot \underbrace{I_s\, a_s\, \Omega_s}_{\substack{\text{Source}\\ \text{factor}}} \cdot \underbrace{n\sigma\ell}_{\substack{\text{Absorption}\\ \text{factor}}} = \underbrace{N}_{\substack{\text{Detector Equivalent}\\ \text{Noise input}}}$$

where N is the equivalent noise input, in watts, of an appropriate detector. An f/2 effective aperture has been assumed for the fluorescence collection system throughout ($\Omega_F/4\pi = 1/64$). f, the fraction of the total fluorescence monitored, is dependent upon the bandwidth of the detector filter. θ, the filter transmission, also depends on the detection wavelength and bandwidth; appropriate values have been taken from manufacturers' literature. For light sources, other than laser beams, the source solid angle is assumed to have an f/2 effective aperture. The noise level, N, and the pathlength, ℓ, depend on the particular detector used. ℓ in each case has been taken as the diameter of the photocathode.

Since detection limits are generally expressed as a fractional unit (ppb) the above equation can be re-written with the substitution

$$n = 9.658 \times 10^9 \, p\chi/T$$

where p (torr) and T (K) are the total pressure and temperature, respectively, of the air sample. χ is the required detection limit expressed in ppb. In cases where only a fraction of the total number of molecules of the particular species is in the absorbing energy level, i, the concentration n must be reduced by the factor n_i/n which can be calculated assuming a Boltzmann distribution over all the available energy levels. Also, in those cases where only a partial overlap occurs between the source line and the absorbing line, a factor has to be included which effectively reduces the absorption cross-section by an appropriate amount. Generally, this factor has been derived in only an approximate manner by considering the relative positions of the lines and assuming particular line shapes. This should be quite sufficient for these basic assessments. A temperature of 250 K has been assumed for the air in the test equipment. For conditions other than those assumed here, simple sealing can often be applied to the calculated detection limits.

ATOMIC CHLORINE, Cl

Atomic resonance fluorescence of atomic chlorine is very sensitive; it occurs in the vacuum ultraviolet being excited in the region of 135 to 140 nm. Clyne and Cruse (1972) have reported a lower limit of detection of about 5 x 10^{10} atoms cm^{-3}, which figure could be improved upon perhaps by a factor of 5 to 10. They found the technique inherently more sensitive than resonance absorption spectrometry. Wavelengths and relative line strengths for the $^4P_{1/2,\ 3/2,\ 5/2} \leftarrow {}^2P_{1/2,\ 3/2}$ and $^2P_{1/2,\ 3/2} \leftarrow {}^2P_{1/2,\ 3/2}$ transitions are given by Davis and Braun (1968) and Clyne and Cruse (1971). Exciting lamp intensities were of the order of 1 x 10^{15} quanta sec^{-1}.

The low-lying, metastable J excited $^2P_{1/2}$ level of the ground electronic state is 881 cm^{-1} above the $^2P_{3/2}$ component. At 298 K its population is only 0.8% that of the $^2P_{3/2}$. Even so, Clyne and Cruse (1971) noted strong fluorescence associated with absorptions from it. At 250 K its population would decrease to 0.3%. In systems free from oxygen this is a particularly sensitive monitor for Cl atoms in either or both of the ground state components. However, it holds no promise for the present task of analyzing stratospheric air samples.

CHLORINE, Cl_2

Chlorine exhibits absorption continua below 480 nm due to several electronic transitions, which are at a maximum around 330 nm. The well characterized $A^3\Pi_{0_u^+} - X^1\Sigma_g^+$ bands occur from this region to about 566.5 nm. Although spin-forbidden, the system is observed for Cl_2. In the heavier iodine molecule this transition is particularly strong and its fluorescence is undoubtedly the most extensively studied for any one gaseous molecule (Table II). Halogens other than iodine do not absorb anything like as strongly in the visible region. The rotational lines of the 0_u^+ state are identical to those for a $^1\Sigma^+$ state; and the structure for Cl_2 is very similar to that of any $^1\Sigma_u^+ - {}^1\Sigma_g^+$ band and shows single P and R branches. Its spectrum is somewhat complicated due to the isotopic components of naturally occurring Cl_2. Vibrational spacings are such that at 250 K only about 4% of the molecules would be in the $\upsilon'' = 1$ level so that absorptions involving the ground state are preferable.

The only detailed fluorescence studies reported in the literature are those for $^{35}Cl_2$ by Holzer et al. (1970a, b) with the 487.986 nm Ar^+ laser line. The transition was identified as arising in the (22, 0) band at $J \sim 38$; at 250 K $n_{\upsilon''=0\ J''=38}/n \sim 0.03$. The fluorescence was particularly weak, in fact an order of magnitude less intense than the Raman fundamental band emission. Plumley (1934) excited fluorescence in Cl_2 with the 546 nm Hg line but noted that the absorption coefficient was 1000 times less than that for Br_2 at this wavelength. Similarly, the fluorescence for Br_2 was about 300 times weaker than that from I_2. Capelle et al. (1971) also have noted the weakness of Cl_2 fluorescence using as the exciting source a pulsed tunable dye laser, pumped with the 337 nm nitrogen laser line and operating in the spectral range 513-626 nm.

It is evident that fluorescence techniques are no use for the detection of Cl_2. Being homonuclear, the molecule is also infrared inactive and can only be stimulated by the weak Raman interaction.

CHLORINE MONOXIDE, ClO

Absorption bands attributed to the $A^2\Pi_i \leftarrow X^2\Pi_i$ system extend from the vicinity of 300 nm to the convergence limit near 263 nm beyond which there is continuous absorption through to the vacuum ultraviolet. The absorption spectrum consists of a strong $v' = 0$ progression. The bands have fairly sharp heads and are degraded to the red. A high resolution study by Durie and Ramsay (1958) showed that the rotational structure for many of the low v' bands is quite diffuse due to predissociation, higher v' bands are sharp. The (7, 0) band is completely diffuse and no individual lines are seen. The most clearly resolved is the (12, 0) band which is also the strongest. Table XVI lists the bandhead wavelengths and the relative band intensities for these transitions from the lowest $v'' = 0$ level.

Table XVI. Absorption Bands of the Main $^2\Pi_{3/2}$ - $^2\Pi_{3/2}$ Subsystem of ClO (from Porter, 1950, and Durie and Ramsay, 1958)

λ	I	v', v''	λ	I	v', v''	λ	I	v', v''
303.45	1	4, 0	277.16	10	12, 0	265.25	5	20, 0
299.30	2	5, 0	274.95	8	13, 0	264.58	3	21, 0
295.43	3	6, 0	272.94	7	14, 0	264.06	2	22, 0
291.80	5	7, 0	271.11	7	15, 0	263.63	2	23, 0
288.40	5	8, 0	269.50	6	16, 0	263.35	-	24, 0
285.18	6	9, 0	268.25	5	17, 0	263.10	-	25, 0
282.24	8	10, 0	267.12	5	18, 0			
279.60	8	11, 0	266.10	5	19, 0			

Several weaker bands of the $^2\Pi_{1/2}$ - $^2\Pi_{1/2}$ subsystem also have been reported by Porter (1950) at the following wavelengths (nm),

297.50 (5, 0)	286.67 (8, 0)	278.14 (11, 0)
293.76 (6, 0)	283.57 (9, 0)	275.80 (12, 0)
290.20 (7, 0)	280.70 (10, 0)	273.53 (13, 0)

Other characterized electronic systems lie in the vacuum ultraviolet (Basco and Morse, 1973). Various studies have been made of the extinction coefficient, ϵ, for several of these bands, where this is defined by:

$$\log_{10}(I/I_0) = -\epsilon c \ell$$

and generally is expressed in cm^2 $mole^{-1}$ units with c the concentration, in mole cm^{-3}. Such ϵ values can be converted to the cross-sections σ (base e), used throughout this report, by multiplying by 3.82×10^{-24}. Values have been reported by two groups of researchers and are listed in Table XVII. The values illustrate the generally strong absorption in this system, peaking in the (12, 0) band. Clyne and Coxon (1966) found that the detection limit for their system (deuterium lamp, 20 cm pathlength) was about 5×10^{13} cm^{-3} which corresponds to about 2 ppm at atmospheric pressure. The detection of ClO using an absorption technique would run into the problem of interferences from SO_2, NO_2 and O_3 which also absorb quite strongly in this spectral region.

No fluorescence studies have been reported for ClO and little data appears to exist concerning its radiative lifetime or its rates of quenching. Since the absorption cross-section obtained with coarse spectral resolution is quite large, that for a particular rotational transition pumped for example with an atomic line, if a coincidence can be found, or a narrow tunable dye laser line, may provide a sufficiently sensitive technique for monitoring ClO if the fluorescence efficiency is favorable. By suitably locating the detector bandpass a potential interference from SO_2 could be avoided. That from NO_2 would have to be minimized.

Table XVII. Absorption Cross-Sections for ClO

Transition	σ, cm^2	Reference
(7, 0) band	4.0×10^{-18}	Basco and Dogra, 1971
(12, 0) band	7.3×10^{-18}	Clyne and Coxon, 1968
	6.5×10^{-18}	Basco and Dogra, 1971
257.7 nm continuum	4.8×10^{-18}	Clyne and Coxon, 1968
	4.4×10^{-18}	Basco and Dogra, 1971

CHLORINE DIOXIDE, ClO_2

For a triatomic molecule, OClO shows a remarkably regular absorption system of well-defined single-headed bands, strongest in the 310 to 380 nm region but extending from about 270 to 480 nm. Coon and Ortiz (1957) list 143 vibronic bands in this region. The sharp-headed bands occur in regularly spaced groups, each of which consists of one strong band and two or three weaker ones to shorter wavelengths. These absorption transitions belong to the $A\,^2A_2 \leftarrow X\,^2B_1$ electronic system and form several progressions, the strongest having the assignment (υ'_1, 0, 0 ← 0, 0, 0), followed in intensity by those belonging to the (υ'_1 , 1, 0 ← 0, 0, 0) and (υ'_1 , 0, 2 ← 0, 0, 0) transitions. Relative intensities of various of these bands have been listed in Table XVIII.

Table XVIII. Relative Intensities for Vibronic Absorption Bands of $^{35}ClO_2$ Originating from the X^2B_1 (0,0,0) Ground State (from Richardson et al., 1969)

Assignment $\upsilon'_1, \upsilon'_2, \upsilon'_3$	λ nm	Relative Intensity*	Assignment $\upsilon'_1, \upsilon'_2, \upsilon'_3$	λ nm	Relative Intensity*
0, 0, 0	475.69	1.00	2, 1, 2	412.62	10.3
0, 1, 0	469.22	0.73	0, 0, 4	412.41	-
1, 0, 0	460.19	6.30	5, 0, 0	408.25	110.
1, 1, 0	454.23	4.39	3, 0, 2	405.79	-
2, 0, 0	445.80	21.5	5, 1, 0	403.82	-
0, 0, 2	442.37	2.24	3, 1, 2	401.51	-
2, 1, 0	440.28	13.6	1, 0, 4	401.37	-
0, 1, 2	437.04	1.72	6, 0, 0	397.28	155.
3, 0, 0	432.42	38.4	4, 0, 2	395.04	-
1, 0, 2	429.40	7.11	6, 1, 0	393.16	-
3, 1, 0	427.31	22.1	4, 1, 2	391.10	-
1, 1, 2	424.45	5.92	2, 0, 4	390.96	-
4, 0, 0	419.94	68.3	7, 0, 0	386.97	-
2, 0, 2	417.23	17.8	5, 0, 2	384.91	-
4, 1, 0	415.18	34.7	7, 1, 0	383.11	-

*Relative intensity for $^{35}ClO_2$ at about 193K

ClO_2 vapor is rapidly photolyzed by ultraviolet radiation and below 385 nm the bands become quite diffuse. Strong bandheads in this region with high absorption cross-sections are at the wavelengths (nm),

377.25
368.05
359.41
351.14
343.40
336.05
329.12
322.60
316.35
310.57
305.09
299.94
295.35

Other electronic absorption systems lie in the vacuum ultraviolet (Basco and Morse, 1974). The maximum absorption coefficient occurs at the 351 nm band center ($\sigma = 1.2 \times 10^{-17} cm^2$, Clyne and Coxon, 1968; Basco and Dogra, 1971). This is as strong as the maximum at 250 nm in the O_3 ultraviolet absorption system. Clyne and Coxon (1966) reported a detection limit for ClO_2 in their system (deuterium lamp, 20 cm pathlength) of $5 \times 10^{13} cm^{-3}$ (2 ppm at atmospheric pressure). Cross-sections are much smaller at longer wavelengths, where predissociation is less (λ nm, σ cm^2; 440.3, 2.6×10^{-19}; 445.8, 3.4×10^{-19}; 454.2, 5.8×10^{-20}; 460.2, 7.4×10^{-20}; 469.2, 8.0×10^{-21}; 475.7, 9.4×10^{-21}, Coon et al., 1962).

Two fluorescence studies of ClO_2 have been reported (Table II), both utilizing the Ar^+ laser as the exciting source. However, the lines used, 458 to 502 nm lie in the region of low absorption cross-section and the resulting fluorescence is very faint as compared visually with that of I_2 or NO_2. There also appears to be considerable photochemical decomposition even at these longer wavelengths. Observations implied that most of the excited molecules predissociate rather than fluoresce. The 476.5 nm (60.00 kcal $mole^{-1}$) line has slightly higher energy than the molecule's bond dissociation energy at 298 K (59.4 kcal $mole^{-1}$, 248.5 kJ $mole^{-1}$). Sakurai et al. (1971c) found that the excited ClO_2 was short-lived, the lifetime being $\leq 5\,\mu$sec at pressures in the range 0.1 to 0.2 torr. The 476.5 nm Ar^+ laser line lies in the middle of the (0, 0, 0 ← 0, 0, 0) transition and excites fluorescence in about 17 bands from 480 to 780 nm. Longer wavelength exciting lines have insufficient energy to pump the (0, 0, 0) ground state and must arise from hot bands, accounting for their additional weakness. As a consequence the fluorescence intensity for these can be expected to decrease at lower temperatures (Sakurai et al., 1971c).

The ClOO isomeric form of chlorine dioxide is very unstable, D_0^o (Cl-OO) = 6 kcal mole^{-1}; 25 kJ mole^{-1} (Benson and Buss, 1957; Clyne and White, 1971) and rapid dissociation is expected even at 250-300 K. Although its uv and infrared spectra have been reported by Morris and Johnston (1968) and Johnston et al. (1969) its low level detection by fluorescence is unlikely.

The more stable OClO form, is probably best monitored via its strong absorption in the ultraviolet. The cross-section of 1.2×10^{-17} cm^2 for the 351 nm band is about 25 times larger than that for NO_2 which also shows continuous absorption in this region, and about 5 orders of magnitude larger than that for O_3.

CARBON MONOXIDE, CO

This molecule has a very rich absorption spectrum in the 100 to 160 nm region with many strong bands, particularly the ubiquitous 4th position system, $A^1\Pi \leftarrow X^1\Sigma^+$. The lowest lying electronically excited states of CO are triplets and although their absorption spectra have been recorded, transitions to all states below $A^1\Pi$ are forbidden and much weaker (Krupenie, 1966; Tilford and Simmons, 1972).

The 4th positive system is dominant in absorption and appears in emission as an impurity in many systems since its spectrum is so readily excited. Unfortunately, its (0, 0) bandhead lies at 154.43 nm in the region where oxygen absorbs strongly, so eliminating it from further detailed study. In passing though it may be noted that the radiative lifetimes of the first six vibrational levels of the $A^1\Pi$ state are all ~10 nsec (Hesser, 1968; Wells and Isler, 1970; Imhof and Read, 1971; Chervenak and Anderson, 1971; Burnham et al., 1972). Collisional quenching is efficient, being of the order of unity for nitrogen, and vibrational relaxational rates within the $A^1\Pi$ state similarly occur with a high probability per collision for many gases (Becker and Welge, 1965; Slanger and Black, 1969; Comes and Fink, 1972). Even so, owing to the short radiative lifetime, fluorescence efficiencies remain reasonably large at most operating pressures, falling to a possible minimum value of about 1% at atmospheric pressure. Slanger and Black (1969, 1970, 1971, 1973a, b, c) have extensively studied the resonance fluorescence, the sensitization with xenon, perturbations between the $A^1\Pi$ state and the triplet levels, and collision-induced interstate conversions in the system. As a consequence, it is now quite well characterized, and in oxygen free systems provides an extremely sensitive technique for monitoring CO.

Its infrared spectrum has been extensively studied owing to its simplicity. The fundamental band is centered at about 4.67 μm with the first overtone, which is about 100 times weaker, at 2.35 μm. Stratospheric concentrations of CO have been measured via its infrared absorption spectrum (Goldman et al., 1973c). The R(2) and R(3) branch lines in the fundamental band are most free from interferences as is apparent from the high resolution spectra of McClatchey and Selby (1974). The interferences arise from overlapping bands of CO_2, N_2O, O_3 and H_2O in the fundamental, and from H_2O and CH_4 in the overtone band. Hanst (1971) has noted that absorption of an iodine laser line at 2056.39 cm^{-1} and xenon laser line at 2168.77 cm^{-1} may have potential for monitoring CO. However, these lines are located about 0.97 cm^{-1} and 0.43 cm^{-1}, respectively, from the center of the CO lines and the extent of the overlap will be small. Green and Hancock (1973b) observed a very close frequency matching between lines of the frequency-doubled CO_2 laser and the R(2), R(6), and P(14) transitions in the fundamental band of CO (Table III) which appear more promising. The degree of mismatch is 0.007, 0.072 and 0.005 cm^{-1}, respectively. Of these the R(2) line of CO at 2154.598 cm^{-1} with an exciting frequency doubled R(18) line of the CO_2 laser at 2154.605 cm^{-1} will be the best for atmospheric air samples. The R(6) and P(14) lines suffer interference from other species. For such a system the Doppler absorption width at this wavelength is ~0.004 cm^{-1} (Table XI). At 250 K the pressure broadened linewidth is ~0.06 cm^{-1} atm^{-1} (Table XII). A CO_2 laser has a typical overall linewidth of about 100 MHz (0.003 cm^{-1}). Consequently, the absorption cross-section will be pressure dependent and at low pressures the laser line will be located in the wing of the absorption line. Using the tables published by Young (1965) for calculating the Voight profile of a line it is possible to estimate the absorption cross-section at the laser frequency. A line strength of 5.643 cm^{-2} atm^{-1} for the R(2) CO line has been used (Benedict et al., 1962). This leads to values for the absorbing cross-sections of 8.3×10^{-21} cm^2 (10 torr), 5.3×10^{-19} cm^2 (100 torr), and 1.8×10^{-18} cm^2 (760 torr). At 250 K, 5% of the molecules are in the $\upsilon'' = 0$, $J'' = 2$ level. The radiative lifetime of $\upsilon'' = 1$ is 0.033 sec (Millikan, 1963; Gerlovin and Orlova, 1964). At room temperature the rate constant for quenching by N_2 is 5.4×10^{-15} cm^3 $molecule^{-1}$ sec^{-1} which corresponds to ~5×10^4 collisions/deactivation. Similar values for O_2 are 7.6×10^{-17} cm^3 $molecule^{-1}$ sec^{-1}, ~3.5×10^6 collisions/deactivation, and for Ar, 3.1×10^{-18} cm^3 $molecule^{-1}$ sec^{-1}, ~8×10^7 collisions/deactivation (Millikan, 1963; Green and Hancock, 1973b; Stephenson, 1973b). Consequently, nitrogen quenching will be predominant in air samples and fluorescence efficiencies are ~(1.8–0.2)% at 10 to 100 torr. If it is assumed that a 100 W cw laser can be frequency-doubled with a 1% efficiency, the detection limits for such an infrared fluorescence arrangement are as listed in Table XIX. The minimum sensitivity that could be hoped for would be about 1 ppm using an atmospheric pressure sample, insufficient for the current application.

Bortner et al. (1973) have established the feasibility of measuring atmospheric CO from a remote platform using a correlation interferometry technique. With such an approach various methods are available for overcoming any spectral interferences. In their application they found that the overtone band was more suitable owing to the effects of certain atmospheric parameters. A sophisticated $C^{16}O$, $C^{18}O$ fluorescent source NDIR detector also has been developed and is being further refined in an attempt to sufficiently lower its range for stratospheric applicability (McClatchie, 1972). Absorption studies utilizing diode lasers have been reported and for a long pathlength are very sensitive (Nill et al., 1971; Sultzmann et al., 1973; Brockman and Seals, 1973). However, in a fluorescence mode of operation these absorption systems are insufficiently sensitive.

Table XIX. Detection Limits for Various CO, HCHO, and HCl Fluorescence Systems

Species	Source, nm	Source Intensity, $I_s a_s \Omega_s$ watts	Fluorescence Efficiency $k_f/(k_f + k_d + k_q[M])$			σ, cm^2	ℓ, cm	f	θ	N, watts	Detector Wavelength, nm	Rayleigh & Mie Scattering at Detector, watts			Detection Limits ppb		
			10 torr	100 torr	760 torr							10 torr	100 torr	760 torr	10 torr	100 torr	760 torr
CO	4.64μm Frequency-doubled R(18) CO_2 laser	1.0 (mean)	$1.8x10^{-2}$	$1.8x10^{-3}$	$2.4x10^{-4}$	$8.3x10^{-21}$ (10torr) $5.3x10^{-19}$ (100torr) $1.8x10^{-18}$ (760torr)	1.0	0.5	0.5	$3x10^{-12}$	P branch filter	$5x10^{-12}$	$1x10^{-10}$	$3x10^{-13}$	$2.7x10^5$	$4.1x10^3$	$1.2x10^3$
HCHO	326.2	1.0	$1.9x10^{-3}$	$3.4x10^{-4}$	$4.8x10^{-5}$	$5.7x10^{-20}$	4.4	0.1	0.4	$6x10^{-17}$	420	$9x10^{-10}$	$1x10^{-8}$	$6x10^{-8}$	5.2	2.9	2.7
	353.2 Tunable laser	1.0	$3.4x10^{-3}$	$3.7x10^{-4}$	$4.9x10^{-5}$	$2.2x10^{-20}$	4.4	0.1	0.4	$6x10^{-17}$	420	$7x10^{-10}$	$8x10^{-9}$	$4x10^{-8}$	7.6	6.9	6.9
HCl	~3.5μm P branch, HCl pulsed laser	10^{-3}(mean)	$4x10^{-3}$	$4x10^{-4}$	$6x10^{-5}$	$1x10^{-18}$	1.0	0.5	0.5	$3x10^{-12}$	R branch filter	$7x10^{-15}$	$7x10^{-14}$	$1x10^{-15}$	$3x10^6$	$3x10^6$	$3x10^6$

HYDROGEN, H_2

The lowest bound excited electronic state of hydrogen that has been characterized, the $B^1\Sigma_u^+$ is 90,633.8 cm^{-1} above the ground state, locating the (0, 0) band of the Lyman system in the vacuum ultraviolet region at 110 nm. Since at 250 K essentially all the molecules are in the $\upsilon'' = 0$ level, absorptions at longer wavelengths than this are out of the question. The only reported fluorescence studies for H_2, Table II, have used the 106.7 nm Ar line to excite the $\upsilon' = 3$ level. Inducing electronic fluorescence from H_2 in air samples is, therefore, out of the question.

A homonuclear diatomic molecule, H_2 is infrared inactive and can only be excited via the Raman effect. The very low cross-sections for spontaneous Raman scattering, enhanced somewhat using novel systems that invoke stimulated anti-Stokes scattering (Regnier et al., 1973; Regnier and Taran, 1973) can only monitor concentration levels down to about 100 ppm. As realized for a long time now, the monitoring of H_2 at low levels in any system constitutes a difficult problem.

FORMALDEHYDE, HCHO

The absorption spectrum of formaldehyde is complex. The lowest lying electronically excited singlet state, designated $\tilde{A}^1A''$ ($^1A_2$), is 28,188 cm^{-1} above the ground $\tilde{X}^1A_1$ state. It is observed in absorption from 230 to 353 nm although 'symmetry forbidden' (Herzberg, 1966). The transition is induced by intensity borrowing from higher $^1B_1$ and $^1B_2$ levels. Its absorption and fluorescence spectrum have been described by Brand (1956). Absorption bands become diffuse at about 275 nm, and to shorter wavelengths the progression continues with increasing diffuseness and rapidly decreasing intensity to about 230 nm. It exhibits a very sharp spectrum in the ultraviolet, the strongest bands forming a long progression in a frequency ~1180 cm^{-1} (ν'_2 , CO stretch vibration). No absorption is apparent between 175 and 230 nm. The vacuum ultraviolet region has been studied by Gentieu and Mentall (1970) and will not be discussed here. The only other system in the visible region at 360 to 397 nm is very weak owing to its $\tilde{a}^3A''(A_2) \leftarrow \tilde{X}^1A_1$ nature and need not be considered further. Vibrational structure of the singlet system is distinct within the molecule and well separated so that selective excitation of a single vibronic band poses no problem with a narrow bandwidth light source. However, rotational branches tend to overlap and if it were required, a selective rotational excitation would only be achieved with sources of a few tenths of a cm^{-1} spectral width. Most levels are sharp and well resolved in spite of the fact that radiationless transitions occur, leading to a near unity quantum yield for dissociation. McQuigg and Calvert (1969) reported two primary processes in the 280 to 355 nm region leading to either H+ HCO or H_2 + CO products. D_0^o (H - CHO) is ~76.0 kcal mole^{-1}, 318 kJ mole^{-1}, which corresponds to a 375 nm wavelength limit. Yeung and Moore (1974) have presented a predissociation model where this collisionless non-radiative decay of the bound vibronic states of the excited $^1A_2$ state strongly couple with high, bound vibronic levels of the ground $^1A_1$ state which then dissociate.

Fluorescence studies of this system have been noted in Table II and involve absorptions in the 4_0^1, $4_0^2 6_0^1$, $2_0^1 4_0^3$ and $2_0^2 4_0^1$ bands. Also, Yeung and Moore (1972) have studied the photopredissociation of HCHO with a high energy frequency-doubled, pulsed, ruby laser at 347.2 nm. However, the absorption cross-section at this wavelength is only 7.6 x 10^{-22} cm^2. The band notation used here is of the form X_m^n, where X is the number of the normal vibration and m and n are the number of quanta in the lower and upper states, respectively. Extinction coefficients and radiative lifetimes have been calculated by

Yeung (1973) for all the progressions in the normal modes. The absorption coefficients also have been measured by McQuigg and Calvert (1969). Intensities of absorptions involving the ν_6 mode are weak. Cross-sections for the stronger 4^1_0 and $2^2_0 4^1_0$ bands are 2.2×10^{-22} and 5.7×10^{-20} cm^2, the latter being about the maximum value noted in this system. Yeung also derived the relative radiative lifetimes from the Einstein coefficients and found them to vary by no more than a factor of 2 for all the bands. That for the $2^2 4^1$ level is 0.75 times the radiative lifetime of 4^1. In comparison, measured lifetimes have been reported as varying by a factor of 100, a fact attributed entirely to non-radiative processes. Estimates of the lifetime from the integrated absorption coefficient data predict a value of about 7 μsec (Sidman, 1958). Yeung and Moore (1973) have obtained radiative lifetimes, $(k_f + k_d)^{-1}$, of 282 nsec (4^1) and 29 nsec ($2^2 4^1$) for these two excited levels, which values have been used in this assessment. Jeunehomme and Duncan (1964) obtained a value of 310 nsec for HCHO excited in a flash discharge. In the latter experiment many levels were excited, and since the higher levels appear to have much shorter lifetimes owing to enhanced rates of non-radiative processes only fluorescence from the lowest vibronic levels would have been observed. Sakurai et al. (1971b) and Aoki et al. (1973) each have investigated the fluorescence excited with a N_2 pulsed laser and report radiative lifetimes of 27 nsec and 18 nsec, respectively. No pressure dependence of this $4^2 6^1$ level was observed in the range 1 to 10 torr. These values are in reasonable accord with the noted lifetime shortening at higher vibronic levels. The fluorescence spectrum observed in these studies extends to about 700 nm, peak emission being in the vicinity of 400 to 450 nm (Aoki et al., 1973; Yeung and Moore, 1973). The collisional quenching rate constants in formaldehyde at room temperature have been measured by Yeung and Moore (1973), who obtained 7.9×10^{-10} and 3.1×10^{-10} cm^3 molecule^{-1} sec^{-1} for the 4^1 and $2^2 4^1$ levels, respectively. These values are comparable to gas kinetic collision rates. Ar appeared to quench the fluorescence about 3.5 times less efficiently than HCHO. Aoki et al. (1973) noted that the effective fluorescence lifetime of the $4^2 6^1$ level decreased from 18 nsec to 14 nsec with air at atmospheric pressure, implying a quenching rate constant of 6.4×10^{-13} cm^3 molecule^{-1} sec^{-1} or 0.002 times the gas kinetic collision rate. At 10 to 100 torr for the longer lived 4^1 level the fluorescence efficiency will be decreased by 30 to 200 fold if collisional quenching is assumed to be at the gas kinetic collision frequency rather than at such a value of 6.4×10^{-13} cm^3 molecule^{-1} sec^{-1}. The shorter lived $2^2 4^1$ level is less affected by such quenching and the corresponding reduction would be from 4 to 30 fold. The dilemma of which rate to use for 4^1 and $2^2 4^1$ levels quenched by air cannot be resolved here and consequently, a value of 1×10^{-10} cm^3 $molecule^{-1}$ sec^{-1} has been used to assure that the detection limits are not overly optimistic. The expected sensitivity limits are shown in Table XIX. They have been calculated assuming the availability of a 1 W tunable, cw laser in this spectral range, although it is realized that this is rather beyond the state of the art at present. It has been further assumed that the line will encompass 10% of the ground state population.

With such a system, the practical sensitivity cannot be on the ppb scale indicated, since the very strong Rayleigh component of the scattered radiation, also listed in Table XIX will necessarily degrade these limits. Either a less intense source would have to be used or means invoked to effectively discriminate against the scattered radiation. Either step, reducing, I^o, or effectively decreasing the filter transmission, θ, will substantially raise the detection limits. Since stratospheric HCHO is most probably at concentration levels below 1 ppb it is unlikely that this fluorescence approach will be fruitful.

As noted by Hanst (1971), coincidences between lines of the infrared bands of HCHO and available laser lines are disappointing. Although the 3.5080 μm strong xenon line is close to an absorption line (Table III), and appears to suffer no absorbing interferences in the atmosphere (McClatchey and Selby, 1974), it lies in a weak absorption region of the spectrum. Johns and McKellar (1973) investigated the coincidences between various CO laser lines and absorption lines in the ν_2 band by Stark spectroscopy. No close matches were noted, the lowest field required was 0.71 kV/cm for the P_{16-15} (13) CO line at 1707.887 cm^{-1}. No infrared fluorescence studies have been reported for formaldehyde, and it is unlikely that it will produce the level of sensitivity required here. Recently, Nill et al. (1973) have, however, illustrated one important new asset of tunable diode lasers by studying part of the HCHO 3.5 μm band with a spectral resolution of 10^{-5} cm^{-1}.

HYDROGEN CHLORIDE, HCl

This stable molecule has no low lying bound electronically excited states and only exhibits continuous absorption at wavelengths less than about 230 nm. The only strong and distinctive spectral system is that of its fundamental vibration centered in the vicinity of 3.5 μm. There have been no reported coincidences of rotational lines in this band with non-tunable exciting line sources other than with HCl lasing transitions.

Fluorescence studies using pulsed HCl lasers have already been listed in Table III, and generally report a weakness of the fluorescence. This is due to the long radiative lifetime of about 0.03 sec for the $\upsilon'' = 1$ state (Margottin-Maclou et al., 1971; Emanuel and Cohen, 1974) and the relatively efficient collisional relaxation with nitrogen. At 250 K, $k_{N_2} = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1} (Chen and Moore, 1971a, b). Consequently, the system is of little use for detecting HCl in low concentrations as illustrated by the crude but sufficient calculation of the potential detection limits which are listed in Table XIX. HCl lasers are operated at a low pulse rate. Assuming the availability of a 1 kW peak power, 1 μsec pulsewidth, 1 pulse sec^{-1} laser, to a first approximation this is basically equivalent to a 10^{-3} W constant power source. The line strengths in the P branch are for example ~8 cm^{-2} atm^{-1} - $H^{35}Cl$ P(4) line (Toth et al., 1970) which corresponds to a peak absorption cross-section of about 1×10^{-18} cm^2. A low J number, P branch laser line, would have to be used since at 250 K only the $J'' = 0$ to 5 levels have a reasonable population. A fractional population of 0.15 has been assumed in these crude estimates. The poor sensitivity consequently arises partly from the low fluorescence efficiency and from the limited detector sensitivity.

HCl is difficult to monitor by any means. However, a feasibility study of the application of existing techniques to remotely monitor HCl in the atmosphere has recently been published elsewhere (Zwick et al., 1973) under contract to NASA. This assessed the suitability of correlation spectrometers and interferometers and also evaluated their possible interferents. Remote monitoring sensitivities down to about 1 ppm-meter appeared possible with the most refined system.

NITROUS ACID, HONO

In the uv-visible region, the absorption spectrum of HNO_2 has been reported by King and Moule (1962) and by Johnston and Graham (1974). Absorption occurs in the 300 to 400 nm region with very diffuse absorption bands indicative of predissociation that form the continuous absorption profile illustrated in Figure 6. The positions of the peaks in the two studies agree well and the cross-sections listed by Johnston and Graham (1974) have maximum values of the order of 10^{-19} cm^2. King and Moule (1962) observed no fine structure in these bands when photographed on a 20-ft grating spectrograph with a resolving power of 150, 000. The dissociation threshold for HNO_2 to OH and NO products is at 590 nm and predissociation appears to occur efficiently in this 300 to 400 nm region. Johnston and Graham (1974) also report that preliminary studies indicate a quantum yield of the order of unity for this process. It therefore appears very unlikely that fluorescence can be excited in this system. Although NO_2 also absorbs in this region, it would have posed no interference problem since wavelengths < 398 nm photodissociate it and produce little if any fluorescence. It may be interesting to note that the HONO exists in two planar tautomeric cis and trans forms. These are separated by about 180 cm^{-1} in energy, the trans being the more stable arrangement. However, the barrier height limiting their interconversion is about 4000 cm^{-1} which will be sufficiently high to prevent their collisional equilibration at 250 K if the molecules are preferentially produced in one form.

The infrared spectrum of HONO is less well characterized but bands have been assigned to the 6 infrared-active vibrational frequencies which are listed in Table XX (Jones et al., 1951; McGraw, 1965). A check of these spectral regions illustrates that nearly all the fundamental bands, possibly with the exception of that at 853 cm^{-1}, lie at wavelengths where absorptions also occur with other atmospheric components (Murcray et al., 1969; McClatchey and Selby, 1974). Infrared fluorescence holds no promise for this species. Moreover, detection by conventional absorption or emission techniques will be very difficult owing to these spectral interferences.

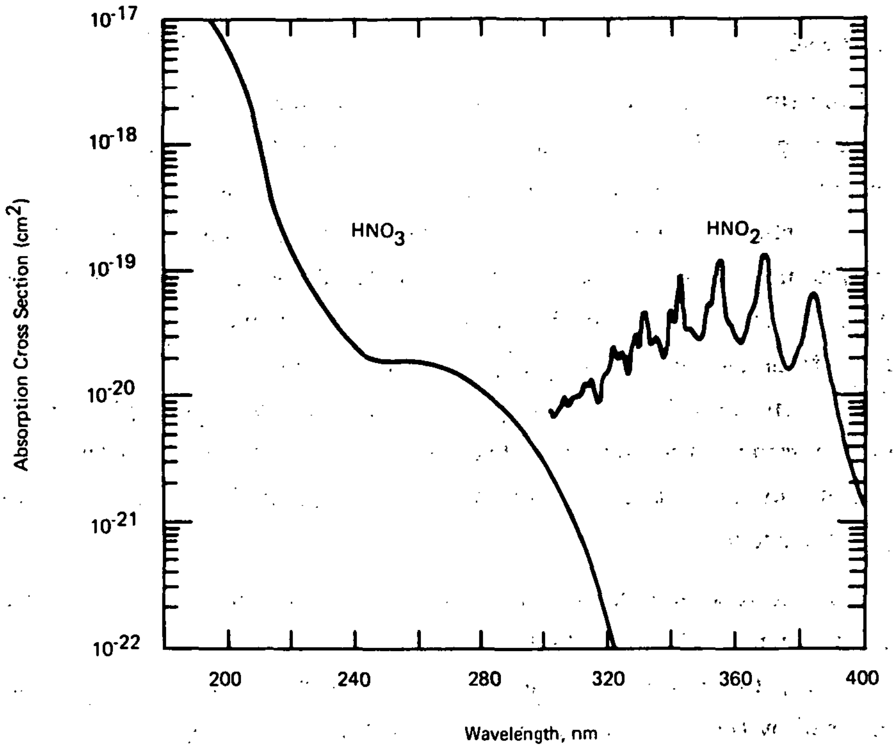

Figure 6. Absorption Cross-Sections for Gaseous Nitric Acid, HNO_3, and Nitrous Acid, HNO_2, in the uv-visible Region (from Johnston and Graham, 1974)

Table XX. Fundamental Vibrations of HONO-cm^{-1}, (from McGraw, 1965)

		cis	trans	Relative Infrared Intensities
ν_1,	O-H stretch	3424	3588	weak
ν_2,	N=O stretch	1640	1699	medium
ν_3,	HON bend	1261	1265	medium
ν_4,	N-O stretch	853	791	strong
ν_5,	ONO bend	608	593	strong
ν_6,	H out of plane	638	540	strong

NITRIC ACID, $HONO_2$

Unlike H_2SO_4 it appears theoretically well justified that nitric acid is present in the stratosphere as a vapor and not as aerosol particles (Toon and Pollack, 1973). The nitric acid absorption spectrum in the uv region has been critically reviewed by Hampson et al. (1973) and further confirmed by more recent work (Biaume, 1973). It is characterized by a continuum profile, Figure 6, and the molecule appears to photodissociate to OH and NO_2 with a primary quantum yield of unity at these wavelengths (Johnston et al., 1974). Cross-sections decrease from 10^{-17} cm^2 at 190 nm, to 10^{-22} cm^2 at 320 nm, and is $\ll 10^{-22}$ cm^2 in the 330 to 370 nm region. Consequently, although the data suggests that a significant portion of the spectrum does result from transitions between bound states, no fluorescent systems are expected to be observed in this or the visible region where it is completely transparent.

The molecule has nine fundamental vibration frequencies, all active in the infrared from 2.8 to 22 μm, the strongest four of which have been observed in atmospheric absorption data (Murcray et al., 1969; Goldman et al., 1971). The 11.3 and 21.9 μm bands have also been monitored by their atmospheric emission (Williams et al., 1972; Murcray et al., 1973). The 5.9 and 7.5 μm bands are in a region where interference by lines of H_2O, O_3 and CH_4 may be severe. The ν_5 band at 11.3 μm lies in a transparent atmospheric window, is relatively free from interfering factors but has a maximum absorption cross-section of about 10^{-21} cm^2 (Goldman et al., 1971). It appears to hold little promise as a sensitive fluorescence detector.

HYDROGEN SULFIDE, H_2S

No fluorescence studies in the uv-visible or infrared spectral regions have been reported. The lowest lying electronically excited state is at 37,000 cm^{-1} and gives rise to a broad absorption continuum from 190 to 270 nm with a maximum at 195 nm, corresponding to a peak absorption cross-section of about 7.4 x 10^{-18} cm^2 (Watanabe and Jursa, 1964). D_o^o (H-SH) = 89.8 kcal $mole^{-1}$, 376 kJ $mole^{-1}$, equivalent to a spectroscopic limit of 318 nm. Consequently, this observed dissociative continuum eliminates the possibility of fluorescence in the uv-visible region.

The intensities of the fundamental bands in the infrared are quite weak when contrasted to the strong bands of isoelectronic H_2O. The ν_1 and ν_3 bands are centered at about 3.81 μm with the ν_2 band at 8.45 μm. Owing to the complexity of these systems (Allen et al., 1956; Allen and Plyler, 1956) and the lack of any reported line coincidences, infrared fluorescence studies of H_2S are not appropriate at present.

Lowder et al. (1971) and Sulzmann et al. (1973) have estimated the limits of detectability for line-center absorption and derivative spectroscopy methods using tunable diode lasers. For the eight species that they considered, detection was the least sensitive for H_2S, even though its strongest ν_2 band was considered. This is primarily due to its weak integrated band intensity. For a laser diode of 2 x 10^{-4} W power output, in a system at atmospheric pressure, a detection limit of 431 ppb-meter was calculated for this line-center absorption approach.

AMMONIA, NH_3

The lowest lying electronically excited state of ammonia, designated $\tilde{A}^1A_2''$, is 46,136 cm^{-1} above the $\tilde{X}^1A_1$ ground state. The absorption system associated with these states consists of rather diffuse double or triple-headed bands in the 170 to 217 nm region, which get stronger at shorter wavelengths and become well defined in the vacuum ultraviolet (Watanabe, 1954). However, none of the bands in this $\tilde{A} \leftarrow \tilde{X}$ system show a resolved rotational fine structure (Douglas, 1963), and predissociation to NH_2 and H occurs on absorption (Okabe and Lenzi, 1967). All the excited states of NH_3 are in fact predissociated. As a consequence, fluorescence from the $\tilde{A}$ state will not occur. The gas is transparent in all other regions of the ultraviolet and visible spectrum.

Ammonia displays four fundamental vibration bands, all infrared active. The ν_1 and ν_3 bands are at about 3.0 μm, ν_4 at 6.1 μm, and the strong ν_2 band at 10.5 μm. The ν_3 fundamental band is particularly weak in NH_3. These bands are subject to potential interferences from other atmospheric gases. ν_1 lies in a region of CO_2 and H_2O absorption, and ν_4 is severely interfered with by H_2O bands. Such invalidating absorptions appear to be least for the ν_2 band at 10.5 μm.

The only reported fluorescence studies with ammonia are those of Borde et al. (1966) and Ronn (1968) listed in Table III. Hanst (1971) has measured the absorption coefficients of NH_3 at 21 CO_2 laser line wavelengths. Four of these were particularly strong, the P(32), R(22), P(34), and P(36) lines. By studying the pressure variation of the absorption it was established that the latter two were due primarily to absorptions in the wings of NH_3 lines. The P(32) line was the most strongly absorbed and quite sensitive to pressure showing it to have the best frequency matching value. Its absorption cross-sections at the pressures being considered here were 2.0×10^{-19} (10 torr), 1.1×10^{-18} (100 torr), and 1.3×10^{-18} cm^2 (760 torr). Shimizu (1970a) studied the Stark spectrum of the NH_3 ν_2 band with CO_2 and N_2O laser lines. The relative positions of the lines was obtained for about 100 potential coincidences. All lines of the CO_2 laser between P(50) and R(50) were investigated together with those for the N_2O laser from P(5) to P(42) and R(5) to R(39). The strong absorption, noted above by Hanst (1971), with the P(32) CO_2 line was found to be mismatched by 950 MHz (0.032 cm^{-1}) illustrating the need for pressure broadening in the absorption line. With the CO_2 laser Shimizu (1970a) did note one closer coincidence for the R(6) CO_2 line, 200 MHz, that has not been otherwise investigated. However, these coincidences appear to be closer than would have been predicted using the available spectroscopic data (Taylor, 1973). For the N_2O laser an almost exact coincidence, within the Doppler width, was found between the P(13) line and the Q(8, 7) NH_3 line, the numbers in parentheses referring to the J, K values, respectively. Shimizu (1970b) reported an absorption coefficient of 0.7 cm^{-1} $torr^{-1}$ for this transition. Assuming this value refers to 298 K and a base 10 definition it corresponds to an absorption cross-section of about 5.0×10^{-17} cm^2. The absorbing level is about 535 cm^{-1} above the ground state and at 250 K will have a population of around 3% of the total number of molecules. This absorption has formed the basis for infrared-microwave double resonance (Shimizu and Oka,1970a, b; Kreiner et al., 1973; Kreiner and Rudolph, 1973; Levy et al., 1973; Kreiner and Jones, 1974; Kano et al., 1974), infrared-infrared double resonance (Freund et al., 1973) and infrared-microwave-microwave triple resonance studies (Jones and Eyer, 1973). Lambert and Salter (1959) found that molecules containig two or more H atoms suffer vibration to translational energy transfer very much more easily than for other molecules. They reported that an average of only 9 collisions deactivate a molecule of NH_3 in its $\upsilon'' = 1$ state (948 cm^{-1}). Such a high relaxation rate implies a very low fluorescence efficiency and it is expected that even with a 5 W N_2O cw laser that the lowest detection limit conceivable would only be on a ppm scale. This system undoubtedly is of value in an absorption mode wherever the use of an N_2O laser is practical, however, for infrared fluorescence it has very limited applicability. It might also be noted that certain organic molecules such as n-butane and ethylene also absorb in this region and interfere if present with the ammonia. The use of tunable diode lasers for the detection of NH_3 by absorption in the ν_2 band at around 10.5 μm has been considered by Hinkley and Kelley (1971), Lowder et al. (1971), and Sulzmann et al. (1973). Such a technique appears quite sensitive for sufficiently long pathlengths.

NITRIC OXIDE, NO

Nitric oxide fluorescence has been extensively studied utilizing numerous atomic line sources in the 191 to 227 nm regions (Table II). As illustrated in Figure 7, the absorption spectrum at room temperature is highly structured from 130 to 230 nm consisting of bands of the $\gamma(A^2\Sigma^+ - X^2\Pi)$, $\beta(B^2\Pi - X^2\Pi)$, $\delta(C\,^2\Pi - X^2\Pi)$, and $\epsilon(D^2\Sigma^+ - X^2\Pi)$ systems. Below 130 nm the spectrum merges into a continuum. Owing to the discrete nature of the absorption spectrum, cross-sections at specific wavelengths have to be obtained from more detailed studies of the line structure of a particular absorption band and should not be taken from Figure 7, which was obtained with a spectral resolution of 0.1 nm. As will be seen later, cross-sections for specific lines are much higher than would be inferred from this low resolution data. Above 190 nm there is very little overlapping of the beta and gamma bands. No laser systems are available in this spectral region and only coincidences with atomic line or discharge sources that radiate the NO bands can be considered. Melton and Klemperer (1973) have undertaken a systematic search for coincidences in the (0, 0) to (3, 0) γ bands and the (3, 0) to (7, 0) β bands. They have measured the separation between the exciting and absorbing lines by using up to 20 kG magnetic fields to Zeeman shift one of the source components into exact coincidence. From their zero field separations it appears that the only atomic lines feasible for fluorescence measurements, in the absence of such fields, are the Cd^+, 214 nm (0.45 cm^{-1}); Ge, 226 (0.0); Se, 196 (0.2); Te 215, (0.1), 214 (0.45); and Zn, 214 (0.86), where the value in parentheses refers to the separation, in wavenumbers, from the nearest NO absorbing line. These lines all populate levels in the $A^2\Sigma^+$ state and induce the strong γ band fluorescence.

Absorption cross-sections at the center of specific Doppler broadened lines in various NO γ bands have been calculated. The nomenclature, and hence consistent formulae for such calculations is quite confused and some care is required. Definitions of the appropriate relationships between oscillator strengths and line strengths have been taken from Schadee (1967) and Tatum (1967). The general working equation for the required cross-section used in these assessments is given by the expression

$$\sigma = \frac{\pi e^2}{mc} \left(\frac{4 \ln 2}{\pi}\right)^{1/2} \frac{f_{\upsilon'\upsilon''} \lambda_{\upsilon'\upsilon''} S_{J'J''} g_e^{J''} \exp(-\epsilon_{J''}/kT)}{\lambda_{J'J''} g_e Q_{vib} Q_{rot} \Delta\nu_D}$$

where: $f_{\upsilon'\upsilon''}$ = vibrational transition probability for the ($\upsilon'\upsilon''$) band. The values 4.0×10^{-4} (0,0); 8.1×10^{-4} (1,0) and 2.4×10^{-4} (3,0) have been taken (Farmer et al., 1972a)

$\lambda_{\upsilon'\upsilon''}$, $\lambda_{J'J''}$ = wavelength of the band origin and the particular (J'J") transition, respectively. The ratio of the two is very close to unity.

$S_{J'J''}$ = line strength of the particular line transition; values taken from Melton (1971)

$g_e, g_e^{J''}$ = electronic degeneracies of the ground state and the particular J" level. Values of $3 \times 2\,(1 - e^{-hcA/kT})$ and 3×2 have been used, respectively, where A is the spin-coupling constant and has a value of 124.2 cm^{-1} for NO.

ϵ_J = energy of the rotational state, J"

Q_{vib}, Q_{rot} = vibrational and rotational partition functions, respectively.

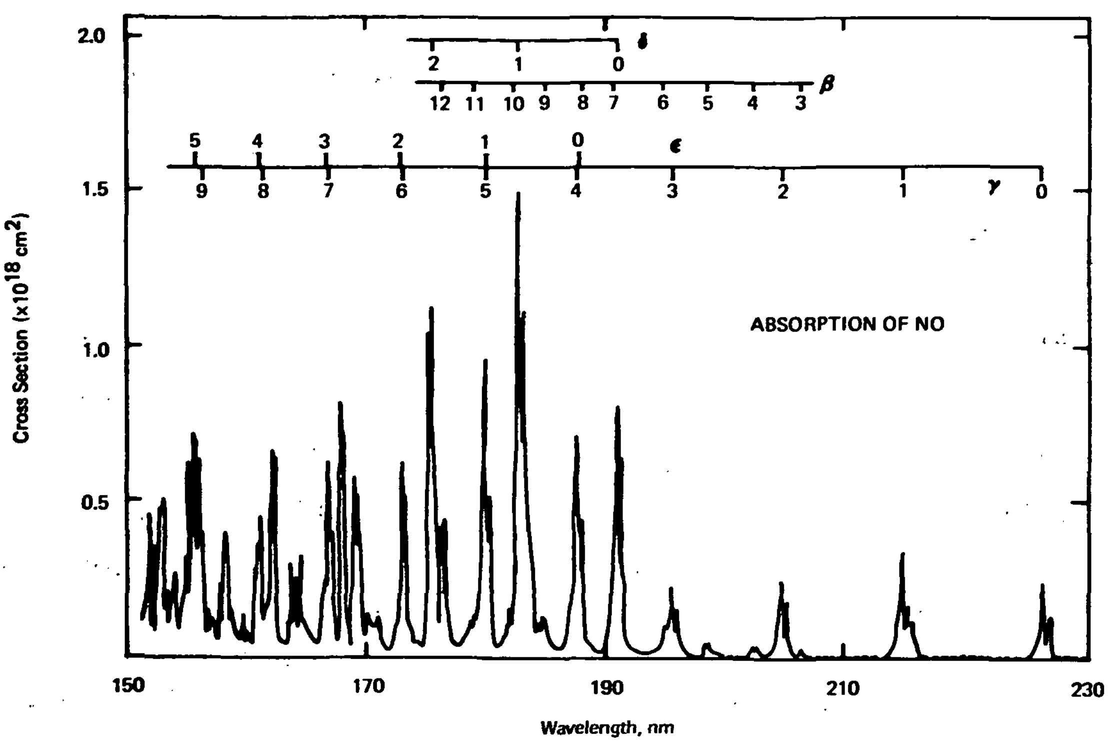

Figure 7. Apparent Absorption Cross-sections for NO in the Wavelength Region 150 to 230 nm, Spectral Resolution About 0.1 nm (from Marmo, 1953)

Absorption cross-section values for the various transitions of interest are given in Table XXI and are seen to be quite large. Also listed are the measured proximity of source to absorption lines and the relative populations of the J" levels at a temperature of 250 K.

Since in this case the fluorescence is excited with atomic line sources, a consideration in each case has to be made of the extent of the overlap between the source and absorbing line. The isotopes of cadmium of even atomic weight, about 75% of the natural abundance (108, 0.88%; 110, 12.39%; 112, 24.07%; 114, 28.86%; 116, 7.58%) all have zero nuclear spin. Those with odd atomic weights (111, 12.75%; 113, 12.26%) have nuclear spin of one-half. Kelly and Sutherland (1956), and Contreras and Kelly (1969) have measured the hyperfine splitting in the $^2S_{1/2}$ ground state of the odd isotopes as 0.5 cm^{-1}. They have noted also that the hyperfine splitting in the $^2P_{3/2}$ state is negligibly small. Isotope effects are small and the line shape is controlled by the nuclear hyperfine components. The approximate line profiles of the Cd^+ 214 nm source and the position of the NO absorbing line are illustrated in Figure 8 for two source linewidths.

Table XXI. Suitable Source and Absorption Lines for NO Fluorescence

	Source Line		NO γ Band				Separation†	$n_{J''}/n$	$S_{J'J''}$	σ,
	λair, nm;	$1/\lambda$ vac, cm^{-1}	Absorbing Line;			$1/\lambda$vac, cm^{-1}	(source-line), cm^{-1}	250 K		($cm^2 \times 10^{18}$)
Se	196.090*	50,996.93	$\upsilon' = 3$ $K' = 1$	$^oP_{12}$	(5/2)	50,997.12	- 0.19	1.82×10^{-2}	0.567	2.65
Zn	213.856	46,745.7	$\upsilon' = 1$ $K' = 29$	Q_{11}	(59/2)	46,746.5	-0.86	6.92×10^{-5}	12.230	0.26_1
Cd^+	214.438	46,618.6	$\upsilon' = 1$ $K' = 13$	R_{11}	(25/2)	46,618.1	+0.45	3.38×10^{-2}	2.196	18.7
Te	214.281	46,653.0	$\upsilon' = 1$ $K' = 22$	Q_{11}	(45/2)	46,652.5	+0.45	1.88×10^{-3}	8.791	3.91
	214.725	46,556.54	$\upsilon' = 1$ $K' = 10$	Q_{11}	(21/2)	46,556.67	-0.13	4.54×10^{-2}	3.536	44.5
Ge	225.600	44,312.5	$\upsilon' = 0$ $K' = 16$	R_{11}	(31/2)	44,312.5	+0.0	1.80×10^{-2}	2.820	6.10

* λ_{vac}

† Melton and Klemperer, 1973

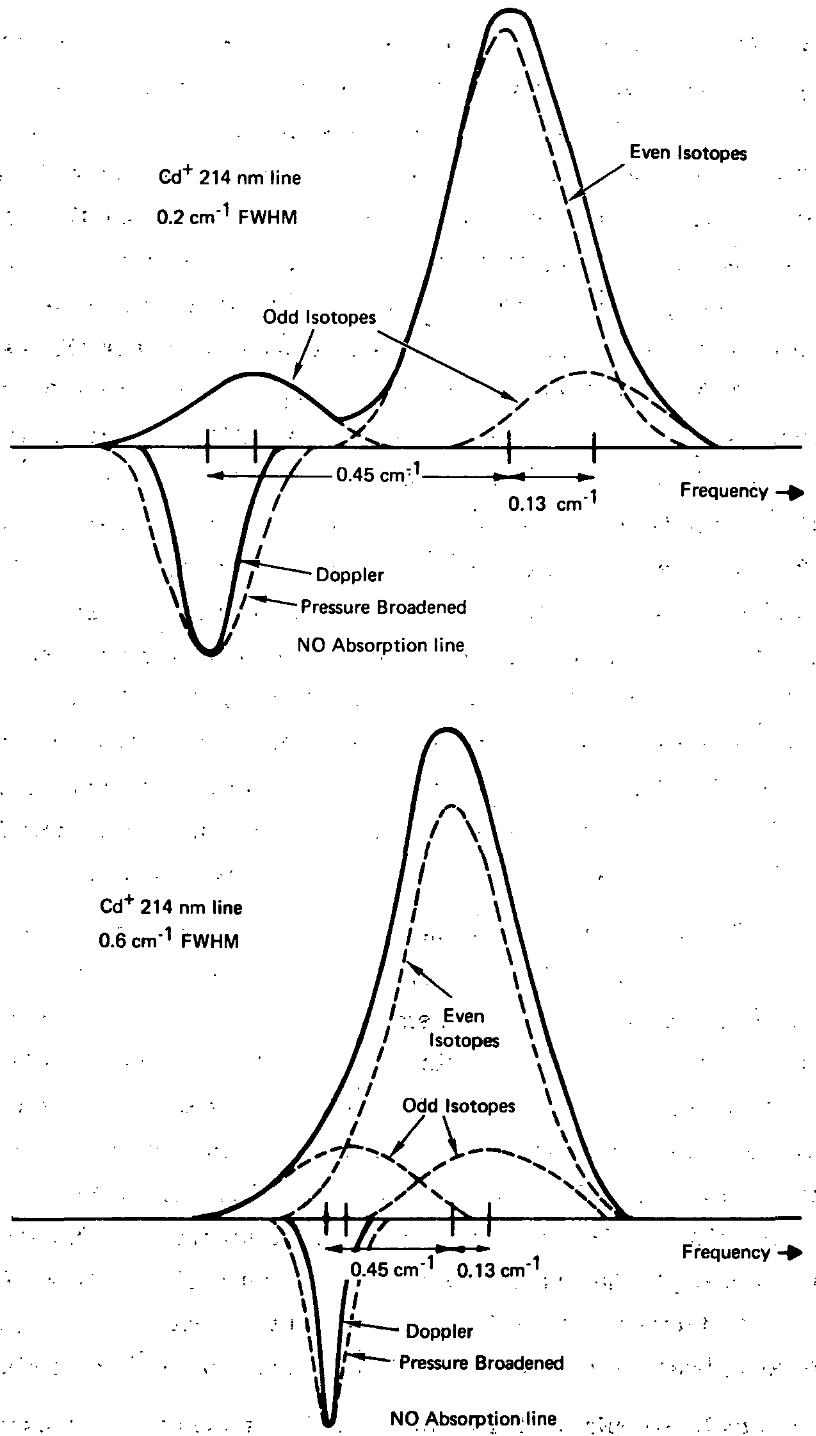

Figure 8. Overlap Between the Source and the Absorption Line in the Cd$^+$/NO System

Overlap is predominantly with one component of the odd isotopes and little interaction occurs with that part of the line produced by the even isotopes unless there is significant line broadening. Such broadening will mainly be a consequence of conditions that enhance self-absorption in the lamp. This has not been indicated in the figure and for a severely broadened source line the even isotope contribution will be less intense than illustrated. Corresponding linewidths for the Doppler broadened (0.1 cm^{-1}) or pressure broadened (0.16 cm^{-1} atm^{-1}) NO absorption line are also illustrated. Considerations of the extent of the overlap in the two cases predict a slightly enhanced absorption using a broadened source. However, a better approach would be to use a cadmium lamp enriched in the odd isotopes. Broida and Carrington (1963) concluded that the linewidth of their source line was 0.7 cm^{-1}, Melton (1971) assessed his at 0.4 cm^{-1} (FWHM). Assuming a value of 0.5 cm^{-1} (FWHM) the fractional overlap can be considered as effectively reducing the peak absorption cross-section by about a factor of 25 for NO at 10 to 100 torr and about a factor of 18 for a sample at atmospheric pressure. Broida and Carrington (1963) did note that at low pressures, NO absorbs NO γ band emission from a discharge through NO more strongly by a factor of 40, than it absorbs the Cd^+ line. Metal vapor lamps appear to be the most intense source of the 214 nm line for our application and it has been assumed that its intensity is about a factor of 25 times weaker than the Cd 229 nm line which intensity is usually quoted. A source area of 0.5 cm^2 and f/2 optics have been assumed. Calculations are for a lamp containing natural Cd.

Isotope splittings in zinc are slight. The mass 64-68 shift is $\sim$0.03 cm^{-1} (Hately and Littlefield, 1958). Mass 67 (4.11% abundance) has a nuclear spin of 5/2 but any resulting hyperfine structure is not expected to play a significant role. There is no hyperfine structure associated with the ground $^1S_0$ state. The 213.8 nm transition is the resonance line of zinc and is about equally intense in metal vapor, hollow cathode or electrodeless microwave discharge lamps. This zinc line is reportedly very easily broadened, a necessary requirement owing to the 0.86 cm^{-1} separation between the source and absorbing line centers. Overlap will be small and limited to the far wings of the absorbing line. Crude estimates imply that the peak absorption cross-section will be effectively reduced in this case by factors of about 1/100 (10 to 100 torr) and 1/60 (sample at atmospheric pressure) based on a source line broadened to 1.0 cm^{-1} (FWHM).

Tellurium exhibits small isotopic splittings and some hyperfine structure owing to odd isotopes (123, 0.9%; 125, 7.0%). The extent of the total splitting appears to be less than the expected linewidths and has not been considered further (Kuhn and Turner, 1961). Since the exactness of the coincidences with the 214.3 nm and 214.7 nm Te lines is only to within +0.45 cm^{-1} and -0.13 cm^{-1}, respectively, some broadening in the source will be necessary. Source lines of 0.4 cm^{-1} (FWHM) will produce an overlap equivalent to reducing the peak absorption cross-section by factors of 1/300 (10 to 100 torr) and 1/200 (atm pressure) for the 214.3 nm line, and 1/6 (10 to 100 torr), 1/4 (atm pressure) for the 214.7 nm line. An electrodeless radio-frequency discharge lamp (Perkin-Elmer) is recommended for Te although in other applications where microwave power can be utilized such a discharge lamp would provide an order of magnitude increased intensity. The 214.7 nm line is assumed to be about five times weaker than that at 214.3 nm.

Selenium has one isotope with nuclear spin ($I = 1/2$, mass 77, 7.58% abundance). Hyperfine and nuclear splittings will be unimportant for a source line broadened to about 0.4 cm^{-1}. The center wavelength is about 0.19 cm^{-1} out of coincidence with that of the NO line, effectively reducing the peak absorption cross-section by factors of about 1/8 (10 to 100 torr) and 1/5 (atm pressure sample). The 196 nm line is a strong feature in the spectrum of atomic Se. An electrodeless radio-frequency discharge lamp (Perkin-Elmer) appears the most intense source. It is assumed to be an order of magnitude brighter than a hollow cathode lamp.

The germanium 225.6 nm line is not a strong feature in its atomic spectrum. The line is much weaker by a factor of about 800 than the strongest Ge lines at 265 nm. Hollow cathode lamps or electrodeless microwave discharge lamps are available. Intensities of this line in such sources are expected only to be about 3×10^{-8} and 6×10^{-7} W cm^{-2} $ster^{-1}$, respectively. Of its five isotopes, the principle four are of even mass (92.2%) and show very small isotopic shifts (< 0.005 cm^{-1} between consecutive even mass numbers) and hyperfine splitting produced in the odd mass component (7.8% abundance, $I = 9/2$) is considered negligible (Deverall et al., 1954; Heilig et al., 1966). Owing to the exact spectral coincidence, the source and absorbing lines will be considered to overlap completely. The extent of the absorption then can be calculated assuming that the cross-section is effectively $\sigma/2^{1/2}$.

Vibrational relaxation within the $A^2\Sigma^+$ state during its lifetime is negligible compared to electronic quenching in systems containing oxygen. Removal of one quantum of vibrational energy by nitrogen requires about 790 collisions for the $\upsilon' = 1$ to $\upsilon' = 0$ transition or 220 collisions for $\upsilon' = 3$ to $\upsilon' = 2$ (Callear and Smith, 1963b). Electronic quenching by oxygen collisions is rapid, $k_{O_2} = 1.7 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} for $\upsilon' = 1$ and 1.6×10^{-10} for $\upsilon' = 0, 3$. Nitrogen is 2000-fold less efficient and can be ignored (Melton and Klemperer, 1972). The generally accepted value for the radiative lifetimes of these vibrational levels, and the value taken here, is about 2×10^{-7} sec [$\upsilon' = 1$ (210 nsec), $\upsilon' = 0$ (230 nsec), Callear and Smith, 1963a; $\upsilon' = 0$ (196.5 nsec), Jeunehomme, 1966; $\upsilon' = 0, 1$ (215 nsec), Bubert and Froben, 1971; $\upsilon' = 1$ (181 nsec), German et al., 1971]. Other workers, though, have reported values that are difficult to reconcile with this [$\upsilon' = 0$, (108 nsec), $\upsilon' = 1$ (106 nsec), Copeland, 1972; $\upsilon' = 0$ (420 nsec), $\upsilon' = 1$ (400 nsec), Fink and Welge, 1968; $\upsilon' = 0$ (449 nsec), $\upsilon' = 1$ (410 nsec), Jeunehomme and Duncan, 1964].

The systems of interest all involve the $A^2\Sigma^+$ state. Consequently, fluorescence for each consists of γ band progressions, the intensities of which are controlled by the respective Franck-Condon factors, $q_{\upsilon'\upsilon''}$ (Jain and Sahni, 1968; Spindler et al., 1970). Each band contains 8 resolvable branches. At low pressures these are represented solely by 8 lines. However, at high pressures rotational relaxation populates many more J' levels. For the exciting wavelengths considered here all Raman scattered components are displaced by less than 13 nm from the source line and would pose no particular detection problem. Band wavelengths and the Franck-Condon factors are listed in Table XXII. For excitation to the $A^2\Sigma^+$, $\upsilon' = 3$ level (Se line) the most suitable, and intense band for monitoring purposes is the (3, 4) transition at 229 nm. At these short wavelengths interference filters are available but their transmission is directly related to their bandwidth and a 10 to 20 nm FWHM filter has only a peak transmission of about 10%. Since the filters main role is to provide a means for rejecting scattered light, in this case at 196 nm, and the nitrogen Raman component at 205 nm, this might be accomplished more efficiently using NH_3 as a filter (Callear and Smith, 1963b) to remove these shorter wavelengths, with a solar blind photomultiplier tube to limit the detector response to about 300 nm. In the other cases, the wavelength cutoff for an ammonia filter is too low and 20 nm FWHM interference filters with a 10% peak transmission might have to be used unless other chemical filters absorbing radiation at <230 nm can be found.

Based on such considerations the calculated detection limits, illustrated in Table XXIII, are seen to be quite high and show little promise for exploitation as an alternate stratospheric monitor. It appears unlikely that the sensitivity of the Se and Cd^+ systems can be sufficiently increased. Zinc loses much of its sensitivity at 250 K primarily due to the reduced concentration of the absorbing level ($n_1/n = 6.9 \times 10^{-5}$). However, the

Table XXII. Wavelengths and Franck-Condon Factors
For Fluorescing γ Bands

υ'	3		1		0	
υ''	λ nm	$q_{\upsilon'\upsilon''}$	λ nm	$q_{\upsilon'\upsilon''}$	λ nm	$q_{\upsilon'\upsilon''}$
0	195.8	0.151	215.1	0.330	226.5	0.162
1	203.3	0.198	224.2	0.107	236.6	0.262
2	211.2	0.045_5	233.9	0.000_6	247.4	0.237
3	219.7	0.039_5	244.3	0.069_3	259.1	0.161
4	228.7	0.112	255.4	0.132	271.7	0.092_0
5	238.3	0.050_2	267.5	0.133	285.4	0.046_9
6	248.5	0.000_6	280.5	0.098_9	300.2	0.022_1
7	259.6	0.022_1	294.6	0.061_9	316.5	0.009_8
8	271.4	0.063_7	310.0	0.034_4	334.2	0.004_2
9	284.1	0.083_5	326.7	0.017_7	353.8	0.001_7
10	297.9	0.078_0	345.0	0.008_5	375.4	0.000_7
11	312.8	0.059_7	365.1	0.004_0	399.3	0.000_3
12	328.9	0.040_2	387.3	0.001_8	425.9	0.000_1
13	346.4	0.024_7	411.9	0.000_8	455.8	0.000_0
14	365.6	0.014_3	439.2	0.000_3	489.6	0.000_0

$q_{\upsilon'\upsilon''}$ values from Jain and Sahni, 1968

Table XXIII. Detection Limits for Various NO Fluorescence Systems

Source, nm	Source Intensity, $I_s a_s \Omega_s$ watts	Fluorescence Efficiency $k_f / (k_f + k_d + k_q [M])$			σ, cm^2	ℓ, cm	f	θ	N, watts	Detector Wavelength, nm	Rayleigh & Mie Scattering at Detector, watts			Detection Limits, ppb		
		10 torr	100 torr	760 torr							10 torr	100 torr	760 torr	10 torr	100 torr	760 torr
196.090 Se RF electrodeless lamp	$1x10^{-5}$	0.28	$3.7x10^{-2}$	$5.1x10^{-3}$	$2.65x10^{-18}$	1.6	0.45	0.8	$5x10^{-18}$	220-300	$2.9x10^{-14}$	$2.9x10^{-13}$	$2.2x10^{-12}$	85	64	39
213.856 Zn vapor lamp	$5x10^{-5}$	0.27	$3.5x10^{-2}$	$4.8x10^{-3}$	$2.61x10^{-19}$	1.6	0.25	0.1	$5x10^{-18}$	262 ± 10	$9.6x10^{-14}$	$9.6x10^{-13}$	$7.3x10^{-12}$	$8.5x10^{6}$	$6.5x10^{6}$	$3.8x10^{6}$
214.438 Cd^+ vapor lamp	$4x10^{-5}$	0.27	$3.5x10^{-2}$	$4.8x10^{-3}$	$1.87x10^{-17}$	1.6	0.25	0.1	$5x10^{-18}$	262 ± 10	$7.7x10^{-14}$	$7.7x10^{-13}$	$5.8x10^{-12}$	76	58	40
214.281 Te	$5x10^{-6}$	0.27	$3.5x10^{-2}$	$4.8x10^{-3}$	$3.91x10^{-18}$	1.6	0.25	0.1	$5x10^{-18}$	262 ± 10	$9.6x10^{-15}$	$9.6x10^{-14}$	$7.7x10^{-13}$	$6.3x10^{5}$	$4.8x10^{5}$	$3.1x10^{5}$
214.725 RF electrodeless lamp	$1x10^{-6}$	0.27	$3.5x10^{-2}$	$4.8x10^{-3}$	$4.45x10^{-17}$	1.6	0.25	0.1	$5x10^{-18}$	262 ± 10	$1.9x10^{-15}$	$1.9x10^{-14}$	$1.5x10^{-13}$	228	175	112
225.600 Ge hollow cathode lamp	$3x10^{-8}$	0.28	$3.7x10^{-2}$	$5.1x10^{-3}$	$6.10x10^{-18}$	1.6	0.10	0.1	$5x10^{-18}$	272 ± 10	$4.6x10^{-17}$	$4.6x10^{-16}$	$3.5x10^{-15}$	$7.9x10^{4}$	$6.0x10^{4}$	$5.8x10^{4}$

possibility of using an NO source to provide sufficient sensitivity cannot be ruled out. Use could be made of the integrated (0, 0) to (3, 0) bands in the 190 to 230 nm region to excite a larger fraction of the NO ground state population, with monitoring of the fluorescent bands in the 240 to 340 nm region. The factors limiting the line source sensitivity are the low source intensity (10^{-5} - 10^{-6} W), the extent of the overlap with absorbing lines and the number density (2-4% of n) of the absorbing state. All these factors would be improved upon with such a system. It is far too involved an exercise to calculate here the ultimate sensitivity for such a system since it is a major task in its own right. The detailed factors involved have been outlined by McGregor et al. (1972, 1973) who isolated various lines in the (0, 0) band to monitor NO by line center absorption. Their source was a high voltage discharge through a flowing mixture of argon, nitrogen and oxygen at 5 torr. It would not be unreasonable to predict two orders of magnitude improvement for such a system if a source of 5×10^{-4} W cm^{-2} $ster^{-1}$ (~ 5×10^{14} quanta sec^{-1}) was available. Whether the detection limit could be lowered to that of the NO chemiluminescent detector (0.02 ppb), requiring a factor of 4000 improvement over an arrangement using a Cd^+ source, would seem unlikely.

Although fluorescence appears not to have been reported in the infrared, various coincidences have been noted and absorption coefficients measured for the lines of the fundamental or overtone band with various laser lines (Table III). The NO fundamental band is centered at about 5.3 μm, a region of appreciable water vapor absorption (Murcray et al., 1969; McClatchey and Selby, 1974). This potential interference becomes less serious if the sample pressure is reduced, and regions free from overlapping bands may exist. However, a detailed assessment would be necessary to establish this fact. At reduced pressure, absorption linewidths at 5 μm decrease from an atmospheric pressure value of about 0.06 cm^{-1} towards the Doppler width of about 0.004 cm^{-1}. At 10 torr the line will still be partially pressure broadened, but even so it is very narrow. Consequently, under such conditions, coincidences have to be quite exact to maintain a suitable overlap. Menzies et al. (1970) have measured the absorption coefficients in NO for various CO laser lines (Table III) at 20 and 50 torr. These correspond to absorption cross-sections in the range 7×10^{-21} to 2×10^{-19} cm^2. Hanst (1971) also has obtained the cross-section of 5×10^{-20} cm^2 for the iodine laser coincidence at atmospheric pressure. Such cross-sections might be considered to be of an intermediate type strength. However, the long radiative lifetime of the $X^2\Pi$ level, 80 msec (Stephenson, 1973a), may produce a low fluorescence efficiency. Quenching cross-sections although low for nitrogen and argon may be quite large for oxygen. No data appears to be available at present. By placing the absorption cell within the CO laser cavity, Chackerian and Weisbach (1973) established that the absorption coefficient becomes enhanced about 250 times, implying an effective cross-section of 1×10^{-16} cm^2. They estimated that 100 ppb could be measured at atmospheric pressure with such an absorption approach. Hinkley (1972b), Sulzmann et al. (1973), and Brockman and Seals (1973) also have discussed the feasibility of using laser diodes tuned to NO absorption line centers in the infrared. Fluorescence in this region does not appear to hold any promise as a high sensitivity detector for NO.

NITROGEN DIOXIDE, NO_2

Nitrogen dioxide fluorescence has been extensively studied with both continuum and line sources (404.6 to 694.3 nm) in the visible spectral range. Absorption appears almost continuous in this region and the complex nature of the spectrum is evident in that fluorescence produced by a narrow line in a system at low pressure is a complex quasi-continuum which is probably a densely packed discrete spectrum. For the 488 nm Ar^+ laser line, Sakurai and Broida (1969b) found no change of transmission with electric or magnetic fields of 3kV cm^{-1} and 2kG, respectively. NO_2 is photodissociated at wavelengths less than 398 nm, its bond dissociation energy D_0^o (NO-O) is 71.8 kcal $mole^{-1}$ (300.5 kJ $mole^{-1}$). Absorption coefficients for the 240 to 700 nm region are illustrated in Figure 9 from which values have been taken. More recent measurements by O'Shea and Dodge (1974) of the absorption coefficients for various mercury and argon ion laser lines confirm these values. Theoretical calculations (Gangi and Burnelle, 1971) predict a linear $^2B_1$ and a bent $^2B_2$ low-lying electronically excited state. Transitions to both appear to occur together over a large portion of the visible spectrum. However, Braslavsky and Heicklen (1973) have argued that the electronic state formed by absorption ($^2B_1$) is not the emitting state ($^2B_2$) and that a mechanism based on two electronic states is insufficient to explain all the observations. The value of the lifetime of these excited states, as with SO_2, has been a long standing anomaly. Values obtained from various studies (Neuberger and Duncan, 1954,; Keyser et al., 1968, 1971; Schwartz and Johnston, 1969; Sakurai and Capelle, 1970; Sackett and Yardley, 1970, 1972; Sidebottom et al., 1972; Stevens et al., 1973) all lie in the range 45 to 85 μsec, which is not only long for an allowed transition, but two orders of magnitude larger than that calculated from the integrated absorption coefficient. Solarz and Levy (1974), and Sackett and Yardley (1971) have found short-lived components that imply at least some excited levels have lifetimes approaching those calculated from the absorption coefficient. The observation and assignment of such short-lived states is difficult as a very large number of excited levels are certainly long-lived and the level density is sufficiently high that even the most narrow banded excitation sources will populate these longer lived states. Measured lifetimes have not been found to be wavelength dependent and in these estimates a value of 60 μsec has been assumed for all the cases considered.

With exciting wavelengths at 400 to 470 nm the fluorescence spectrum is essentially a continuum extending from the line to about 800 nm. For 435.8 nm and 546.1 nm Hg lines, Clyne et al. (1964) have measured the intensity distribution in the 500 to 800 nm range (Table XXIV).

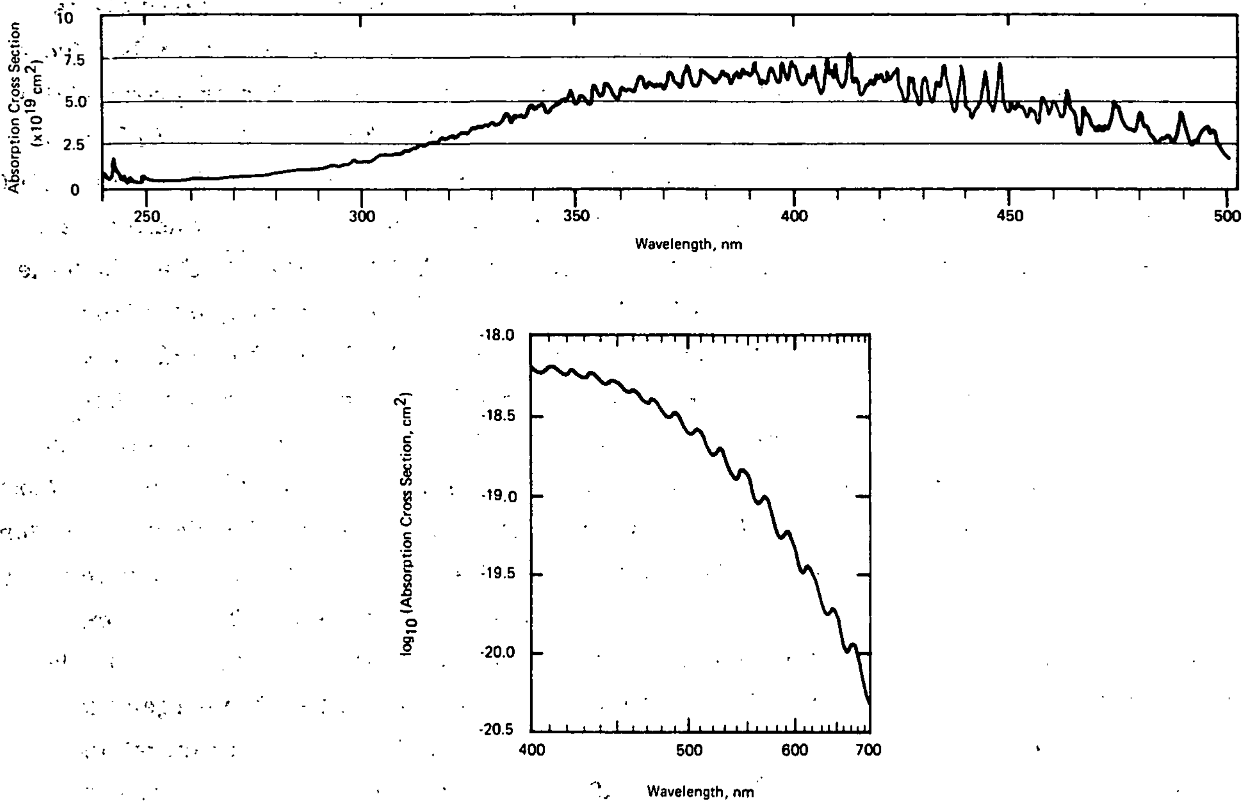

Figure 9: Absorption Cross-sections for NO_2 (from Hall and Blacet, 1952; Dixon 1940)

Table XXIV: Relative Intensities of NO_2 Fluorescence -Quanta Sec^{-1} (from Clyne et al., 1964)

Exciting line, nm		Wavelength range,nm		
	495-570	615-670	670-720	720-775
435.8	0.36	1.0	0.82	0.46
546.1	-	1.0	1.01	0.53

There is a marked red-shift in the fluorescence spectrum with increasing wavelength of excitation or an increase in pressure. Distributions are fairly similar above 600 nm. Sakurai and Broida (1969b) exciting fluorescence with Ar^+ and Kr^+ laser lines between 457.9 and 520.8 nm found that the intensity of the continuum increases with increasing wavelength. Less pronounced with shorter wavelength excitation, but increasingly so for wavelengths >440 nm, discrete bands are evident, particularly at low pressures, with laser excitation in the 590 to 650 nm region (Brand et al., 1973a; Stevens et al., 1973). These bands are displaced from the excitation frequency by ν_2, ν_1, $2\nu_2$, $\nu_1 + \nu_2$ and $3\nu_2$ etc. of the ground electronic state and represent ground state progressions such as the ν_2, $2\nu_2$, $3\nu_2$ bands (Abe et al., 1971; Abe, 1973). Sakurai and Broida (1969b) have shown that these line features are quenched to a greater extent than the continuum background. Problems associated with monitoring the bands displaced by ν_1 (1318 cm^{-1}), $2\nu_2$ (1499.6 cm^{-1}) or $3\nu_2$ (2249.4 cm^{-1}) arise owing to their close proximity to Raman scattered bands of CO_2 (1285, 1388 cm^{-1}), O_2 (1566 cm^{-1}) and N_2 (2330 cm^{-1}). The $\nu_1 + 2\nu_2$ band displaced by 2818 cm^{-1} is the first that might be monitored with some assurance. It has to be assumed that particularly at higher pressures the continuum fluorescence is most persistent and the more desirable for monitoring purposes, otherwise attempts to include the band displaced by $\nu_1 + 2\nu_2$ within the accepted detection bandpass would be necessary. For exciting wavelengths up to 500 nm a detection bandwidth located anywhere from 600 to 720 nm would appear most appropriate. For the other exciting lines, filters have to be used with a short wavelength cutoff that will efficiently exclude the N_2 Raman band which can be several orders of magnitude above the dark current noise level of the photomultiplier tube. This factor is very important in positioning the detection bandwidth to insure sufficient blocking at the Raman band position. Appropriate detection wavelengths and bandwidths have been listed in Table XXVII. Estimates of the fraction of the fluorescence monitored, f, have been drawn mainly from the intensity distributions reported by Clyne et al. (1964). Collisional quenching rate constants are dependent on both the exciting wavelength and the fluorescence detection wavelength. Values are largest for fluorescence near the exciting wavelength and decrease with increasing energy separation between the exciting and fluorescent radiations, an effect explained assuming the importance of vibrational relaxation processes within the excited state. Quenching rates are high and are a reasonable fraction of the gas kinetic collision rate ($\sim 2.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}). Reported values have been listed in Table XXV for the self-quenching rate constant, k_{NO_2}.

Table XXV. Collisional Self-Quenching Rate Constants for NO_2 Fluorescence at 298 K (x10^{11} cm^3 $molecule^{-1}$ sec^{-1})

	λ fluorescence, nm																					
λ exciting	436	458	>462	468	470	475	>480	489	509	546	548	566	580	592	599	>630	633	635	660	700	725	785
405	18		(4.2)						6.4			5.5						3.7		3.6		3.5
436		(8.0)	(5.1)	(8.2)	13*	11†	4.8†	(6.5)	8.2	6.6*	(4.2)	5.6	(3.1)	(2.9)	5.1	3.0†	(2.4)	3.8*	3.7	3.3*	3.2	2.7*

	570	>570	583	>594	599	>600	603	623	635	660	700	>720	725	785
532	9.0†	7.1†				7.5†								
546		(9.5)	(8.2)		19		(8.2)	(8.2)	12	11	11		8.6	7.6
578				(10)					20	16	14		12	10
694												8.1†		

No identifying mark - Keyser et al., 1971
( ) - Meyers et al., 1966
* - Keyser et al., 1968
† - Sidebottom et al., 1972

Rates for other gases relative to that for NO_2 show no pronounced dependence on exciting and detecting wavelengths, and values for k_M/k_{NO_2} of 0.36 (M = Ar), 0.44 (M = O_2), and 0.40 (M = N_2) are suggested (Table XXVI). Lee and Uselman (1972) have measured the fluorescence efficiency at sufficiently low pressures that collisional quenching becomes negligible. Efficiencies approached unity for most exciting wavelengths. However, below 415 nm it declined sharply, being attributed to an early onset of predissociation. From their data a value for k_d of 1 x 10^4 sec^{-1} can be derived for the 404.6/407.8 nm Hg exciting lines. At 10 torr or higher pressures this makes a negligible contribution to the fluorescence efficiency at these wavelengths owing to the predominance of collisional quenching.

As seen from Table XXVII the potential detection limits for the various systems considered are remarkably low. Scattering is a severe problem though and a limiting factor. In order to reduce it to manageable levels, it may be necessary to use less intense sources and degrade the limits proportionally. Mie scattering is expected to produce a one-quarter to three-quarter contribution to the total scattering. Values from Figure 5 have been used to estimate its magnitude, the 30 km data for a 10 torr system and that at

Table XXVI. Quenching Rate Constants for NO_2 Fluorescence With Various Gases Relative to k_{NO_2} (1.0)

λ exciting, nm	λ fluorescing, nm	k_{Ar}	k_{O_2}	k_{N_2}	Reference
404.7	557.7		0.29	0.29	Braslavsky and Heicklen, 1973
	630.0		0.40	0.39	
435.8	486.0		0.42	0.38	
	557.7		0.43	0.38	
	630.0		0.35	0.36	
480.0	557.7		0.26	0.29	
	630.0		0.35	0.36	
435.8	>462.0	0.30	0.48	0.44	Myers et al., 1966
	468.0	0.39			
	489.0	0.36			
	548.0	0.36			
	> 570.0		0.55		
	592.0	0.39			
	633.0	0.37			
Recommended values		0.36	0.44	0.40	

Table XXVII. Detection Limits for Various NO_2 Fluorescence Systems

Source, nm	Source Intensity, $I_s a_s \Omega_s$ watts	Fluorescence Efficiency $k_f/(k_f + k_d + k_q [M])$			σ, cm^2	ℓ, cm	f	σ	N, watts	Detector wavelength, nm	Rayleigh & Mie Scattering at Detector, watts			Dectection Limits, ppb		
		10 torr	100 torr	760 torr							10 torr	100 torr	760 torr	10 torr	100 torr	760 torr
441.56	0.05, cw	$2.7x10^{-3}$	$2.7x10^{-4}$	$3.6x10^{-5}$	$5.4x10^{-19}$	1.0	0.30	0.50	$1x10^{-18}$	660±30	$3.6x10^{-12}$	$4.3x10^{-11}$	$2.0x10^{-10}$	0.015	0.015	0.015
He. Cd laser																
457.934	0.3, cw	$2.4x10^{-3}$	$2.4x10^{-4}$	$3.2x10^{-5}$	$4.6x10^{-19}$	1.0	0.30	0.50	$1x10^{-18}$	660±30	$2.0x10^{-11}$	$2.4x10^{-10}$	$1.0x10^{-9}$	0.003_3	0.003_3	0.003_3
465.789	0.3	$2.2x10^{-3}$	$2.2x10^{-4}$	$2.9x10^{-5}$	$4.2x10^{-19}$	1.0	0.30	0.50	$1x10^{-18}$	660±30	$1.8x10^{-11}$	$2.2x10^{-10}$	$9.7x10^{-10}$	0.004_0	0.004_0	0.004_0
472.685	0.2	$2.0x10^{-3}$	$2.0x10^{-4}$	$2.7x10^{-5}$	$3.9x10^{-19}$	1.0	0.30	0.45	$1x10^{-18}$	660±30	$1.1x10^{-11}$	$1.4x10^{-10}$	$5.9x10^{-10}$	0.007_9	0.007_9	0.007_7
476.486	0.5	$2.0x10^{-3}$	$2.0x10^{-4}$	$2.6x10^{-5}$	$3.7x10^{-19}$	1.0	0.30	0.45	$1x10^{-18}$	660±30	$2.9x10^{-11}$	$3.5x10^{-10}$	$1.5x10^{-9}$	0.003_3	0.003_3	0.003_4
487.986	2.0	$1.8x10^{-3}$	$1.8x10^{-4}$	$2.3x10^{-5}$	$3.2x10^{-19}$	1.0	0.30	0.45	$1x10^{-18}$	670±30	$1.0x10^{-10}$	$1.3x10^{-9}$	$5.3x10^{-9}$	0.001_1	0.001_1	0.001_1
496.507	1.0	$1.6x10^{-3}$	$1.7x10^{-4}$	$2.2x10^{-5}$	$2.8x10^{-19}$	1.0	0.25	0.45	$1x10^{-18}$	680±30	$5.1x10^{-11}$	$6.2x10^{-10}$	$2.5x10^{-9}$	0.003_3	0.003_1	0.003
501.715	0.6	$1.6x10^{-3}$	$1.6x10^{-4}$	$2.0x10^{-5}$	$2.6x10^{-19}$	1.0	0.25	0.45	$1x10^{-18}$	680±30	$3.0x10^{-11}$	$3.9x10^{-10}$	$1.4x10^{-9}$	0.005_9	0.005_9	0.006
514.532	2.0	$1.4x10^{-3}$	$1.4x10^{-4}$	$1.8x10^{-5}$	$2.1x10^{-19}$	1.0	0.25	0.45	$1x10^{-18}$	680±30	$9.2x10^{-11}$	$1.9x10^{-9}$	$4.3x10^{-9}$	0.002_5	0.002_5	0.002_6
Ar$^+$laser																
404.656 407.781	0.01	$3.0x10^{-3}$	$3.0x10^{-4}$	$4.0x10^{-5}$	$6.4x10^{-19}$	1.0	0.30	0.50	$1x10^{-18}$	660±30	$9.5x10^{-13}$	$1.1x10^{-11}$	$5.6x10^{-11}$	0.057	0.057	0.057
435.835	0.01	$2.8x10^{-3}$	$2.8x10^{-4}$	$3.7x10^{-5}$	$5.7x10^{-19}$	1.0	0.30	0.50	$1x10^{-18}$	660±30	$7.6x10^{-13}$	$9.1x10^{-12}$	$4.2x10^{-11}$	0.069	0.069	0.069
546.074	0.01	$1.0x10^{-3}$	$1.1x10^{-4}$	$1.4x10^{-5}$	$1.2x10^{-19}$	1.0	0.25	0.45	$1x10^{-18}$	720±30	$3.8x10^{-13}$	$5.1x10^{-12}$	$1.7x10^{-11}$	1.23	1.23	1.15
576.959 579.065	0.01	$9.6x10^{-4}$	$9.6x10^{-5}$	$1.3x10^{-5}$	$6.4x10^{-20}$	1.0	0.25	0.40	$1x10^{-18}$	750±30	$3.3x10^{-13}$	$4.7x10^{-12}$	$1.3x10^{-11}$	2.70	2.70	2.62
Hg vapor lamp																
420.0	1.5, cw	$2.9x10^{-3}$	$2.9x10^{-4}$	$3.9x10^{-5}$	$6.2x10^{-19}$	1.0	0.30	0.50	$1x10^{-18}$	660±30	$1.3x10^{-10}$	$1.5x10^{-9}$	$7.4x10^{-9}$	0.000_{41}	0.000_{41}	0.000_{40}
520.0	1.5	$1.3x10^{-3}$	$1.3x10^{-4}$	$1.7x10^{-5}$	$2.0x10^{-19}$	1.0	0.25	0.45	$1x10^{-18}$	680±30	$6.6x10^{-11}$	$8.5x10^{-10}$	$3.1x10^{-9}$	0.003_8	0.003_8	0.003_8
620.0	1.5	$8.8x10^{-4}$	$8.8x10^{-5}$	$1.2x10^{-5}$	$2.6x10^{-20}$	1.0	0.20	0.40	$1x10^{-18}$	750-900	$4.1x10^{-11}$	$5.9x10^{-10}$	$1.5x10^{-9}$	0.060	0.060	0.058
Tunable dye laser																
532.4	2.0, cw	$1.1x10^{-3}$	$1.1x10^{-4}$	$1.5x10^{-5}$	$1.6x10^{-19}$	1.0	0.25	0.45	$1x10^{-18}$	700±30	$8.2x10^{-11}$	$1.1x10^{-9}$	$3.7x10^{-9}$	0.004_2	0.004_2	0.004_0
Doubled Nd. Yag laser																
632.82	0.05, cw	$9.6x10^{-4}$	$9.6x10^{-5}$	$1.3x10^{-5}$	$2.0x10^{-20}$	1.0	0.20	0.40	$1x10^{-18}$	760-900	$1.3x10^{-12}$	$1.9x10^{-11}$	$4.5x10^{-11}$	2.16	2.16	2.10
He. Ne laser																
647.088	4.0, cw	$9.6x10^{-4}$	$9.6x10^{-5}$	$1.3x10^{-5}$	$1.5x10^{-20}$	1.0	0.20	0.40	$1x10^{-18}$	780-900	$9.9x10^{-11}$	$1.4x10^{-9}$	$3.3x10^{-9}$	0.036	0.036	0.035
Kr$^+$laser																
694.3	10.0, pulsed	$1.3x10^{-3}$	$1.3x10^{-4}$	$1.7x10^{-5}$	[illegible]$.6x10^{-21}$	1.0	0.20	0.40	$1x10^{-18}$	840-900	$2.2x10^{-10}$	$3.3x10^{-9}$	$6.2x10^{-9}$	0.028	0.028	0.029
Ruby laser																

15 km for 100 torr. It has been assumed that in a pressurized system at 760 torr particulates will be largely removed and for this only the Rayleigh component is quoted. The sensitivity expressed in ppb is seen to be independent of altitude (pressure). Since stratospheric concentrations appear to be in the range of 1 to 10 ppb a system utilizing excitation in the 405 to 465 nm region is recommended. The He.Cd laser has been reported to be a little noisy (Brown and Ginsburg, 1974) and unless a suitably amplitude-stabilized model can be attained, a source of the blue Hg lines may be superior for incorporation in a piece of flight hardware.

Gelbwachs et al. (1972) and Tucker et al. (1973) have measured the sensitivity of laser fluorescence systems at atmospheric pressure using a 100 mW, 488 nm Ar^+ laser, and a 15 mW, 441.6 nm He.Cd laser. They noted that concentrations of 1 ppb could readily be detected. No interferences from NO, SO_2, O_3, or H_2O were observed, and it is unlikely that other gaseous atmospheric constituents are likely to produce interfering signals. However, they did note that large particles ($>5\,\mu m$ diameter) did contribute to the fluorescence signal (Gelbwachs and Birnbaum, 1973). Stratospheric particles are of a much smaller size though and should only Mie scatter.

Infrared fluorescence from NO_2 appears not to have been studied, but various coincidences have been noted (Table III) between CO laser lines and absorption lines in the strong ν_3 fundamental band centered at about $6.2\,\mu m$ ($1618\ cm^{-1}$). The wavelengths of the latter system have been measured recently to high accuracy and it appears that several coincidences are sufficiently exact to be within the Doppler width of the lines even at reduced pressure. However, potential interferences from the H_2O lines particularly in its ν_2 band in this same spectral region appears severe (Murcray et al., 1969; McClatchey and Selby, 1974). Time does not permit a more detailed assessment of such spectrally overlapping interferences, but a preliminary examination does appear to rule out such an infrared fluorescence approach for NO_2 in the atmosphere.

NITROUS OXIDE, N_2O

In the uv-visible region, N_2O shows only a continuous, dissociative absorption in the far ultraviolet, which is composed of three overlapping transitions. That associated with $\tilde{a}\,^3\Pi \leftarrow X^1\Sigma^+$ is weak and lies at 280 to 306.5 nm having a flat maximum in the vicinity of 290 nm (absorption cross-section $\sim 5 \times 10^{-24}$ cm^2). From 260 to 280 nm an equally weak $\tilde{b}\,^3\Pi \leftarrow X^1\Sigma^+$ transition has a maximum value at 273 nm and a similar absorption cross-section. Below 260 nm absorption rises sharply to a maximum value at 182 nm (1.2×10^{-19} cm^2) and has been assigned to transitions to the lowest singlet state, $\tilde{A}\,^1\Sigma^+$. Absorption cross-sections for these regions have been given by Bates and Hayes (1967). The first discrete region of absorption lies in the vacuum ultraviolet between 140 and 160 nm. Preston and Barr (1971) have established that the primary quantum yield for photolysis of N_2O in these spectral regions is unity and that radiation at 180 to 300 nm produces $N_2 + O\,(^1D)$. As a consequence of the repulsive nature of the upper state involved in absorption in the uv region (Holliday and Reuben, 1968) it will not be possible to stimulate fluorescence from N_2O at these wavelengths.

The likelihood that the infrared region holds any promise is equally remote since all three fundamental bands lie in regions where there is significant absorption by other atmospheric species. Goldman et al. (1970, 1973a) and Murcray et al. (1969) have managed to reduce solar absorption data for a spectral region near the center of the 4.5 μm band (N-N stretch frequency), which is otherwise overlapped by CO and $^{13}CO_2$ lines, and have observed the 7.8 μm band (N-O stretch frequency), although the latter is quite severely obscured by overlapping bands of CH_4 and H_2O. The possibility of exciting fluorescence in these or the 17 μm band (bending frequency) for analytical purposes appears remote. Some care has to be taken in discussing the frequencies since the commonly labelled ν_1 (1285 cm^{-1}) and ν_3 (2224 cm^{-1}) frequencies have been interchanged in Shimanouchi's (1972) tabulation of molecular vibrational frequencies so that the 2224 cm^{-1} value is labelled ν_1.

The only fluorescence studies with N_2O, Table III, have involved the N_2O 10.6 μm laser, resonantly pumping from 001 (1285 cm^{-1}) to 100 (2224 cm^{-1}), fluorescence being observed at 4.5 μm from the latter. This transition cannot of course occur in room-temperature N_2O samples. Recently, Mills and Long (1974) have reported absorption measurements for N_2O pressure broadened samples (atm pressure) using 5 DF laser wavelengths between 2546.42 and 2594.25 cm^{-1} lying in the N_2O overtone band (N-O stretch frequency). Two of these lines are nearly coincident with absorption lines and measurements are reportedly in progress to establish the extent of the frequency mismatch. Lowder et al. (1971) and Sulzmann et al. (1973) have also assessed the potential of center line absorption and derivative spectroscopy for lines in the 4.5 μm band using tunable diode lasers. However, such approaches appear to hold little promise in a fluorescence mode of detection.

HYDROXYL RADICAL, OH

As was noted in Table I, the concentrations of OH in the stratosphere are expected to be particularly low and may be of the order of 10 parts per trillion or less; consequently, fluorescence systems for its detection will have to be efficient, use a reasonably intense source, and be relatively free from spectral interferences. The extreme sensitivity of OH fluorescence has long been recognized and was utilized several years ago aboard rocket flights through the upper atmosphere for which the resonance fluorescence of the (0, 0) band of the $A^2\Sigma^+ - X^2\Pi$ transition at 306.4 nm was monitored in evening twilight conditions (Anderson, 1971a, b). More recently, its potential has been clearly illustrated by the work of Wang (1974) and Wang and Davis (1974) who measured OH concentrations in atmospheric pressure air down to 5×10^6 cm^{-3} (0.2 parts per trillion). Other reported fluorescence studies using line excitation are listed in Table II. Anderson (1974) also is finalizing the development of a highly sensitive system using an OH source of the (0, 0) band radiation (10^{15} photons cm^{-2} sec^{-1}) and predicts a lower limit of detection in the stratosphere $\sim 10^5$ cm^{-3}.

The systems that are most sensitive have been fully described in detail by Wang and Davis (1974) and by Anderson (1974). The former tunes a pulsed, frequency doubled dye laser to the $P_1(1)$ or $P_1(2)$ line at 282.17 nm or 282.58 nm, respectively (Engleman, 1972) to pump the (1, 0) transition in the $A^2\Sigma^+ \leftarrow X^2\Pi$ system. Frequency narrowing of the line was accomplished using a Littrow grating and an intracavity Fabry-Perot etalon, fine tuning being achieved by varying the mixture of helium and propylene in the etalon spacing. An output of up to 6 mJ per pulse ($\sim 8 \times 10^{15}$ quanta) of the 2nd harmonic was obtained. Fluorescence near 309 nm ascribed to (0, 0) radiation was monitored, it lying sufficiently removed from the N_2 Raman band (695 cm^{-1}) to eliminate any interference from this. They calculated an absorption cross-section of 1.2×10^{-17} cm^2 for this transition and a detection limit of 5×10^6 cm^{-3}. Earlier development work was reported by Baardsen and Terhune (1972). Lengel and Crosley (1974) have noted that gases such as N_2 or Ar rapidly relax $\upsilon' = 1$ to $\upsilon' = 0$ in the $A^2\Sigma^+$ state. Transfer is only slightly less efficient than rotational relaxation. For N_2 a preliminary value of ~ 0.15 nm^2 was quoted which corresponds to $\sim 3.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}. This explains the presence of intense (0, 0) fluorescence in this system even though pumping is to $\upsilon'=1$, and also the extreme weakness of the (1,1) fluorescence in spite of its large Franck-Condon factor. To convey the relative spectral positions of these OH bands of interest their approximate bandhead wavelengths are

(0,1) 342.8 nm, (1,1) 312.2 nm, (0,0) 306.4 nm, and (1,0) 281.1 nm. Wang and Davis (1974) have discussed the background signals observed and the potential interferences. SO_2 and NO_2 can constitute an interference since they absorb at these wavelengths and fluoresce in the detection bandpass. Becker et al. (1972, 1974) similarly have worked with a pulsed, frequency doubled tunable dye laser but in the 300-320 nm region pumping the resonance (0, 0) fluorescence excitation and using a monochromator to isolate a section of the band. Such systems are rather sophisticated and require occasional adjustment. Consequently, although satisfactory sensitivity is attainable it is an impractical approach for placement aboard a U2 plane for automated stratospheric OH concentration monitoring.

The system that has been fully described in an as yet unpublished report by Anderson (1974) appears a more feasible approach for flight hardware. This utilizes either an RF or microwave discharge in an Ar/H_2O mixture to produce the intense (0, 0) $A^2\Sigma^+ - X^2\Pi$ radiation ($\sim10^{15}$ photons cm^{-2} sec^{-1}). Rayleigh and Raman scattering effects are avoided by monitoring the (0, 1) band. Assessments of the detection limit give values of about $\sim10^5$ cm^{-3}, sufficiently sensitive for stratospheric applications.

The natural lifetime of the $\upsilon' = 0$, and 1 levels has been extensively studied. Recently reported values all fall within the range of about 514 to 830 nsec and have been summarized by Becker and Haaks (1973) and Becker et al. (1974). Older literature values, which show a wider spread are given by DeZafra et al. (1971) and German et al. (1973). The lifetimes of the two levels are quite similar and a mean value of about 670 nsec appears a best estimate, and has been used here. Several states are known to exist that cross the $A^2\Sigma^+$ state. However, although predissociation is observed in the OH ($A^2\Sigma^+ - X^2\Pi$) system it is only apparent at high K levels in the $\upsilon' = 0$ ($K \geq 30$) and $\upsilon' = 1$ ($K \geq 21$) bands and will not be of concern here (Sutherland and Anderson, 1973) Electronic quenching of the $A^2\Sigma^+$ vibrational levels has been studied with various gases. For nitrogen, values range from about 5×10^{-12} to 5×10^{-11} cm^3 $molecule^{-1}$ sec^{-1} and a mean value of about 1.2×10^{-11} might be assumed (Kaneko et al., 1968; Kley and Welge, 1968; Becker and Haaks, 1973). With argon, values are lower, being in the range $< 2 \times 10^{-13}$ to 1×10^{-12}; a value of 5×10^{-13} has been taken (Kley and Welge, 1968; Becker and Haaks, 1973; Becker et al., 1974). For oxygen, data have only been obtained in flames and correspond to a rate constant of about 5×10^{-11} (Carrington, 1959; Hooymayers and Alkemande, 1967). Consequently, nitrogen and oxygen will contribute equally to the quenching of OH ($A^2\Sigma^+$) in air samples. Fluorescence efficiencies are 0.16 (10 torr), 0.019 (100 torr), and 0.0025 (760 torr).

The fluorescence excited with the Bi 306.7 nm resonance line has been studied in flames by Carrington (1959, 1960) and Hooymayers and Alkemade (1967). This source line is composed of 4 hyperfine components that lie between the $R_2(9)$ and $R_2(10)$ lines in the (0, 0) band of OH. In a reduced pressure sample the extent of the overlap will become significantly reduced. Also at a temperature of 250 K the absorbing population density is quite low since these transitions are from levels that are at 1693.2 and 2056.5 cm^{-1} respectively, above the ground state (Hooymayers and Alkemade, 1967). Consequently, since a Bi line source of only 5×10^{-3} W $ster^{-1}$ cm^{-2} is available (Table IX) it would seem unlikely that such a system could be refined to measure the exceedingly low concentrations of OH that are predicted for the atmosphere. Similarly the possibility of using the Zn 307.2 nm line (Table II) to pump the ground rotational level can be discarded since this line is weak, being only 10^{-2} times that of the zinc resonance line which has been seen elsewhere in this report to be available with intensities of about 5×10^{-4} W $ster^{-1}$ cm^{-2}. This is unfortunate since its coincidence with an OH line is very close, which fact has been used by Hollander and Broida (1967, 1969) to measure line profiles in flames by the Zeeman scanning technique.

Although OH can also be monitored in absorption (McGregor et al., 1972) the fluorescence mode is more sensitive and less subject to spectral interferences. Infrared fluorescence is not possible for OH detection with atmospheric samples owing to severe interferences by H_2O.

SULFUR DIOXIDE, SO_2

The spectroscopy of the low-lying electronically excited states of SO_2 has long been a difficult problem. Much work has been devoted to elucidating the nature of the two excited states $^3B_1$, $^1B_1$ produced by absorption of radiation at wavelengths greater than 250 nm where no photochemical dissociation occurs. The dissociation limit of the ground state $\tilde{X}\,^1A_1$ corresponds to a wavelength of about 219 nm, D_0^o (SO-O) = 130.8 kcal mole^{-1} (547.3 kJ mole^{-1}), and absorption at this or shorter wavelengths is accompanied by predissociation of the molecule.

In the near ultraviolet there are three main regions of absorption. A very weak 'forbidden' absorption to the $^3B_1$ electronic state in the region 340 to 390 nm. A strong absorption between 250 and 340 nm generally attributed to the $^1B_1 \leftarrow {}^1A_1$ transition, but probably consisting of more than one electronic transition. Brus and McDonald (1973) have presented evidence for the existence of two emitting singlet states. A still stronger absorption lies in the 190 to 235 nm range and has been identified with the $^1B_2 \leftarrow {}^1A_1$ and possibly other systems. Cross-sections for these absorptions are illustrated in Figures 10 and 11 and show a complex coarsely structured nature.

The lowest excited state, $^3B_1$, phosphoresces with a radiative lifetime of about 9×10^{-4} sec (Otsuka and Calvert, 1971; Sidebottom et al., 1971; Strickler et al., 1974) and is quenched by air species at a rate of about 5×10^{-14} cm^3 molecule^{-1} sec^{-1} at 250 K (Wampler et al., 1973). The very low absorption cross-section ($\sim 3 \times 10^{-22}$ cm^2) together with the small fluorescent efficiency is sufficient to eliminate this region from further consideration.

Absorptions in the 250 to 340 nm region populate the $^1B_1$ electronic state and possibly others. Resulting fluorescence emission extends in a continuous band from the exciting line to about 500 nm, peak emission being in the vicinity of 340 nm. The spectral distribution of the envelope is fairly independent of the exciting wavelength (Mettee, 1968). As with NO_2, the measured fluorescent collision-free lifetime is at least 2 orders of magnitude larger than that computed from the integrated absorption coefficient (0.2 μsec). This anomaly discussed by Douglas (1966) has been ascribed to the mixing and perturbation of vibrational levels of the state with those of other electronic states. Previous considerations as to whether the measured collision-free lifetime was entirely radiative or whether additional non-radiative unimolecular internal conversions played a role have now been discarded (Brus and McDonald, 1973; Calvert, 1973). Absorption in this region can best

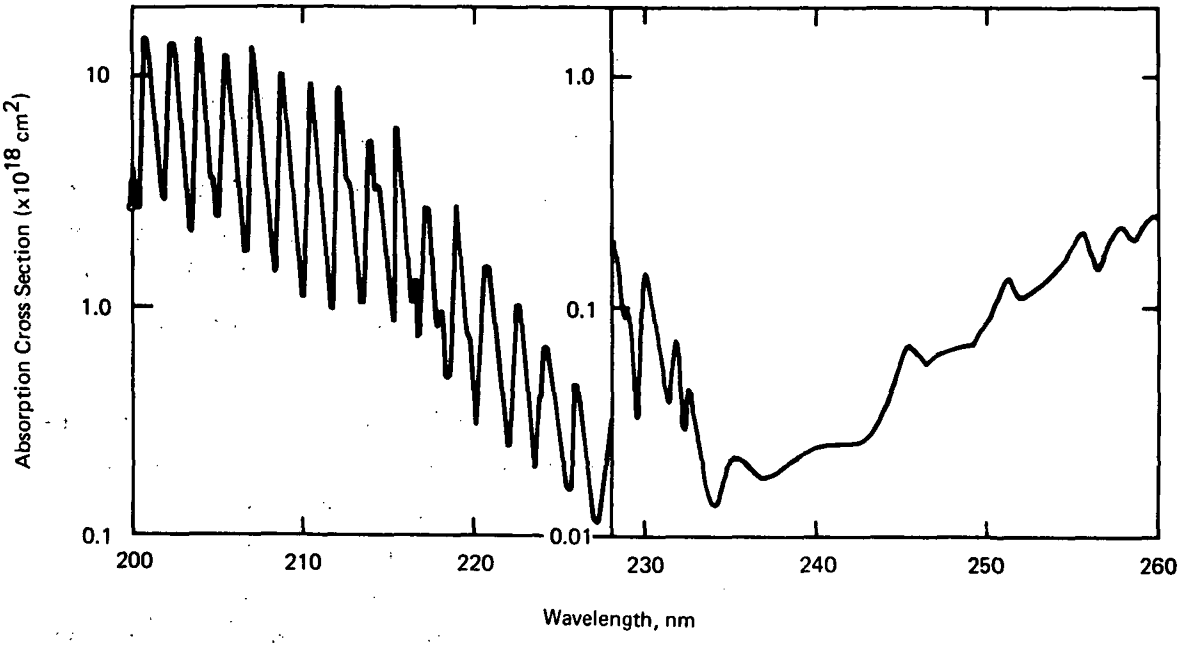

Figure 10. Absorption Cross-sections of SO_2 at 200 to 260 nm, 0.2 nm Spectral Resolution (from Warneck et al., 1964)

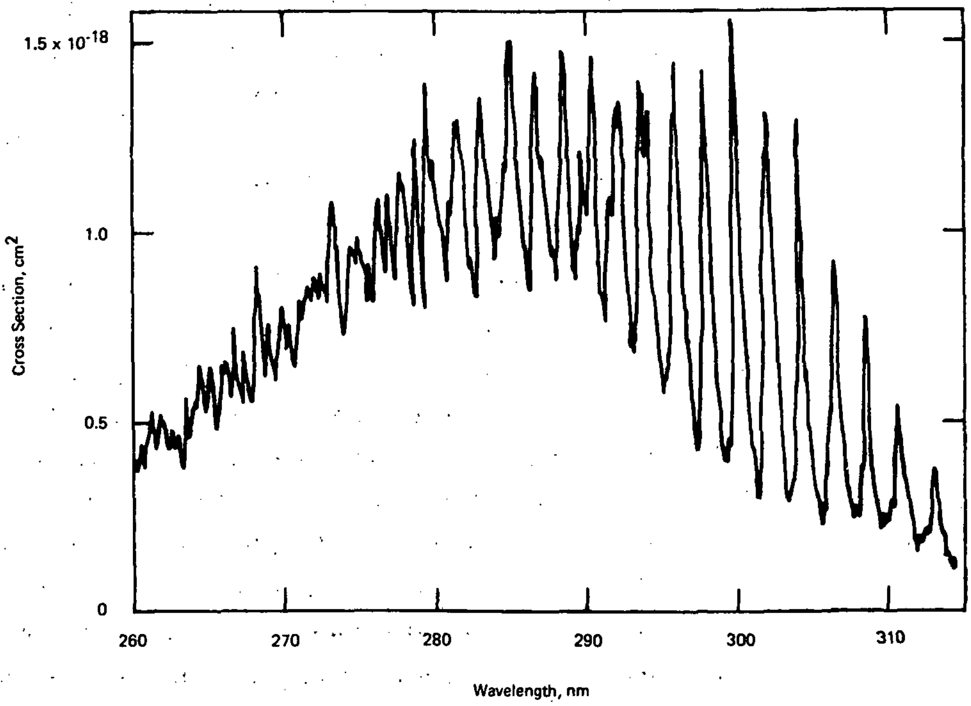

Figure 11. Absorption Cross-sections of SO_2 at 260 to 315 nm (from Martin, 1973)

be interpreted as producing two different states which appear to have different quenching rates and zero pressure lifetimes (Brus and McDonald, 1973). The principal group has unusually long radiative lifetimes (80 to 600 μsec) decreasing to shorter excitation wavelength. The second group has lifetimes of about 49 μsec. Collisional quenching rates are very high. For the long-lived states these are within a factor of 2 to 5 of the collision frequency, which is $\sim 2.5 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1} (Mettee, 1969; Sidebottom et al., 1972; Brus and McDonald 1973). The short-lived states have quenching rates that appear to be larger than this. In spite of the many detailed studies, available data for the radiative lifetime are still inconsistent. Greenough and Duncan (1961) obtained a value of 42 μsec using broadband flashlamp excitation, Brus and McDonald's values range from 79 μsec (261.7 nm) to 532 μsec (320 nm), and Martin (1973) obtained 35 to 57 μsec (250 to 315 nm). Disagreement is particularly evident at the longer wavelengths. In these assessments a value of 80 μsec and a collisional quenching rate of one-quarter the gas kinetic frequency has been assumed. The very low fluorescence efficiency reflects the high collisional quenching rate. The detection limits have been calculated for the two sources that have been used to excite fluorescence in this region, namely the fourth harmonic of the neodymium laser and the strong 253.6 nm Hg line which is the predominant radiation from a low-pressure lamp. Values are listed in Table XXVIII. A 10 nm (FWHM) interference filter centered at 340 nm has been assumed. The dark current noise level of the photomultiplier tube corresponds to about 100 quanta sec^{-1} at this detection wavelength. A frequency-doubled tunable, cw dye laser also could be used as a source operating in the 260 to 310 nm region. At these short wavelengths the Rayleigh scattering is very severe. Raman scattering from the air components will fall outside of the filter bandpass and poses no problem. The nitrogen Raman band at 284 nm lies closest to the 340 nm detection channel. For these 0.1 W sources, the magnitude of the scattering is listed in Table XXVIII. Contributions from Mie scattering are negligible at these wavelengths. It will therefore be necessary to provide 6 to 8 orders of magnitude attenuation to sufficiently reduce the Rayleigh component. An interference filter provides about 5 orders. The photomultiplier, fitted with a lime-soda window will provide a further attenuation factor. Additional Corning filters might also be used, for example filter number 0-54, or polarizers. The calculation has simply assumed the use of two interference filters, each with a peak transmission of 25%, in series, so producing an overall transmission of 6%. Since the scattering is so severe at these short wavelengths, little is to be gained by using higher power cw sources or pulsed systems to lower the sensitivity

Table XXVIII. Detection Limits for Various SO_2 Fluorescence Systems

Source, nm	Source Intensity, $I_s a_s \Omega_s$ watts	Fluorescence Efficiency $k_f/(k_f + k_d + k_q [M])$ 10 torr	100 torr	760 torr	σ, cm^2	ℓ, cm	f	θ	N, watts	Detector Wavelength, nm	Rayleigh & Mie Scattering at Detector, watts 10 torr	100 torr	760 torr	Detection Limits ppb 10 torr	100 torr	760 torr
266.2 4th Harmonic Nd laser	0.1	5.2×10^{-4}	5.2×10^{-5}	6.8×10^{-6}	0.64×10^{-18}	4.4	0.10	0.06*	6×10^{-17}	340± 5	1.9×10^{-10}	1.9×10^{-9}	1.4×10^{-8}	11	11	11
253.6 Hg low pressure lamp	0.1 (assumed)	5.2×10^{-4}	5.2×10^{-5}	6.8×10^{-6}	0.13×10^{-18}	4.4	0.10	0.06*	6×10^{-17}	340± 5	2.4×10^{-10}	2.4×10^{-9}	1.8×10^{-8}	56	56	56
213.86 Zn vapor lamp	5×10^{-5}	0.12	0.10	0.044	5.6×10^{-18}	4.4	0.08	0.25	6×10^{-17}	330± 5	2.6×10^{-13}	2.6×10^{-12}	2.0×10^{-11}	3.4	0.40	0.12
228.80 Cd vapor lamp	1×10^{-3}	0.84	0.34	0.064	0.10×10^{-18}	4.4	0.08	0.25	6×10^{-17}	330± 5	3.9×10^{-12}	3.9×10^{-11}	3.0×10^{-10}	1.3	0.33	0.23

* Double interference filter

limits. Some assessments have been made by Measures and Pilon (1972) of the potential of SO_2 laser fluorescence for mapping pollution in the air at ground level. They use the second harmonic of a high-power ruby laser at 347.2 nm and lidar techniques comparing the fluorescence approach with the differential absorption and scattering method. The absorption coefficient is much reduced at this wavelength and consequently fluorescence levels are very low.

From the analytical point of view, emphasis has been placed on the third spectral region, 190 to 235 nm, owing to its much reduced radiative lifetime. However, less is known of the $\tilde{C}$ and $\tilde{D}$ states lying more than 40,000 cm^{-1} above the ground state. The radiative lifetime has been taken as 10 nsec (Smith, 1969, 1971b; Okabe, 1971), however, Hui and Rice (1972, 1973) have reported a value of 32 nsec. Fluorescence quantum yields have been measured by Okabe (1971), and Hui and Rice (1972, 1973) in the 200 to 230 nm region. At low pressures these fall away sharply for excitation energies of less than 220 nm due to predissociation of the electronically excited SO_2 state. This shortens the effective fluorescent lifetime by about a factor of 8 from which a value of $k_d \doteq 7 \times 10^8$ sec^{-1} can be derived. Collisional quenching rates for the state are high, $\sim 5 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1} (Okabe, 1971) which is about 0.2 times the gas kinetic collision frequency. Fluorescence studies in this region have used Zn, Zn^+, Cd line sources. Zn^+ (210 nm) sources are very weak and do not merit further consideration. Zn (213.86 nm) and Cd (228.80 nm) are the strongest lines of these elements. Cd appears to be most intense in metal vapor discharge lamps, whereas comparable intensities are emitted from hollow cathode, metal vapor or electrodeless microwave discharge lamps for Zn. The assumed intensities used in these calculations are 10^{-2} W cm^{-2} $ster^{-1}$ for cadmium and 5×10^{-4} W cm^{-2} $ster^{-1}$ for zinc. A source area of 0.5 cm^2 is assumed. The fluorescence spectrum appears to be continuous over the range 240 to 420 nm with a broad maximum at about 320 nm (Okabe et al., 1973). Although the zinc source is twenty times weaker and also predissociates a fraction of the excited SO_2 the absorption cross-section is 56 times larger. Calculated detection limits (ppb) for these systems are listed in Table XXVIII and are smallest for Cd, decreasing with increasing pressure.

Okabe et al. (1973) have investigated experimentally the analytical potential of SO_2 fluorescence excited by these Zn and Cd lines. Their preliminary system produced a detection limit of 20 ppb which is consistent with these calculated estimates. They also investigated possible interferences from a series of gases known to be present in ambient air and found the system interference free for the current application. Although NO also fluoresces when excited with the Zn 213.86 nm line it is very weak at room temperatures and predominantly in the 215 to 280 nm region.

Infrared fluorescence appears not to have been studied for SO_2. However, various line coincidences have been noted of potential interest for absorption techniques. Hanst (1971) has observed that a neon laser line at 7.4237 μm (1347.04 cm^{-1}) lies in the strongest SO_2 infrared band (ν_3) centered at about 7.35 μm. However, this lies in a region seriously overlapped with water bands which might produce a severe interference for any ppb detector. Also, owing to the narrowness of infrared laser lines in this region (< 0.002 cm^{-1}) and the Doppler width of an absorbing SO_2 line (0.002 cm^{-1}) little absorption would be expected at reduced pressure for such systems unless an almost exact coincidence occurs. The same considerations also apply to the possible coincidences noted by Menzies (1971) between some very high vibrational CO laser and SO_2 lines (Table III). Brockman and Seals (1973) have assessed the feasibility of absorption measurements in this region using tunable diode lasers. The low sensitivity derived by them would apply equally well to any fluorescent type approach. Similarly, Hinkley (1972a) has also considered the use of diode lasers but operating on the slightly weaker ν_1 band centered at 8.7 μm, a region less susceptible to spectral interferences.

It appears that a system based on Cd (228.8 nm) induced fluorescence is feasible for SO_2. Rayleigh scattering can be eliminated by the combined interference filters and photomultiplier attenuation factors. Mie and Raman scatterings pose no problems.

SUMMARY AND RECOMMENDATIONS

It may be appropriate at this point to briefly summarize the conclusions reached for the individual species considered here. It will also serve to concisely illustrate the promise and limitations of this molecular fluorescence approach for future stratospheric monitoring applications.

Cl Although atomic fluorescence is extremely sensitive for chlorine, absorptions lie in the vacuum ultraviolet and so are inappropriate for air samples.

Cl_2 Fluorescence is too weak for chlorine to be of any analytical value. Otherwise, it can only be stimulated by the weak Raman interaction.

ClO Although predissociation is evident in several of the absorption bands, the (12, 0) at 277 nm is sharp. Absorption cross-sections are large and it may offer some promise. However, its fluorescence is as yet uninvestigated and the ClO $(A^2\Pi_{3/2})$ state is poorly characterized concerning its radiative lifetime and its quenching rates.

ClO_2 The strongest region of absorption at 351 nm photodissociates the stable OClO molecular form. Longer wavelength excitation with, for example, an Ar^+ laser line is weak, partly due to a small absorption cross-section and also due to extensive dissociation, which appears to be predominant at all these wavelengths. The cross-section for the 351 nm band is such that an absorption technique may be suitable for this species. The isomeric form ClOO is very unstable and its detection at low concentration levels is unlikely with a fluorescence technique.

CO The very sensitive CO (4th positive) fluorescence lies at wavelengths < 154 nm and is unsuitable for air samples. Although CO infrared fluorescence can be induced, a minimum detection of no less than 1 ppm is feasible.

H_2 Since ground state absorption lies at wavelengths ≤ 110 nm the direct detection of hydrogen other than by Raman scattering poses a difficult task.

HCHO Absorptions in the 280 to 350 nm region produce fluorescence from the $\tilde{A} - \tilde{X}$ system. Levels are sharp in spite of the fact that radiationless transitions lead to a near unity quantum yield for dissociation. Lifetimes of some of the vibronic levels are sufficiently short that in spite of this and the fast collisional quenching rates reasonably strong fluorescence is still observed. However, the system is limited by Rayleigh scattering and a practical detection limit of about 50 to 100 ppb may be about the best achievable; too high for stratospheric application.

HCl The only spectral feature of interest for this molecule is the infrared fundamental band at 3.5 μm. Low fluorescence efficiencies and limited detector sensitivity predict such high detection limits that the system is of little use analytically.

HONO Nitrous acid vapor appears to photodissociate in the ultraviolet with a primary quantum yield of unity. The infrared fundamental bands have been characterized but lie in regions where other atmospheric components absorb. Fluorescence techniques hold no promise. Moreover, detection by any absorption or emission technique may prove to be difficult.

$HONO_2$ This molecule is photodissociated with a primary quantum yield of unity in the ultraviolet where its absorption spectrum is continuous. Infrared bands are either severely interfered with by overlapping H_2O, O_3 and CH_4 lines or too weak to show any promise for fluorescence detection.

H_2S This only exhibits a dissociative continuum in the far ultraviolet and weak infrared bands. No fluorescence studies have been reported, or are likely to be.

NH_3 Its only uv-visible region absorption system lies at 170 to 217 nm. Predissociation is evident with no fluorescence. In the infrared an almost exact coincidence between the P(13) line of the N_2O laser and a line in the strong ν_2 band of NH_3 at 10.8 μm (928 cm^{-1}) may have potential, in fact more than any other infrared fluorescence system considered, for monitoring ammonia. However, sensitivity at best will be in terms of ppm.

NO Several atomic lines coincide to various extents with absorptions in the γ bands of NO. However, the lowest calculated fluorescence detection limits are in the range 40 to 80 ppb, the most sensitive systems being those with Cd^+ or Se line sources in the vicinity of 200 nm. The low sensitivity results from a combination of factors, source intensities, a low concentration in the absorbing level, and only partial overlap between the source and absorbing lines. Sensitivity could be improved several fold by using a Cd^+ lamp enriched in its odd isotopes or by using an NO γ band molecular source. However, these systems will never be serious competitors for the NO chemiluminescent detector.

NO_2 As a result of its complex nature, although NO_2 fluorescence has been extensively studied, various spectral features are still not entirely characterized. However, potential detection limits can be calculated and for various exciting line sources are remarkably low, the monitoring of concentrations at the 1 ppb level being easily attainable. Light scattering can be severe and may ultimately control the lower limit of detection. A system using a He.Cd laser or the blue Hg lines appears best for incorporation in flight hardware.

N_2O This only shows dissociative absorption continua in the far ultraviolet. The infrared region is equally inappropriate since the three fundamental bands lie in regions where there is significant absorption by other species.

OH A tunable laser system is sufficiently sensitive for OH measurements but impractical for the fully automated system demanded by a U2 plane. Its application to lower altitude measurements aboard larger aircraft is probably assured. A system incorporating an RF discharge source of OH radiation is particularly appropriate and appears to have a detection limit near 10^5 cm^{-3}, quite sufficient for flights through the stratosphere.

SO_2 Of the three main regions of absorption in the ultraviolet the most sensitive is that lying at 190 to 235 nm. Zn and Cd exciting systems are appropriate in this region, the latter being the more sensitive. Measurements down to about 1 ppb appear feasible.

It should be noted therefore, that as a result of various factors, infrared fluorescence techniques in general cannot be exploited in sensitive analyzers. The species OH, NO_2, and SO_2 all can be monitored using uv-visible fluorescence systems with a sufficient sensitivity to warrant their development as analytical flight hardware. It might also be appropriate, at some period, to obtain the data required to permit a characterization of the potential of ClO fluorescence.

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