

Hydrogen Halide Trace Detection Using Diode Lasers

David S. Bomse, Joel A. Silver, and Alan C. Stanton
Southwest Sciences, Inc.
1570 Pacheco Street, Suite E-I1
Santa Fe, NM 87505
(505) 984-1322

Abstract

Diode-laser-based optical spectroscopy is ideally suited to the quantitative measurement of hydrogen halides resulting from the decomposition of potential Halon replacements. Near-infrared diode **lasers** offer a rapid, reliable, sensitive and highly selective method for the detection of all HX species except hydrogen iodide. Room temperature detection limits are 0.2, 0.9, and 19 part per *billion* for HF, HCl, and HBr, respectively, assuming a 10 m optical path. Real time *in situ* measurements are possible including measurements made at high temperatures.

Introduction

The formation of gaseous hydrogen halides (HF, HCl, HBr, and possibly HI) by thermal decomposition of Halon replacements is an important safety issue. The hydrogen halides attack the respiratory system and the eyes and probably exacerbate pulmonary risks from smoke inhalation.' Hydrogen fluoride, for example, can be fatal at concentrations of 50 ppm.' Testing of potential Halon replacements, therefore, requires sensitive analyzers for rapid, quantitative measurement of the concentrations of the individual hydrogen halides.

Southwest Sciences has demonstrated that optical spectroscopy using near-infrared diode lasers is particularly well suited to detecting hydrogen fluoride (HF) and hydrogen chloride (HCl).² Detection limits below 1 part per *billion* are possible for a 1 second measurement time. Available spectroscopic data imply minimum detectable HBr concentrations are in the sub-ppm range.' Our approach uses the type of diode lasers originally developed for the communications industry. These solid-state devices are extremely reliable, compact, operate at room temperature, require little power and are compatible with fiber optics. Their narrow spectral linewidth allows high selectivity for detecting the target compound — even at trace concentrations — while minimizing the likelihood of interferences due to background gases. *In situ* measurements and extractive gas sampling are both possible. High frequency wavelength modulation techniques developed at Southwest Sciences provide exceptional detection **sensitivity**.⁴⁻⁵

Detection of Trace Gases Using Diode Lasers

Types of Diode Lasers. Diode lasers are commercially available at wavelengths extending from the red (–650 nm) to the far infrared (–25 μm). Although mid-infrared wavelengths are best-suited for most gas detection schemes—these wavelengths overlap with strong fundamental vibrational bands—the mid-infrared diode lasers require cryogenic cooling, show poor long term

stability, and need cryogenically cooled detectors. We have demonstrated that excellent sensitivity can be obtained, instead, using near-infrared lasers tuned to vibrational overtones.^{2,4-6} The advantages of working with near-infrared lasers more than compensate for the one- to two-order of magnitude smaller line strength exhibited by the overtones. Near-infrared lasers manufactured for the communications industry operate at room temperature, are rugged and reliable. These lasers are sold in standard DIP packages containing the laser, a monitor photodiode, a thermoelectric heater/cooler, and an optical isolator. The laser light comes out through an optical fiber. Special types of lasers, fabricated using the distributed feedback (DFB) design, guarantee single wavelength operation at all times. This spectral purity is necessary for trace gas detection.

Diode lasers are wavelength tunable. Coarse wavelength adjustment is performed by changing the laser temperature (typical useful temperatures are -20° to 50° C). Fine wavelength control is accomplished by changing the laser drive current. This current tunability also allows a simple method for wavelength modulation (described below) by adding a small sinusoidal AC component to the DC current. Typically, the DC current is in the range of 40 to 150 mA and the AC current is about 10% of the DC magnitude. The lasers draw less than 200 mW electrical power and optical output powers are in the 1 to 10 mW range. When used for open air measurements, the laser beam is expanded to ~1 cm diameter so that the irradiances are eye safe.

Optical Spectroscopy Using Diode Lasers. Detection sensitivity is determined, in large part, by the smallest optical absorbance that can be measured. Absorbance, a , is a dimensionless quantity defined by Beer's Law,

$$I/I_0 = \exp(-a) \tag{1}$$

with

$$a = \sigma N \ell ,$$

where I is the laser intensity reaching the detector, I_0 is the laser intensity in the absence of absorption, σ is the absorption cross section, N is the number density (concentration) of the absorbing species, and ℓ is the optical path length. Typically, σ and ℓ are known so that measurement of absorbance yields the species concentration.

Conventional spectrometers such as FTIR instruments or grating devices can measure absorbances down to about $\alpha = 10^{-3}$, whereas using diode lasers we and other groups have demonstrated **minimum** detectable absorbances as small as 10^{-7} (1 Hz). Our experience with field instruments translates into minimum detectable absorbances of $\sim 3 \times 10^{-6}$ for a 1 second measurement.

The detection method that we employ with diode lasers is a high frequency version of what is described in the literature by the terms "Wavelength modulation spectroscopy," "derivative spectroscopy," or "harmonic detection."⁷⁻⁹ High sensitivity is obtained by shifting the absorbance measurement to high frequencies where laser $1/f$ noise is unimportant. A small sinusoidal modulation is superimposed on the diode laser injection current. This current modulation

produces a modulation of the laser wavelength, since the laser wavelength changes with current. Typically, the amplitude of the current modulation is chosen such that the wavelength excursions are comparable to the width of the spectral feature under study. Optical absorption converts the wavelength modulation of the light into an amplitude modulation which shows up as AC components in the detector output. Phase sensitive electronics are then used to detect the signal at the modulation frequency, f , or one of its harmonics, nf . The resulting spectral waveforms look like the n^{th} derivative with respect to wavelength of the direct transmission spectrum. High sensitivity absorbance measurements are possible using a single optical beam. Absolute absorbances are obtained by dividing the demodulated AC signal by the detector DC output. Calibration is straightforward and can be maintained over large ranges of absorbances and laser power levels. Absorbance measurement dynamic ranges of 10^5 are possible. Wavelength modulation spectroscopy is implemented using inexpensive rf electronic components. Figure 1 shows an isolated absorption line and its corresponding $2f$ lineshape. Figure 2 shows a typical experimental schematic diagram. Herriott-style multiple pass optical cells can be included to obtain long path lengths (tens of meters) within a compact two-mirror design.¹⁰⁻¹¹

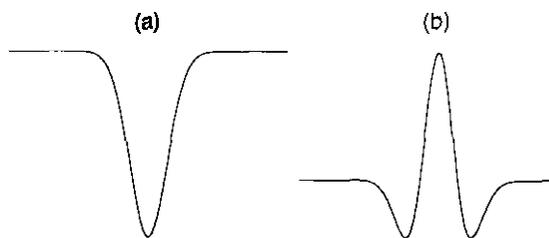


Figure 1. Representative absorption (a) and $2f$ lineshapes (b).

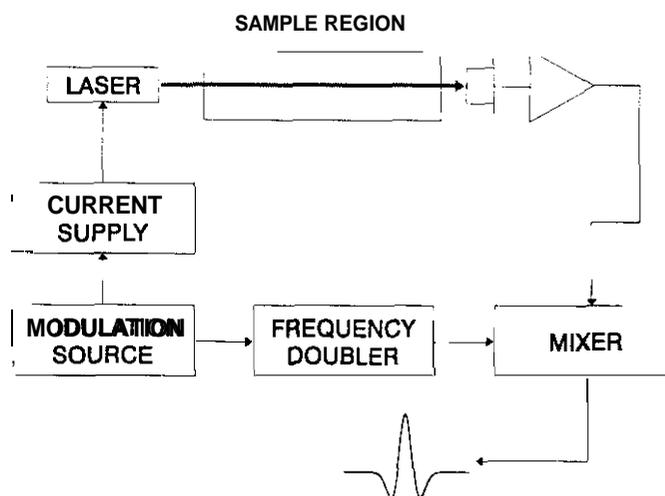


Figure 2 - Schematic diagram for wavelength modulation spectroscopy

Our recent measurements using both mid-IR and near-IR diode lasers achieved minimum detectable absorbances ($S/N = 1$) of 1 to 2×10^{-7} with a time constant of 1 second or less.⁴ These results represent an improvement by at least two orders of magnitude over the sensitivity typically achieved in diode laser experiments employing lower frequency (~ 1 kHz) laser modulation due to the negligible laser noise at the higher (MHz) frequencies. The near-IR results were achieved using a 3 mW diode laser operating near 760 nm and the mid-IR experiments used an 11 μ W Pb-salt laser operating at 8 μ m.

Detection of Hydrogen Halides

Diode laser methods can provide detection limits of 0.2, 0.9, and 19 part per *billion* for HF, HCl, and HBr, respectively, assuming a minimum detectable absorbance of 3×10^{-6} , an optical path length of $\ell = 10$ m, and measurement at room temperature. Expected results for high temperature (1200 K) are about a factor of five worse.

The following tables list anticipated detection limits for HF, HCl, and HBr at 300 K and 1200 K using near-infrared wavelengths. We assume a minimum detectable absorbance of 3×10^{-6} and a 10 m optical path length. Hydrogen fluoride is easiest to observe because the compound shows an overtone band that is stronger than the fundamental transition of many molecules and the optimum detection wavelength, $\sim 1.3 \mu\text{m}$, is available from InGaAsP diode lasers sold for long-haul fiber-optic communications. The preferred detection wavelengths for HCl, near $1.75 \mu\text{m}$, are due to the $2 \leftarrow 0$ overtone. The next higher overtone has lines near $1.2 \mu\text{m}$ and can provide part per million detection limits for both room temperature and 1200 K conditions. In the case of hydrogen bromide, we also consider two overtones. Lines near $2.0 \mu\text{m}$, the $2 \leftarrow 0$ vibrational overtone band, are a factor of 35 stronger than lines in the $3 \leftarrow 0$ overtone near $1.3 \mu\text{m}$; but the longer wavelength band may be preferred, despite the lower line strengths, because lasers are more readily available in that wavelength range.

Entries in the tables were calculated using data from the HITRAN spectroscopic data base.³

Transition cross sections, σ , calculated from,

$$\sigma = \frac{S}{\pi \cdot \Delta \nu}, \quad (2)$$

where S is the line strength and $\Delta \nu$ is the collisional broadening parameter. Typical linewidths range between 0.05 and 0.10 cm^{-1} at 1 atm .³ The line strength is temperature dependent, reflecting the changes in molecular rotational partition function and Boltzmann factors with temperature. For measurements at **high** temperature, one can select a rotational line with a relatively high ground state energy in order to compensate for the reduction in S due to the larger partition function.

Table I - HF Line Parameters

Wavelength (μm)	Line	Detection Limit 300 K (ppb)	Detection Limit 1200 K (ppm)
1.310	P(5)	0.52	0.019
1.321	P(4)	0.37	0.006
1.312	P(3)	0.29	0.003
1.305	P(2)	0.27	0.002
1.297	P(1)	0.39	0.002
1.284	R(0)	0.33	0.001
1.278	R(1)	0.19	0.001
1.273	R(2)	0.18	0.001
1.268	R(3)	0.19	0.002
1.264	R(4)	0.23	0.004
1.261	R(5)	0.40	0.015

λ (μm)	Line	Detection Limit 300 K (ppb)	Detection Limit 1200 K (ppb)	λ (μm)	Line	Detection Limit 300 K (ppb)	Detection Limit 1200 K (ppb)
1.778	P(2)	1.8	9	2.003	P(2)	33	158
1.771	P(1)	3.2	14	1.996	P(1)	73	309
1.758	R(0)	3.2	13	1.983	R(0)	70	278
1.754	R(1)	1.4	6	1.977	R(1)	30	126
1.747	R(2)	1.1	5	1.972	R(2)	23	109
1.742	R(3)	0.9	6	1.967	R(3)	19	110
1.738	R(4)	1.0	8	1.962	R(4)	19	135
1.734	R(5)	1.1	13	1.958	R(5)	20	193
1.730	R(6)	1.3	25	1.954	R(6)	23	324
1.727	R(7)	1.8	58	1.951	R(7)	30	652
1.208	P(3)	232	1460	1.357	P(2)	1440	6860
1.204	P(2)	280	1403	1.353	P(1)	3050	13000
1.201	P(1)	500	2180	1.348	R(0)	2690	10800
1.195	R(0)	440	1770	1.345	R(1)	1110	4760
1.193	R(1)	214	924	1.343	R(2)	828	3970
1.191	R(2)	155	782	1.341	R(3)	679	3880
1.189	R(3)	135	851	1.339	R(4)	639	4650

The tabulated data show several spectral lines for each compound to help emphasize that the diode laser method is useful when detecting a trace species in the presence of myriad other compounds. Even though water, for **example**, exhibits numerous overtone absorption lines in the 1.3 to 1.4 μm region, the narrow linewidths available from the diode lasers make it possible to selectively quantify absorption lines due to trace HF or HBr in the same spectral region.

Note that Tables II and III only include entries for the majority isotopic species: H^{35}Cl and H^{79}Br , respectively. In most cases, the other isotopic variant (H^{37}Cl and H^{81}Br) gives rise to a separate absorption line having a line strength scaled by the relative abundances of the isotopes.

Southwest Sciences has demonstrated detection of both HF and HCl using diode lasers. The HF work, currently in progress, is being performed for a consortium of petrochemical companies and is targeted for open path perimeter monitoring. A five month long field test of the first prototype instrument was recently completed. Although most details of the test are proprietary, we can report that the instrument performance matched nearly all design specification. Work done at Southwest Sciences in 1988 demonstrated the usefulness of diode lasers for HCl detection even though the only laser available at that time was a multimode device operating at $1.2\ \mu\text{m}$.² The measured detection limit was 3 ppm for a 50 torr sample using a 1.5 m path length sample and tuning the laser coincident with the H^{35}Cl P(3) line. We now expect the same absorption line to provide a room temperature detection limit of 1.5 ppm for the same optical path in a 1 atm sample. (Data in Table II were calculated assuming a 10 m path.) When the effects of pressure broadening on cross section are included, the entries in Table II represent a twelve-fold improvement over the 1988 results in the expected detection limit. Most of the improvement is due to the lower noise expected from the types of single mode DFB diode lasers now available.

Conclusions

Optical spectroscopy using near-infrared diode lasers offers a rapid, reliable, sensitive and highly selective method for the detection of hydrogen halides HF, HCl, and HBr. The laser-based technology is ideally suited to the quantitative measurement of hydrogen halide formation resulting from the decomposition of potential Halon replacements. Real time *in situ* measurements are possible including measurements made at high temperatures.

Acknowledgments

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