LA-UR -83-1044

LA-UR--83-1044

DE83 011327

CONF-830425--10

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-30

TITLE Infrared-Laser Spectroscopy, 1980-1983

AUTHOR(S) Robin S. McDowell

SUBMITTED TO Los Alamos Conference on Optics, April 11-15, 1983

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

By acceptance of this article the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

MASTER
Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Infrared Laser Spectroscopy, 1980-1983*

Robin S. McDowell

University of California, Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Abstract

The text for the Short Course on Infrared Laser Spectroscopy given at the Los Alamos Conference on Optics '83 is R. S. McDowell, "Vibrational Spectroscopy Using Tunable Lasers," in Vibrational Spectra and Structure, J. R. Durig, ed. (Elsevier, Amsterdam, 1981) 10, 1-151, which includes references through 1979. The present paper summarizes progress in this field from 1980 to early 1983.

Introduction

The review article used as a text for the Short Course on Infrared Laser Spectroscopy¹ was completed in January 1980 and included only a few references after that date. There has ensued three years of progress, during which spectroscopy using tunable infrared lasers has become an increasingly used tool both for basic research and for analytical and industrial applications. The present paper, which follows closely the outline of the earlier review,¹ updates the latter to early 1983.

The reader is referred to several recent review articles treating tunable infrared sources²⁻⁸ and infrared laser spectroscopy.^{3-6,9}

Generation of tunable monochromatic infrared radiation

The current status of tunable infrared sources is summarized in Table 1. It should be emphasized that demonstration of laser action in a given region does not always imply that a useful spectroscopic tool has been developed. Figure 1 shows those regions in which the results of high-resolution spectroscopic studies have actually been reported using various tunable infrared lasers, and is a more realistic guide to the spectral coverage available.

Figure 1. Regions in which high-resolution infrared spectroscopy has been performed using various tunable sources

* This work was supported by the United States Department of Energy.

Semiconductor diode lasers

Semiconductor diode lasers continue to be the most commonly used tunable infrared source, and they are now produced commercially in Europe and Japan as well as at several locations in the United States. Several detailed reviews are available.¹⁰⁻¹² Numerous papers on the fabrication and characteristics of lead-salt diodes have appeared; only some representative recent references are cited here.¹³⁻¹⁵ Recent attention has focused on achieving wide single-mode tunability, less complex multimode structure, higher-temperature operation, and improved lifetime, with particular concentration on the details of the confinement structure. Improved ohmic contacts have been designed that significantly reduce long-term degradation.¹⁶⁻¹⁸ Single modes continuously tunable over 20 cm^{-1} near 780 cm^{-1} have been obtained with distributed-feedback devices.¹⁹ Almost all SDL's are current-tuned, but pressure tuning continues to be investigated as a method of extending the tuning range.²⁰

A detailed study of SDL linewidths has been carried out,²¹ using both heterodyne techniques and a Fabry-Perot etalon. Linewidths of 2×10^{-5} to 0.02 cm^{-1} were observed for different lasers, and the width depended strongly on the junction temperature and injection current. Resolution is significantly degraded by the vibration of closed-cycle refrigerators, even when an "ultrastable" commercial laser mount was used.

Several designs for double-beam SDL spectrometers have been reported^{22,23}; features include a stable digital signal processing system²⁴ and current modulation with improved cali-

Table 1. Generation of Continuously Tunable Monochromatic Infrared Radiation

Device ^a	Spectral coverage		Highest reported resolution (cm^{-1})	Approximate power (W) ^c	
	overall (μm)	continuous (cm^{-1}) ^b		cw	peak pulsed
*Semiconductor diode lasers	0.4-34	2	2×10^{-6}	10^{-5} (0.3)	1 (10^2)
Gas lasers:					
*Waveguide CO_2 lasers	9-11 ^d	0.05	3×10^{-7}	1 (7)	10^4
Multiatmosphere lasers	9.1-12.5	50	5×10^{-3}	...	10^6 (3×10^7)
*Zeeman-tuned gas lasers	0.6-9 ^d	5	1×10^{-3}	10^{-3}	...
*Spin-flip Raman lasers	3.0-3.3	15	?	...	10^2
	5.0-6.5	50	1×10^{-6}	0.1 (3)	10^2 (10^4)
	9.0-16.8	100	3×10^{-5}	10^{-3}	10^2 (10^5)
	87-100	15	~ 6	...	10^{-4}
Other Raman scattering processes:					
Polariton lasers	16-20, 40-1000	200	0.25	...	10 (10^3)
Raman frequency shifting	0.5-18	500	<0.02	0.5	10^6 (10^9)
	39-360 ^d	5	?	...	10^5
Optical parametric oscillators	0.3-16.5		$<1 \times 10^{-3}$	10^{-3} (0.03)	10^3 (10^8)
Nonlinear optical mixing techniques:					
*Difference frequency generation	0.7-24.3	5	1×10^{-4}	10^{-6}	1 (10^4)
	52-8300	100	$<3 \times 10^{-6}$	10^{-7}	10^{-2} (0.2)
*Tunable sideband generation	3.4	$<10^{-5}$	2×10^{-10}	?	...
	9.1-11.3	0.5	1×10^{-5}	10^{-3} (0.2)	?
Four-wave parametric mixing	2-31		0.07	...	10^{-3} (10)
*Color-center lasers	0.35-4.0	0.1 ^e	9×10^{-6}	10^{-2} (3)	10^2 (2×10^4)
Miscellaneous techniques:					
Free electron lasers	f		0.5	...	10^4 (10^6)
Landau emission	62-500	50	1	10^{-8}	10^{-6}
Vibronic transition lasers	1.1-2.3		1×10^{-3}	0.1	10^2 (10^5)

^a Asterisks indicate devices that have actually been used for high-resolution spectroscopy.

^b Coverage that can be expected in a single scan, without changing optical elements or shifting modes.

^c Typical values given, with the highest that have been reported in parentheses.

^d Tunable only near discrete lines in this region.

^e Typical single-mode operation; up to 500 cm^{-1} with full computer control, or at low resolution.

^f Potentially tunable throughout the visible and infrared regions.

bration accuracy.²⁵ The combination of a diode source with an existing large high-resolution vacuum grating spectrometer has been described.²⁶ One can improve wavenumber accuracy using a feedback loop to correct accidental drift in the laser emission.²⁷ Dubs et al.²⁸ describe a method of stabilizing the output of a SDL by locking onto the side of an absorption line. Harmonic detection with SDL's has been discussed in detail.^{29,30} Baseline drift due to variations in diode output energy can be eliminated by ultra-low-frequency filtering.³¹ Diode lasers can be used in conjunction with an integrating sphere to provide tunable sources with a high dynamic range.³²

Gas lasers

High-pressure gas lasers. Modest improvements have been made in this class of lasers over the past few years. Crocker and Butcher³³ have developed a microprocessor-controlled spectrometer based on a boron nitride waveguide CO₂ laser. This operates in the 9-11 μm region with a linewidth of $5 \times 10^{-6} \text{ cm}^{-1}$ and a 0.02-cm^{-1} tuning range, and has been used for saturation spectroscopy. Dithering the resonator length of a waveguide laser to tune over two adjacent frequencies for differential absorption measurements has been demonstrated.³⁴ The highest reported resolution for a multiatmosphere CO₂ laser is now $5 \times 10^{-3} \text{ cm}^{-1}$.³⁵ Reviews on transversely-excited lasers in general³⁶ and on using isotopic species to extend the range of sealed-off CO₂ lasers³⁷ have appeared.

Zeeman-tuned gas lasers. Uehara et al.³⁸ describe a Zeeman-tuned He-Xe laser with a tuning range of $200 \text{ GHz} = 7 \text{ cm}^{-1}$ for use in Stark modulation spectroscopy; particular attention was paid to eliminating the effects of mode-hopping.

Stark tuning. Electrical fields of up to 10 kv/cm have been used to Stark tune a NH₃ laser line at 927 cm^{-1} over a range of $1 \text{ GHz} = 0.03 \text{ cm}^{-1}$.³⁹

Raman processes

There has been little new development in either spin-flip Raman⁴⁰ or polariton lasers. Advances in Raman frequency shifting have been in the direction of high-power, relatively low-resolution, pulsed sources.

Optical parametric oscillators

OPO's have still not been developed for high-resolution applications, though they have found increasing use in monitoring atmospheric constituents by lidar techniques (see under Atmospheric Studies).

Nonlinear optical mixing techniques

Difference frequency generation. Zueva et al.⁴¹ have described a novel difference-frequency spectrometer in which radiation from argon-ion and dye lasers is mixed in LiIO₃ for absorption spectroscopy between 1900 and 5000 cm^{-1} with a resolution of 0.001 cm^{-1} ; these two lasers are simultaneously used to record the coherent anti-Stokes Raman spectrum of the sample.

Tunable sideband generation. Magerl et al.⁴² describe a tunable CO₂ laser sideband spectrometer that operates 9-11 μm with continuous tuning ranges of $\pm(0.41\text{-}0.60, 0.87\text{-}1.23, \text{ and } 1.73\text{-}1.83) \text{ cm}^{-1}$ about each of ca. 80 CO₂ lines. The resolution is 10^{-5} cm^{-1} and measurement accuracy is $\pm 2 \times 10^{-4} \text{ cm}^{-1}$. Spectroscopy in the 26 to 36 cm^{-1} region has been performed by mixing tunable klystron radiation with output of a HCN laser.⁴³

Color-center lasers

Several recent reviews should be consulted.⁴⁴⁻⁴⁶ An important advance is the development of $(\text{F}_2^+)_A$ centers for lasing in the infrared out to 4 μm . An $(\text{F}_2^+)_A$ center consists of a single electron trapped by two adjacent anion vacancies (F_2^+ center) adjacent to a single substitutional impurity cation. $(\text{F}_2^+)_A$ centers are rather complex to produce and handle and are usually optically and thermally unstable; some of these problems are being overcome.⁴⁷ They are not yet available commercially. Typical characteristics are summarized in Table 2.

Table 2. $(\text{F}_2^+)_A$ color center lasers

Crystal	Tuning range (μm)	Pump	Mode	Refs.
KCl: (Li, Na)	1.67-2.46	Nd:YAG (1.3 μm)	CW	48
KCl:Li	2.00-2.50	Nd:YAG (1.3 μm)	CW	47,49
KI:Li	2.38-3.99 ^a	Er:YLF (1.73 μm)	P	50

^a Also 1.98-2.56 μm from coexisting F_2^+ centers.

The problem of adjusting multiple dispersive elements to continuously tune a CCL requires computer control. Curl et al.^{51,52} have described the conversion of a commercial Burleigh CCL into a minicom-

puter-controlled high-resolution spectrometer for the 2.3-3.3 μm region with a resolution of $3 \times 10^{-5} \text{ cm}^{-1}$, continuous scan capability of 10 cm^{-1} , and automatic calibration to within 0.003 cm^{-1} . A less expensive microcomputer-controlled spectrometer with 100-cm^{-1} scan capability and a resolution of 0.01 cm^{-1} has been built.⁵³ The use of color-center lasers with magnetic rotation (Faraday) spectroscopy has been demonstrated for high-sensitivity detection of paramagnetic species.⁵⁴⁻⁵⁶

Calibration methods

Absolute frequency calibration

Some recently reported gas spectra suitable for frequency calibration are summarized in Table 3. The use of isotopic CO_2 lasers as secondary frequency standards has been discussed by Freed.⁵⁷

Table 3. Some recently-published infrared frequency standards

Spectral region (cm^{-1})	Molecule and band	No. of lines	Method ^a	Refs.
372-432	CS_2 , ν_2 (& isotopes, hot bands)	665	I	58
501-714	H_2O , rotation	65	I	59
622-722	CO_2 , ν_2	95	I	59
812-1117	CO_2 laser (& isotopes)	960	H,C	60
815-893	OCS , ν_1	193	H	61
825-886	OCS , ν_1 (& isotopes, hot bands)	464	G	62
826-985	OCS , ν_1	144	I	59
1066-2297	H_2O , ν_2 (& isotopes)	2019	I	63
1116-1343	N_2O , ν_1 (& isotopes, hot bands)	1457	I,C	64
1655-1738	OCS , $2\nu_1$	944	G	62
1661-1739	OCS , $2\nu_1$	191	H	61
3234-3379	HCN , ν_3	49	W	65

^a C = calculated from selected molecular constants; G = grating spectra; H = heterodyne frequency measurements; I = high-resolution interferometer; W = wavemeter.

Direct measurement of tunable laser radiation with wavelength meters has been reviewed with emphasis on measuring dye laser output.⁶⁶ Nagai et al.⁶⁷ have described a wavelength meter specifically designed for use with diode lasers. This is based on a Michelson interferometer, counting fringes relative to the 6328-Å He-Ne frequency, and achieves an accuracy of about 10^{-4} cm^{-1} at $10 \mu\text{m}$.

Calibration of laser tuning rate

The technique of internal calibration using the Doppler width of an absorption line has been improved by least-squares fitting a Voigt profile to the observed line contour.⁶⁸

Etalon calibration is still by far the most frequently used technique. Detailed reviews of the refractive indices of air⁶⁹ and germanium⁷⁰ have recently appeared. Because the refractive index may vary among different samples of germanium, it is preferable to calibrate germanium etalons at the wavelength of interest against known calibration lines.⁷¹ The shift of etalon fringes with temperature has been confirmed by heterodyne measurements.^{72,73}

Heterodyne measurements of line positions have been reported more frequently in the last few years. A SDL spectrometer with heterodyne calibration, in use at NBS, has been described by Wells et al.⁷⁴ Typical HgCdTe photomixers now in use are usable to about 9 GHz (0.30 cm^{-1}) from the reference line. By non-linear mixing with harmonics of a microwave frequency, heterodyne calibration has been achieved over a 1.7-cm^{-1} range.⁷⁵

Special experimental techniques

Laser modulation

First and second derivative detection reduces noise and increases sensitivity in analytical applications of diode lasers.^{29,30,76,77} It has been demonstrated that true lineshapes can be recovered from experimental $2f$ signals.^{29,30} A diode laser spectrometer has been specifically designed to allow derivative spectroscopy with high calibration accuracy using etalons.²⁵ Amplitude and frequency modulation using a color-center laser have been compared.⁶⁵

Optoacoustic detection

See the review by Ferguson.⁷⁸ Design optimization of optoacoustic cells for high-resolution infrared spectroscopy indicated that a small-volume (0.4 cc) non-resonant cell was more sensitive than a resonant cell in the pressure range of interest (<50 torr).⁷⁹ Such a cell has been used with a color-center laser for saturation spectroscopy of HCN.⁸⁰

Heterodyne detection

Recent discussions of laser heterodyne spectroscopy consider the use of tunable infrared sources as local oscillators.^{81,82} A high-resolution IR heterodyne spectrometer designed for both laboratory and field use and using a diode laser as the LO has been described in some detail.⁸³ Katzberg et al.⁸⁴ discuss the signal-to-noise performance of SDL heterodyne spectrometers.

Intraresonator absorption

A theoretical analysis shows that enhancement in detection sensitivity over single-pass absorption spectroscopy of the order of 10^4 is possible for a single-mode CW laser when the absorbing medium is in the laser cavity.⁸⁵

Linewidth reduction in gases

Papers in which nozzle expansion has been used to reduce linewidth can be located by reference to Table 4. In a study of NH_3 , a non-Boltzmann rotational energy distribution was observed below 100 K.⁸⁶ Rotational temperatures in helium expansions were reported to be 40 K for hexafluoride molecules⁸⁷ and 10 K for CF_2Cl_2 .⁸⁸

Apparatus for the bolometric detection of the energy deposited in a molecular beam by a color-center laser has been described^{88,89} and used to study the formation and predissociation of $(\text{CO}_2)_n$ clusters⁸⁸ and the dipole moment of HF and HCN.⁸⁹ Boughton et al.⁹⁰ have described a similar apparatus employing two crossed supersonic beams, which achieved a linewidth of 8 MHz for HF. Studies of translational relaxation downstream from the nozzle orifice and collisional processes between atoms and state-selected molecules were carried out.⁹⁰ Room-temperature pyroelectric detectors can be used instead of more complex and expensive helium-cooled bolometers in this type of study, with only a small loss of sensitivity.⁹¹

A different technique for reducing the Doppler linewidth as observed in high-resolution, low-noise spectra is numerical deconvolution, assuming a Gaussian line profile.⁹² This can enhance the resolution by factors of 3 to 4, and has been applied to spectra obtained using diode lasers⁹³ and difference-frequency spectrometers.^{94,95}

Matrix isolation

The linewidths and lineshapes of CO in a N_2 matrix have been studied in detail with a diode laser⁹⁶; linewidths as narrow as 0.013 cm^{-1} were observed in dilute samples.

Hole-burning experiments in matrices allow one to separate the homogeneous linewidth (determined by radiative decay, excited-state relaxation, and dephasing) from the inhomogeneous linewidth caused by the differing matrix surroundings of each molecule. A detailed series of experiments on $t\text{-CH}_2\text{F}\cdot\text{CH}_2\text{F}$ using diode lasers established the two widths to be 0.002 and 0.25 cm^{-1} , respectively, and polarization experiments helped to elucidate the rotational behavior of the molecules.^{28,97} Diode-laser spectroscopy of matrix-isolated ReO_4^- ions exhibit hole widths of as little as $7 \times 10^{-4} \text{ cm}^{-1}$ in a transition whose inhomogeneously-broadened width may reach 1 cm^{-1} .⁹⁸

Linear absorption spectroscopy

Work of the past few years is summarized in Table 4, which updates Table 7 of Ref. 1. Results on line contours and widths, intensities, rotational fine structure, and band analyses can be located by referring to the "Results" column of Table 4.

Perhaps the most significant recent development has been in intensity work, where critical treatments of tunable laser data have resolved some of the previously noted disagreements among various measurements. A systematic assessment of errors in diode intensity measurements has revealed that additional off-axis mode structure may be present and can influence the results.⁷³ Other papers that consider intensity measurements in some detail are Refs. 107,111,139,141,167,169.

Table 4. Linear absorption spectra obtained using tunable infrared laser sources

Molecule	Band ^a	Laser ^b	Freq. range (cm ⁻¹) ^c	Calibration		Results ^f	Special techniques used ^g	References
				Absolute freq. ^d	Tuning rate ^e			
<u>Atoms and monatomic ions</u>								
Ar ⁺	*2p _{1/2} -2p _{3/2}	SDL	~1431.6	A	E	F(n), I		99
Br	*2p _{1/2} -2p _{3/2}	CCL	~3685	A	E	F(n), I	D, MR	100
Cl	*2p _{1/2} -2p _{3/2}	SDL	~882	M	E	F(n), I	D	101, 101a
F	2p _{1/2} -2p _{3/2}	SDL	403.8-404.4	A	E	F(n)		102, 103
He	4 ³ p-4 ³ s	SDL	918.9-919.1	L	E	A, B, F	D	104
	3 ¹ p-3 ¹ s, 6F-5D	SDL	1344.1-1345.3	A, W	E	A, B, F	D	104
	(n=6)-(n=4)	CCL	3719-3829	A		A	G	104a
<u>Diatomic molecules and radicals</u>								
AlF	1-0 (H)	SDL	827-849	A	E	A, B		105
BCl	*1-0 (H)	SDL	828-871	A	E	A, B		106
l ¹ BF	1-0, P(11)	SDL	~1343.5	A	A	S		107
CCl	*1-0 (H)	SDL	864-880	A	E	A, B, F(Δ), I	D, Z	108
CF	1-0	SDL	(1250-1332)	A	E	A, B, F(Δ)	Z	109
CN	1-0	SDL	1994-2131	A	E	F(sp)	C	110
CO	1-0	SDL	2028-2231		E	C, S, W(p)	C	111, 112
	1-0	SDL	~2140	A	E	C, W	M	96
	1-0	SDL	(2107-2162)		E	W(p)	C, F	113
C ¹⁸ O	*1-0	SDL	829-882	A	E	A, B	D	114
HF	1-0, P	DFS	(3540, 3694)		I	C, W(n)		115
KF	2-0 (H)	SDL	832-855	A	E	A, B		105
NF	1-0	SDL	(1114-1207)	A	E	A, B, F(n)	F	116
NP	1-0	DFS	2949-3294	A	E	A, B	Z	117
NO	rotation	IMM	28-36	F		A, B		43
	*1-0	SFR	~1870-1900	T	C	W(p)	Z	118
	1-0, R	SDL	1906-1910		E	C, S, W		119
	1-0, R	SDL	(1887-1933)		E	W(p)		120
	2-0	CCL	~3700			F(Δ)	MR, Z	64
NS	1-0	SDL	(1185-1239)	A	E	A, B, F(Δ)	D	121
OH	1-0	CCL	3663-3785			A, B, F(Δ)	MR	54, 55
PN	1-0 (H)	SDL	(1217-1319)	A	E	A, B		122
SF	1-0 (H)	SDL	821-839	A	E	A, B	D, Z	123
SiO	*1-0 (H)	SDL	(1212-1294)	A	E	B		124
<u>Triatomic molecules, radicals, and ions</u>								
BO ₂	ν ₃ (H)	SDL	1245-1345	A, W	E	A, B	D, Z	125
CF ₂	ν ₁	SDL	1242-1275	A	E	A, B, F(a)		101a, 126
C ₂ H	A ² Σ ⁺ -X ² Π	CCL	~3772			A, B	MR	56
CO ₂	ν ₂ , R (H)	SDL	(683-709)			S, W(p)		127
¹³ CO ₂	*ν ₂ , Q	SDL	538-641	A	E	A, B		128
ClBO	*ν ₃	SDL	654-695	A	E	A, B, I	D	129
ClO ₂	ν ₁	SDL	(957-1320)	L	E	A, B, F(sp)	D, Z	130
FCO	ν ₁	SDL	1852-1876	A, W	E	A, b	D, Z	131
	ν ₂	SDL	1013-1047	A	E	A, B	D, Z	131
F ¹³ CO	ν ₁	SDL	1817-1836	A, W	E	A, B	Z	131

Molecule	Band ^a	Laser ^b	Freq. range (cm ⁻¹) ^c	Calibration		Results ^f	Special techniques used ^g	References
				Absolute freq. ^d	Tuning rate ^e			
H ₃ ⁺	v ₂	DFS	2457-2919	A		A, B	D	132
HCN	v ₃	CCL	3234-3379	W		A, B, W(p)	D, O	65
HO ₂	v ₂	SDL	1371-1416	W, A	E	A, B	D, Z	133
H ₂ O	v ₂	SDL	(1652-1700)		E	S, W(p)	D	73
HDO	v ₁	ZTG	2848-2854	I	C	A, F(k)	S	38
H ₂ S	v ₂	SDL	(1082-1258)	A	E	A, B		134
HOCl	v ₂	SDL	1266-1272	A	E	A, B		135
NF ₂	v ₁	SDL	~1100		E	A, B, F(sp)	D	101a, 136
NH ₂	v ₁ , v ₃	DFS	3126-3399	A		A, B	D, Z	137
NO ₂	v ₂	SDL	(687-720, 825-863)	A	E	A, B, S, W(p)		138, 139
	v ₃ (H)	SDL	(1567-1612)		E	F(sp), S, W(p)		26
N ₂ O	v ₁ +v ₂ -v ₂ , R(8)	SDL	~1298.9		E	C, T(l), S, W(p)	D	140
O ₃	v ₃	SDL	(1069-1104)		E	W(p)		120
OCS	v ₁ (H)	SDL	(824-866)		E	S, W(p)		141
	*v ₁	SDL	(834-887)	L	H	A, B	D	74
	*2v ₁ (H)	SDL	(1690-1723)	A	E	A, B		62
	2v ₂ (H)	SDL	(1037-1091)	L	H	A, B		142
SO ₂	v ₁	SDL	(1068-1086)	L	E, H	A, B		143
	v ₁ +v ₃	DFS	2497-2500	A	I	S		144
<u>4-atomic molecules and radicals</u>								
CF ₃	v ₃	SDL	(1233-1276)			A, B	Z	145
CH ₃	v ₂ (H)	SDL	~606, 681, 730	A, W	E	A, B, F(sp), S	D, Z	146, 147
	v ₃	DFS	3077-3248	A	E	A, B	D, Z	148
C ₂ H ₂	*v ₃ (H)	SDL	(717-731)	A	E	A, B		149
HNCO	v ₂	SDL	~2250-2270	A	E	A, B	D, S	150
HN ₃	v ₃	SDL	1247-1283	A	E	A, B	D, S	151
H ₂ CO	*v ₂ , Q	SDL	(1706-1755)	A	E	A, B		152
NH ₃	v ₂	SDL	(1177-1213)		E	A, F		153
	v ₂	SDL	931-954	A	E	A, F		154
	v ₂	SDL	1033.0-1035.5			B	Z	155
	v ₂ , aP(4,2)	SDL	852.7	A	D	W(p)		68
	*v ₂ (H)	SDL	(924-1085)	L	H	A		72, 156
ND ₃	*v ₂	SDL	(819-859)	A	E	A, B		157
<u>5-atomic molecules</u>								
CF ₂ Cl ₂	v ₈ , Q	SDL	921.2-922.1	A		A, B, S	W	158
CF ₄	v ₃ , Q	SDL	1282.7-1283.5	A	E	A, B, F(t)	S	159
	v ₄ , P(16,17)	SDL	622.5-623.1	M	E	F(t)		160
	v ₂ +v ₄ , R(29)	CTG	1073.3	L	E	C, W(p)		161
	(v ₂ +v ₄)-v ₂	SDL	(1064-1074)	A	E	A, B, F(t)		162
	2v ₁ +v ₄ , Q	DFS	2444.2-2445.6	A	E	A, B, F(t)		163
CH ₄	v ₂ , R	SDL	1586.9-1589.8			S, W(p)		164
	v ₄	SDL	1243-1374		E	S		165
	v ₄	SDL	~1295-1310		E	F(t)		166
	v ₄	SDL	1170-1317			S		167
CH ₃ Br	*v ₆	SDL	927.0-935.3	A	E	A, B		168

Molecule	Band ^a	Laser ^b	Freq. range (cm ⁻¹) ^c	Calibration		Results ^f	Special techniques used ^g	References
				Absolute freq. ^d	Tuning rate ^e			
CHF ₃	ν ₄	SDL	~1376.9		A	S		169
CHF ₃	ν ₂ , Q	SDL	(1094-1112)	A	E	A,B		170
	ν ₅ , Q	SDL	(971-978)	A	E	A,B		170
CH ₃ F	ν ₃	SDL, HPG	1044.8-1048.6	L	H	A,B	S	171
	ν ₃	IMM	(1039-1076)	L	F	A,B,F(s)	S	172
CH ₃ I	ν ₆	SDL	(824-863)	A	E	A,B,F(n)		173
¹³ CH ₃ I	ν ₆	SDL	(820-867)	A	E	A,B		174
CH ₂ DI	ν ₆ ''	SDL	(820-859)	A	E	A,B,F(n)		174
GeH ₄	ν ₃	DFS	2109-2112	W		A,B,F(t)		41
	*ν ₄	SDL	818-842	A	E	A,B,F(t), I		175
HCCCN	ν ₃ (H)	SDL	2068-2095	A	E	A,B,F(l)	D	176, 177
HCC ¹³ CN	ν ₂ (H)	SDL	2224-2244	A	E	A,B,F(l)		178
HNO ₃	ν ₂	SDL	1690-1727	A	E	A,B		179
OsO ₄	ν ₃	SDL	970.9-972.1	A	E	A,B,F(t)		180
SiF ₄	ν ₃	SDL, CTG	1023-1038	A, L	E, H	A,B,F(t), S		181, 182
	ν ₄	SDL	379-405	A	E	A,B,F(t)		183
	3ν ₃	DFS	3061-3073	A	I	A,B,F(t), S		184
SiH ₄	ν ₃	DFS	2187-2190	W		A,B,F(t)		41
<u>6-atomic molecules</u>								
C ₂ H ₄	ν ₇ +ν ₈ , ν ₄ +ν ₈ , ν ₈ +ν ₁₀	SFR	1830-1905	A	C	A,B		185
C ₂ D ₄	ν ₄	SDL	2174-2227	A	E	A,B		186
CHF-CHF	ν ₄ , ν ₉	SDL	(926-981)	L	H	A,B		187
CD ₃ OH	ν(C-O)	SDL	973-996	A	E	A,B	F, S	188, 189
<u>7-atomic molecules</u>								
CH ₃ CCH	ν ₁	CCL	3305-3370	A	E	A,B	O	53
SF ₆	ν ₃	SDL	935.8-938.8	A	E	W	M	190
	ν ₅ +ν ₆	SDL	(870-890)	A	E	A,B,F(o)		191
	2ν ₁ +ν ₇	DFS	2483-2492	A	J	A,B,F(o), S		192
	3ν ₃	DFS	2819-2850	A	I	A,B,F(o), S		193
³⁴ SF ₆	ν ₃	SDL	929.2-931.9	A	E	A,B,F(o)	W	194
UF ₆	*ν ₃ , Q	SDL	~628	A	E	I	F, W	87
WF ₆	*ν ₃ , Q	SDL	~714	A	E	I	F, W	87
<u>8-atomic molecules</u>								
C ₂ H ₆	ν ₅ , ν ₇ , ν ₈ +ν ₁₁	DFS	2862-3054	A	I	A,B,F(tor)		195
	ν ₉	SDL	785-845	A	E	A,B,F(tor)	DC, F	93
	ν ₉ , RQ ₀	SDL	822.0-822.4	A	E	A,B,F(l, tor)		196
CH ₃ CH ₂ Cl	ν ₉ , Q	SDL	(973.0-976.2)	A	E	A,B		197
<u>9-atomic molecule</u>								
C ₃ H ₆ (cyclo- propane)	ν ₁₀ +ν ₁₁	SDL	1880-1920	A	E	A,B	F	198
<u>12-atomic molecule</u>								
C ₆ H ₆	ν ₁₂	DFS	3020-3125	A	I	A,B	DC	95

^a An asterisk indicates that the studied band includes isotopic species, where these are not listed separately. (H) indicates that hot bands were recorded in addition to the listed band.

^b CCL = color-center laser; CTG = cavity-tuned gas laser; DFS = difference-frequency spectrometer; HPG = high-pressure gas laser (i.e., CO₂ waveguide laser); IMM = infrared-microwave mixing (tunable sideband generation); SDL = semiconductor diode laser; SFR = spin-flip Raman laser; ZTG = Zeeman-tuned gas laser.

^c Parentheses indicate incomplete coverage.

^d A = absorption lines of gases; F = direct frequency measurement; L = gas laser frequencies; M = monochromator; T = laser tuning curve; W = wavelength meter.

^e A = absorption lines of gases; C = calculated from laser tuning parameters; D = Doppler width of known lines; E = etalon; F = direct frequency measurement; H = heterodyne techniques; I = interferometer.

^f A = assignments; B = band analysis and molecular constants; C = line contour and shape studies; F = fine structure, including (a) = asymmetry doubling, (k) = K-type doubling, (l) = l-doubling, (Λ) = Λ-doubling, (n) = nuclear hyperfine structure, (o,t) = octahedral and tetrahedral splitting in spherical tops, (s) = Stark splitting, (sp) = spin-rotation interaction, (tor) = torsional splitting; I = isotope shifts; S = line strengths, absorption coefficients, and intensity measurements; W = linewidths, including (n) = collisional narrowing, (p) = pressure broadening coefficients.

^g C = computer averaging to improve S/N ratio; D = derivative spectra; DC = deconvolution; F = fast-scan techniques; G = optogalvanic spectroscopy; M = matrix isolation; MR = magnetic rotation (Faraday) spectroscopy; O = optoacoustic detection; S = Stark modulation; W = linewidth reduction by beam or nozzle techniques; Z = Zeeman spectra.

Nonlinear spectroscopy

CO₂ waveguide lasers have been used to obtain saturation spectra in the 9-11 μm region for HCOOH,³³ CH₃Br,¹⁹⁹ CH₃I,³³ and C₂H₄.²⁰⁰ Spectra of CH₃I have also been reported using optoacoustic detection.²⁰¹ A widely-tunable color-center laser has been used for Doppler-free optoacoustic saturation spectra of HCN near 3.0 μm.⁸⁰ Doppler-free two-photon spectroscopy of the (inactive) 2ν₃ band of SF₆ has been reported using a waveguide CO₂ laser,²⁰² and Doppler-free two-photon absorptions in NH₃ were observed using a CO₂ pump with a diode laser probe.²⁰³

Double-resonance spectroscopy

There has been an increasing amount of work using tunable infrared lasers in double-resonance spectroscopy. Takami^{159,204-206} has described infrared-radiofrequency experiments in which diode lasers were used as tunable pump sources, with radiofrequency/microwave detection of pure rotational transitions; molecules studied included CF₄,^{204,206} ¹³CF₄,²⁰⁵ and SiH₄.²⁰³

Double-resonance spectroscopy of the 2ν₃ + ν₃ band of SF₆, using a CO₂ pump laser with a tunable diode probe, have been described.^{207,208} Information on the parameters that govern the multiphoton absorption ladder in SF₆ have been obtained from this work,²⁰⁷ and collisional relaxation has been studied.²⁰⁸ An analysis of line shapes in SF₆ double-resonance experiments was reported.²⁰⁹

Doppler-free double-resonance spectroscopy of NH₃ has been carried out with a CO₂ pump and a diode probe,²¹⁰ and of several molecules (CH₃F, NH₃, PH₃, GeH₄, SiH₄, CH₃D) using a CO₂ laser with radiofrequency modulation sidebands.²¹¹

Applications

Laboratory analytical techniques

Some recent general applications of tunable infrared lasers to problems in physics and chemistry are summarized in Table 5. Laser absorption methods for characterizing high-temperature gases have been reviewed.²²⁵ A measurement of the absorption coefficient of liquid water with an accuracy of 0.01 absorbance unit (AU) throughout the range 0 to 9 AU has been described.²²⁶ The use of high-resolution spectroscopy for elucidating multiphoton absorption processes was reviewed.²²⁷

Atmospheric studies and pollution monitoring

Table 6 summarizes some atmospheric trace gases that have been analyzed using tunable sources. The application of diode lasers to atmospheric monitoring of trace gases has been considered in several laboratories,^{77,229,230,232-234} with particular attention paid to detection sensitivity,^{77,231} calibration,²²⁹ and special techniques such as sweep integration.²³⁴ Applications have ranged from laboratory analyses such as gases in cigarette smoke^{232,235} to tropospheric N₂O measurements.²³⁰ Patel has reviewed such applications of spin-flip Raman lasers.⁴⁰ Optical parametric oscillators with linewidths of about 0.1 cm⁻¹ have been used as continuously-tunable laser sources for monitoring temperature and humidity of the atmosphere from H₂O transitions.^{236,237}

Table 5. Some applications of infrared laser spectroscopy

Topic	Laser ^a	Region (μm)	References
<u>Flame and combustion measurements</u>			
CO concentrations and halfwidths in flames	SDL	4.5-4.7	212-215
<u>Isotopic analysis</u>			
CO ₂ isotopic ratios	SDL	10.0	76
¹⁴ CO ₂ anal.; radiocarbon dating	SDL	4.5	216
Os isotopic anal. in OsO ₄	CTG	10.2-10.5	217
<u>Chemical reactions and kinetics</u>			
N ₂ F ₄ ⇌ 2NF ₂ equilibrium	SDL	9.1	218
HO ₂ radical reactions	SDL	8.9	219
CH ₃ radical reactions	SDL	16.4	220
UF ₆ ⇌ UF ₅ + F kinetics	SDL	17.0	221
<u>Solid-state physics</u>			
Refractive index of Ge	SDL	~8,10	71
Oxygen concentration in Si	SDL	9.0	222
<u>Miscellaneous</u>			
Gain in optically pumped NH ₃	SDL	12.1	223
Helical pitch in a chiral smectic liquid crystal	CCL	2.2-2.9	224

^a CCL = color-center laser; CTG = cavity-tuned gas laser; SDL = semiconductor diode laser

Table 6. Analysis of atmospheric trace gases

Gas	Laser ^a	Region (μm)	Special techniques ^b	Detection limit (ppm)	Refs.
CO	SDL	4.8	O	50	228
H ₂ O	SDL	6.0	D	0.2	229
N ₂ O	SDL	8.7	D	0.02	77,230
NO ₂	SDL	6.2	D	0.0001	231
HCN	SDL	13.0	D		232
CH ₄	SDL	7.9	D	0.3	233
C ₂ H ₄	HPG	10.5-10.7	DA	1.2	34

^a HPG = high-pressure gas laser (CO₂ waveguide); SDL = semiconductor diode laser.

^b D = derivative spectra; DA = differential absorption; O = optoacoustic detection.

Laser development

The $\nu_2 + \nu_4 - \nu_2$ hot band of CF₄ has been completely analyzed, allowing the prediction of CF₄ laser frequencies with an accuracy of ca. 0.005 cm⁻¹.¹⁶² Saturation spectroscopy of the ν_6/ν_8 interacting bands of HCOOH using a CO₂ waveguide laser, has led to a reassignment of the formic acid laser transitions in the far infrared.²³⁸

Acknowledgement

The free radical entries in Table 4 are based in part on a bibliography compiled by Stephen L. Baughcum.

References

1. R. S. McDowell, Vibrational Spectra and Structure, J. R. Durig, ed. (Elsevier, Amsterdam, 1981) 10, 1-151.
2. H. M. Preier, SPIE Proc. 197, 311 (1979).
3. W. Demtröder, in Quantum Dynamics of Molecules, R. G. Woolley, ed. (Plenum Press, New York, 1979), p. 377.
4. H. R. Schlossberg and P. L. Kelley, in Spectrometric Techniques, G. A. Vanasse, ed. (Academic Press, New York, 1981), Vol. 2, p. 161.
5. W. Demtröder, Laser Spectroscopy: Basic Concepts and Instrumentation (Springer-Verlag, 1982).
6. R. S. Eng and R. T. Ku, Spectrosc. Lett. 15, 803 (1982).

7. B. D. Guenther and R. G. Fuser, *IEEE J. Quantum Electron.* QE-18, 1179 (1982).
8. A. S. Pine, *Phil. Trans. Roy. Soc. Lon.* A307, 481 (1982).
9. W. Krieger, *Acta Phys. Polon.* A61, 571 (1982).
10. H. Kressel, in *Quantum Electronics*, C. L. Tang, ed. (Methods of Experimental Physics, Vol. 15, Part A; Academic Press, New York, 1979), p. 209.
11. R. S. Eng, J. F. Butler, and K. J. Linden, *Opt. Eng.* 19, 945 (1980).
12. J. F. Butler, in *Applied Optics and Optical Engineering*, R. Kingslake and B. J. Thompson, eds. (Academic Press, New York, 1980), Vol. 6, p. 53.
13. F. Bryant, M. Ekin-Uddin, J. Reed, and E. L. Thomas, *Infrared Phys.* 22, 97 (1982).
14. J. P. Moy and J.-Ph. Reboul, *Infrared Phys.* 22, 163 (1982).
15. Y. Horikoshi, M. Kawashima, and H. Saito, *Jpn. J. Appl. Phys.* 21, 77 (1982).
16. W. Lo, *Jpn. J. Appl. Phys.* 18, Suppl. 1, 367 (1979).
17. W. Lo and F. E. Gifford, *J. Electrochem. Soc.* 127, 1372 (1980).
18. W. Lo, *J. Appl. Phys.* 52, 900 (1981).
19. H.-H. Hsieh and C. G. Fonstad, *IEEE J. Quantum Electron.* QE-16, 1039 (1980).
20. V. B. Anzin, M. V. Glushkov, Yu. V. Kosichkin, A. I. Nadezhdinskii, A. N. Perov, and A. M. Shirokov, *Appl. Phys.* 22, 241 (1980).
21. J. Reid, D. T. Cassidy, and R. T. Menzies, *Appl. Opt.* 21, 3961 (1982).
22. D. E. Jennings, *Appl. Opt.* 19, 2695 (1980).
23. J. N.-P. Sun, M. L. Olson, D. L. Griebel, and P. R. Griffiths, *Appl. Opt.* 19, 2762 (1980).
24. R. S. Eng, C. Simpson, A. W. Mantz, and C. G. Venkatesh, *Appl. Opt.* 19, 1973 (1980).
25. G. Tränkle and W. Hüttner, *Appl. Opt.* 21, 4151 (1982).
26. V. Malathy Devi, B. Fridovich, G. D. Jones, D. G. S. Snyder, P. P. Das, J.-M. Flaud, C. Camy-Peyret, and K. Narahari Rao, *J. Mol. Spectrosc.* 93, 179 (1982).
27. Yu. V. Kosichkin, A. I. Kuznetsov, A. I. Nadezhdinskii, A. N. Perov, and E. V. Stepanov, *Sov. J. Quantum Electron.* 12, 518 (1982).
28. M. Dubs, L. Ermanni, and Hs. H. Günthard, *J. Mol. Spectrosc.* 91, 458 (1982).
29. J. Reid and D. Lzbie, *Appl. Phys.* B26, 203 (1981).
30. D. T. Cassidy and J. Reid, *Appl. Phys.* B29, 279 (1982).
31. A. K. Atakan, W. E. Blass, and D. E. Jennings, *Appl. Spectrosc.* 34, 369 (1980).
32. C. G. Venkatesh, R. S. Eng, and A. W. Mantz, *Appl. Opt.* 19, 1704 (1980).
33. D. Crocker and R. J. Butcher, *Infrared Phys.* 21, 85 (1981).
34. M. Khelkhal, F. Herlemont, M. Lyszyk, and J. Lemaire, *Appl. Phys.* B29, 227 (1982).
35. S. V. Efimovskii and A. K. Zhigalkin, *Sov. J. Quantum Electron.* 12, 102 (1982).
36. P. W. Smith, O. R. Wood II, P. J. Maloney, and C. R. Adams, *IEEE J. Quantum Electron.* QE-17, 1166 (1981).
37. C. Freed, *IEEE J. Quantum Electron.* QE-18, 1220 (1982).
38. K. Uehara, K. Takagi, and T. Kasuya, *Appl. Phys.* 24, 187 (1981).
39. P. Pinson, G. Girard, and M. Michon, *Appl. Phys.* B28, 55 (1982).
40. C. K. N. Patel, *Phil. Trans. Roy. Soc. Lon.* A293, 257 (1979).
41. G. Ya. Zueva, D. N. Kozlov, P. V. Nickles, A. M. Prokhorov, V. V. Smirnov, and S. M. Tchuksin, *Opt. Comm.* 35, 218 (1980).
42. G. Magerl, W. Schupita, and E. Bonek, *IEEE J. Quantum Electron.* QE-18, 1214 (1982).
43. F. C. van den Heuvel, W. L. Meerts, and A. Dymanus, *J. Mol. Spectrosc.* 84, 162 (1980).
44. Yu. L. Gusev, S. I. Marennikov, and V. P. Chebotaev, *Izvest. Akad. Nauk SSSR* 44, 2018 (1980).
45. V. A. Arkhangel'skaya and P. P. Feofilov, *Sov. J. Quantum Electron.* 10, 657 (1980).
46. W. Gellermann, K. P. Koch, and F. Luty, *Laser Focus* 18(4), 71 (April 1982).
47. I. Schneider and C. L. Marquardt, *Opt. Lett.* 5, 214 (1980).
48. I. Schneider and S. C. Moss, *Opt. Lett.* 8, 7 (1983).
49. C. R. Pollock and D. A. Jennings, *Appl. Phys.* B28, 308 (1982).
50. I. Schneider, *Opt. Lett.* 7, 271 (1982).
51. J. V. V. Kasper, C. R. Pollock, R. F. Curl Jr., and F. K. Tittel, *Appl. Opt.* 21, 236 (1982).
52. G. Litfin, C. R. Pollock, J. V. V. Kasper, R. F. Curl Jr., and F. K. Tittel, *IEEE J. Quantum Electron.* QE-16, 1154 (1980).
53. E. Kyrö, S. G. Lieb, and J. W. Bevan, *Rev. Sci. Instrum.* 53, 1550 (1982).
54. G. Litfin, C. R. Pollock, R. F. Curl Jr., and F. K. Tittel, *J. Chem. Phys.* 72, 6602 (1980).
55. J. Pfeiffer, D. Kirsten, P. Kalkert, and W. Urban, *Appl. Phys.* B26, 173 (1981).
56. P. G. Carrick, J. Pfeiffer, R. F. Curl Jr., E. Koester, F. K. Tittel, and J. V. V. Kasper, *J. Chem. Phys.* 76, 3336 (1982).
57. C. Freed, *IEEE J. Quantum Electron.* QE-18, 1220 (1982).
58. K. Jolma and J. Kauppinen, *J. Mol. Spectrosc.* 82, 214 (1980).
59. J. Kauppinen, K. Jolma, and V.-M. Horneman, *Appl. Opt.* 21, 3332 (1982).
60. C. Freed, L. C. Bradley, and R. G. O'Donnell, *IEEE J. Quantum Electron.* QE-16, 1195 (1980).
61. J. S. Wells, F. R. Petersen, A. G. Maki, and D. J. Suple, *Appl. Opt.* 20, 1676, 2874 (1981).
62. A. G. Maki, W. B. Olson, and R. L. Sams, *J. Mol. Spectrosc.* 81, 122 (1980).
63. G. Guelachvili, *J. Opt. Soc. Am.* 73, 137 (1983).

64. G. Guelachvili, *Can. J. Phys.* **60**, 1334 (1982).
65. K. R. German and W. S. Gornall, *J. Opt. Soc. Am.* **71**, 1432 (1981).
66. J. J. Snyder, *Laser Focus* **18**(5), 55 (May 1982).
67. K. Nagai, K. Kawaguchi, C. Yamada, K. Hayakawa, Y. Takagi, and E. Hirota, *J. Mol. Spectrosc.* **84**, 197 (1980).
68. T.-Y. Chang, R. N. Morris, and F. S. Yeung, *Appl. Spectrosc.* **35**, 587 (1981).
69. F. E. Jones, *J. Res. Natl. Bur. Standards* **86**, 27 (1981).
70. H. H. Li, *J. Phys. Chem. Ref. Data* **9**, 561 (1980).
71. D. E. Jennings and J. P. Sattler, *Appl. Opt.* **21**, 3236 (1982).
72. J. P. Sattler, L. S. Miller, and T. L. Worcnesky, *J. Mol. Spectrosc.* **88**, 347 (1981).
73. J. A. Mucha, *Appl. Spectrosc.* **36**, 141 (1982).
74. J. S. Wells, F. R. Petersen, A. G. Maki, & D. J. Sucke, *J. Mol. Spect.* **89**, 421 (1981).
75. M. Lyszyk, J. C. Depannemaeker, J. G. Bantegnie, F. Herlemont, J. Lemaire, and Y. Piant, *Opt. Comm.* **37**, 53 (1981).
76. G. J. Kemeny, R. S. Eng, and A. W. Mantz, *Acta Phys. Acad. Sci. Hungary* **48**, 93 (1980).
77. D. T. Cassidy and J. Reid, *Appl. Opt.* **21**, 1185 (1982).
78. A. I. Ferguson, *Phil. Trans. Roy. Soc. Lon.* **A307**, 645 (1982).
79. H. G. Kraft and J. W. Bevan, *Infrared Phys.* **21**, 337 (1981).
80. J. N. Dahiya, K. Iqbal, H. G. Kraft, W. C. Eue, & J. W. Bevan, *Infrared Phys.* **22**, 77 (1982).
81. G. Wijntjes, *SPIE Proc.* **191**, 33 (1979).
82. J. A. R. Griffith, *Phil. Trans. Roy. Soc. Lon.* **A307**, 563 (1982).
83. D. Glenar, T. Kostjuk, D. E. Jennings, D. Buhl, & M. J. Mumma, *Appl. Opt.* **21**, 253 (1982).
84. S. J. Katzberg, H. R. Kowitz, and C. W. Rowland, *Appl. Phys. Lett.* **39**, 688 (1981).
85. H. J. Kimble, *IEEE J. Quantum Electron.* **QE-16**, 455 (1980).
86. G. Baldacchini, S. Marchetti, and V. Montelatici, *Chem. Phys. Lett.* **91**, 423 (1982).
87. G. S. Baronov, A. D. Britov, S. M. Karavaev, A. I. Karchevskii, S. Yu. Kulikov, A. V. Merzlyakov, S. D. Sivachenko, and Yu. I. Shcherbina, *Sov. J. Quantum Elect.* **11**, 947 (1981).
88. T. E. Gough, R. E. Miller, and G. Scoles, *J. Phys. Chem.* **85**, 4041 (1981).
89. T. E. Gough, R. E. Miller, and G. Scoles, *Chem. Soc. Lon. Faraday Disc.* **71**, 77 (1981).
90. C. V. Broughton, R. E. Miller, and R. O. Watts, *Aust. J. Phys.* **35**, 611 (1982).
91. R. E. Miller, *Rev. Sci. Instrum.* **53**, 1719 (1982).
92. B. Fridovich, V. Malathy Devi, & P. P. Das, *J. Mol. Spectrosc.* **81**, 269 (1980).
93. J. Susskind, D. Reuter, D. E. Jennings, S. J. Daunt, W. E. Blass, and G. W. Halsey, *J. Chem. Phys.* **77**, 2728 (1982).
94. J. Pliva, A. S. Pine, and P. D. Willson, *Appl. Opt.* **19**, 1833 (1980).
95. J. Pliva and A. S. Pine, *J. Mol. Spectrosc.* **93**, 209 (1982).
96. H. Dubost, R. Charneau, and M. Harig, *Chem. Phys.* **69**, 389 (1982).
97. M. Dubs and H. H. Günthard, *J. Mol. Struct.* **60**, 311 (1980).
98. A. R. Chraplyvy, W. E. Moerner, and A. J. Sievers, *Opt. Lett.* **6**, 431 (1981).
99. P. B. Davies and P. A. Hamilton, *Chem. Phys. Lett.* **94**, 565 (1983).
100. J. V. V. Kasper, C. R. Pollock, R. F. Curl Jr., & F. K. Tittel, *Chem. Phys. Lett.* **77**, 211 (1981).
101. P. B. Davies and D. K. Russell, *Chem. Phys. Lett.* **67**, 440 (1979).
- 101a. P. B. Davies and D. K. Russell, *J. Mol. Struct.* **60**, 201 (1980).
102. A. C. Stanton and C. E. Kolb, *J. Chem. Phys.* **72**, 6637 (1980).
103. G. A. Laguna and W. H. Beattie, *Chem. Phys. Lett.* **88**, 439 (1982).
104. K. Nagai, K. Tanaka, and E. Hirota, *J. Phys.* **B15**, 341 (1982).
- 104a. D. J. Jackson, H. Gerhardt, and T. W. Hänsch, *Opt. Comm.* **37**, 23 (1981).
105. A. G. Maki and F. J. Lovas, *J. Mol. Spectrosc.* **95**, 80 (1982).
106. A. G. Maki, F. J. Lovas, and R. D. Suenram, *J. Mol. Spectrosc.* **91**, 424 (1982).
107. M. S. Zahniser and M. E. Gersh, *J. Chem. Phys.* **75**, 52 (1981).
108. C. Yamada, K. Nagai, and E. Hirota, *J. Mol. Spectrosc.* **85**, 416 (1981).
109. K. Kawaguchi, C. Yamada, Y. Hamada, & E. Hirota, *J. Mol. Spectrosc.* **86**, 136 (1981).
110. P. B. Davies and P. A. Hamilton, *J. Chem. Phys.* **76**, 2127 (1982).
111. P. L. Varghese and R. K. Hanson, *J. Quant. Spectrosc. Rad. Transfer* **24**, 479 (1980).
112. P. L. Varghese and R. K. Hanson, *J. Mol. Spectrosc.* **88**, 234 (1981).
113. A. Picard-Bersellini, R. Charneau, and P. Brechignac, *Nuovo Cim.* **63B**, 343 (1981).
114. A. G. Maki, F. J. Lovas, and W. B. Olson, *J. Mol. Spectrosc.* **92**, 410 (1982).
115. A. S. Pine, *J. Mol. Spectrosc.* **82**, 435 (1980).
116. P. B. Davies, P. A. Hamilton, and M. Okumura, *J. Chem. Phys.* **75**, 4294 (1981).
117. P. F. Bernath and T. Amano, *J. Mol. Spectrosc.* **95**, 359 (1982).
118. W. Rohrbach, R. Winter, W. Herrmann, J. Wildt, & W. Urban, *Mol. Phys.* **39**, 673 (1980).
119. J. A. Sell, *J. Quant. Spectrosc. Rad. Transfer* **25**, 19 (1981).
120. S. Lundqvist, J. Margolis, and J. Reid, *Appl. Opt.* **21**, 3109 (1982).
121. K. Matsumura, K. Kawaguchi, K. Nagai, C. Yamada, and E. Hirota, *J. Mol. Spectrosc.* **84**, 68 (1980).
122. A. G. Maki and F. J. Lovas, *J. Mol. Spectrosc.* **85**, 368 (1981).
123. Y. Endo, K. Nagai, C. Yamada, and E. Hirota, *J. Mol. Spectrosc.* **97**, 213 (1983).
124. F. J. Lovas, A. G. Maki, and W. B. Olson, *J. Mol. Spectrosc.* **87**, 449 (1981).
125. K. Kawaguchi, E. Hirota, and C. Yamada, *Mol. Phys.* **44**, 509 (1981).
126. P. B. Davies, W. Lewis-Bevan, and D. K. Russell, *J. Chem. Phys.* **75**, 5602 (1981).

127. G. L. Tetterer and W. G. Planet, *J. Quant. Spectrosc. Rad. Transfer* **24**, 343 (1980).
128. N. Nereson, H. Flicker, and M. J. Reissfeld, *J. Mol. Spectrosc.* **82**, 452 (1980).
129. K. Kawaguchi, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **93**, 381 (1982).
130. Y. Hamada and M. Tsuboi, *J. Mol. Spectrosc.* **83**, 373 (1980).
131. N. Nagai, C. Yamada, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **90**, 249 (1981).
132. T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
133. N. Nagai, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **89**, 520 (1981).
134. L. L. Strow, *J. Mol. Spectrosc.* **97**, 9 (1983).
135. R. L. Sams and W. B. Olson, *J. Mol. Spectrosc.* **84**, 113 (1980).
136. P. B. Davies, B. J. Handy, and D. K. Russell, *Chem. Phys. Lett.* **68**, 395 (1979).
137. T. Anano, P. F. Bernath, and A. R. W. McKellar, *J. Mol. Spectrosc.* **94**, 100 (1982).
138. J.-M. Flaud, C. Camy-Peyret, V. Malathy Devi, P. P. Das, and K. Narahari Rao, *J. Mol. Spectrosc.* **84**, 234 (1980).
139. V. Malathy Devi, P. P. Das, A. Bano, K. Narahari Rao, J.-M. Flaud, C. Camy-Peyret, and J.-P. Chevillard, *J. Mol. Spectrosc.* **88**, 251 (1981).
140. D.-W. Chen, E. R. Niple, and S. K. Poultney, *Appl. Opt.* **21**, 2906 (1982).
141. V. Malathy Devi, P. P. Das, A. Bano, & K. Narahari Rao, *J. Mol. Spectr.* **87**, 578 (1981).
142. J. P. Sattler, T. L. Worchesky, A. G. Maki, and W. J. Lafferty, *J. Mol. Spectrosc.* **90**, 460 (1981).
143. J. P. Sattler, T. L. Worchesky, & W. J. Lafferty, *J. Mol. Spectrosc.* **88**, 364 (1981).
144. A. S. Pine and M. Dang-Nhu, *J. Mol. Spectrosc.* **84**, 132 (1980).
145. C. Yamada and E. Hirota, *J. Chem. Phys.* **78**, 1703 (1983).
146. C. Yamada, E. Hirota, and K. Kawaguchi, *J. Chem. Phys.* **75**, 5256 (1981).
147. C. Yamada and E. Hirota, *J. Chem. Phys.* **78**, 669 (1983).
148. T. Anano, P. F. Bernath, C. Yamada, Y. Endo, & E. Hirota, *J. Chem. Phys.* **77**, 5284 (1982).
149. P. P. Das, V. Malathy Devi, and K. Narahari Rao, *J. Mol. Spectrosc.* **84**, 313 (1980).
150. B. Lemoine, K. Yamada, & G. Winnewisser, *Ber. Bunsenges. Phys. Chem.* **86**, 795 (1982).
151. K. Yamada and M. Takami, *J. Mol. Spectrosc.* **84**, 431 (1980).
152. D. M. Swager and R. L. Sams, *J. Mol. Spectrosc.* **87**, 18 (1981).
153. S. Giorgianni, F. Cappellani, and G. Restelli, *J. Mol. Spectrosc.* **83**, 228 (1980).
154. G. Baldacchini, S. Marchetti, and V. Montelatici, *J. Mol. Spectrosc.* **86**, 115 (1981).
155. V. G. Koloshnikov, Yu. A. Kuritsyn, I. Pak, N. I. Ulitskiy, B. M. Kharlamov, A. D. Bri-tov, I. I. Zasavitsky, and A. P. Shotov, *Opt. Comm.* **35**, 213 (1980).
156. J. P. Sattler and T. L. Worchesky, *J. Mol. Spectrosc.* **90**, 297 (1981).
157. V. Malathy Devi, P. P. Das, K. Narahari Rao, S. Urban, P. Papoušek, and V. Špirko, *J. Mol. Spectrosc.* **88**, 293 (1981).
158. G. Baldacchini, S. Marchetti, and V. Montelatici, *Appl. Phys.* **B29**, 269 (1982).
159. M. Takami, *J. Chem. Phys.* **74**, 4276 (1981).
160. H. Niki, Y. Izawa, and C. Yamanaka, *Jpn. J. Appl. Phys.* **19**, 1801 (1980).
161. R. Eckhardt, J. Telle, and L. Haynes, *J. Mol. Spectrosc.* **90**, 321 (1981).
162. C. W. Patterson, R. S. McDowell, and N. G. Nereson, *IEEE J. Quantum Electron.* **QE-16**, 1164 (1980).
163. A. S. Pine, *J. Mol. Spectrosc.* **96**, 395 (1982).
164. V. Malathy Devi, B. Fridovich, D. G. S. Snyder, G. D. Jones, and P. P. Das, *J. Quant. Spectrosc. Rad. Transfer* **29**, 45 (1983).
165. G. Restelli and F. Cappellani, *Chem. Phys. Lett.* **92**, 439 (1982).
166. K. Shinohara, T. Akamatsu, and R. Ueda, *Jpn. J. Appl. Phys.* **20**, 439 (1981).
167. D. E. Jennings and A. G. Robiette, *J. Mol. Spectrosc.* **94**, 369 (1982).
168. G. Baldacchini, S. Marchetti, and V. Montelatici, *Lett. Nuovo Cim.* **33**, 267 (1982).
169. S. Sofue, K. Kawaguchi, E. Hirota, & T. Ujiyama, *Bull. Chem. Soc. Jpn.* **54**, 3546 (1981).
170. Z. Qingshi and J. I. Steinfeld, *J. Mol. Spectrosc.* **89**, 405 (1981).
171. F. Herlemont, M. Lyszyk, J. Lemaire, & J. Demaison, *Z. Naturforsch.* **36a**, 944 (1981).
172. G. Magerl, W. Schupita, E. Bonek, and W. A. Kreiner, *J. Mol. Spectrosc.* **83**, 431 (1980).
173. P. P. Das, V. Malathy Devi, and K. Narahari Rao, *J. Mol. Spectrosc.* **84**, 305 (1980).
174. P. P. Das, V. Malathy Devi, and K. Narahari Rao, *J. Mol. Spectrosc.* **86**, 202 (1981).
175. P. P. Das, V. Malathy Devi, K. Narahari Rao, and A. G. Robiette, *J. Mol. Spectrosc.* **91**, 494 (1982).
176. K. Yamada, R. Schieder, G. Winnewisser, and A. W. Mantz, *Z. Naturforsch.* **35a**, 690 (1980).
177. K. Yamada and G. Winnewisser, *Z. Naturforsch.* **36a**, 23 (1981).
178. K. Yamada and G. Winnewisser, *J. Mol. Spectrosc.* **90**, 596 (1981).
179. A. G. Maki and J. S. Wells, *J. Mol. Spectrosc.* **82**, 427 (1980).
180. M. V. Glushkov, Yu. V. Kosichkin, A. I. Nadezhdinskii, I. I. Zasavitskii, A. P. Shotov, G. A. Gerasimov, and V. V. Fomin, *Sov. J. Quantum Electron.* **10**, 521 (1980).
181. R. S. McDowell, C. W. Patterson, N. G. Nereson, F. R. Petersen, and J. S. Wells, *Opt. Lett.* **6**, 422, 647 (1981).
182. C. W. Patterson, R. S. McDowell, N. G. Nereson, B. J. Krohn, J. S. Wells, and F. R. Petersen, *J. Mol. Spectrosc.* **91**, 416 (1982).
183. R. S. McDowell, M. J. Reissfeld, C. W. Patterson, B. J. Krohn, M. C. Vasquez, and G. A. Laguna, *J. Chem. Phys.* **77**, 4337 (1982).
184. C. W. Patterson and A. S. Pine, *J. Mol. Spectrosc.* **96**, 404 (1982).

185. Ch. Lambeau, M. de Vleeschouwer, D. Van Lerberghe, A. Fayt, J. P. Kupfer, H. Pascher, and H. G. Haefele, *Mol. Phys.* **46**, 981 (1982).
186. N. Ohashi, K. Kawaguchi, and E. Hirota, *J. Mol. Spectrosc.* **85**, 427 (1981).
187. W. J. Lafferty, J. P. Sattler, T. L. Worchesky, and K. J. Ritter, *J. Mol. Spectrosc.* **87**, 416 (1981).
188. W. H. Weber, D. H. Leslie, and C. W. Peters, *J. Mol. Spectrosc.* **89**, 214 (1981).
189. W. H. Weber and P. D. Maker, *J. Mol. Spectrosc.* **93**, 131 (1982).
190. N. J. Bristow, M. Poliakoff, P. B. Davies, and P. A. Hamilton, *Chem. Phys. Lett.* **84**, 462 (1981).
191. S. Marchetti, *J. Phys.* **B14**, L827 (1981).
192. A. S. Pine and C. W. Patterson, *J. Mol. Spectrosc.* **92**, 18 (1982).
193. C. W. Patterson, B. J. Krohn, and A. S. Pine, *J. Mol. Spectrosc.* **88**, 133 (1981).
194. G. Baldacchini, S. Marchetti, and V. Montelatici, *J. Mol. Spectrosc.* **91**, 80 (1982).
195. A. S. Pine and W. J. Lafferty, *J. Res. Natl. Bur. Standards* **87**, 237 (1982).
196. C. W. Patterson, H. Flicker, R. S. McDowell, and N. G. Nereson, *Mol. Phys.* **43**, 517 (1981).
197. Z. Qingshi, J. S. Francisco, and J. I. Steinfeld, *J. Mol. Spectrosc.* **92**, 257 (1982).
198. W. H. Weber, D. H. Leslie, C. W. Peters, and R. W. Terhune, *J. Mol. Spectrosc.* **81**, 316 (1980).
199. F. Herlemont, J. Fleury, J. Lemaire, and J. Demaison, *J. Chem. Phys.* **76**, 4705 (1982).
200. F. Herlemont, M. Lyszyk, J. Lemaire, Ch. Lambeau, M. De Vleeschouwer, and A. Fayt, *J. Mol. Spectrosc.* **94**, 309 (1982).
201. A. Di Lieto, P. Minguzzi, and M. Tonelli, *J. Phys.* **E14**, 429 (1981).
202. F. Herlemont, M. Lyszyk, and J. Lemaire, *Appl. Phys.* **24**, 369 (1981).
203. R. Guccione-Gush, H. P. Gush, R. Schieder, K. Yamada, and G. Winnewisser, *Phys. Rev. A23*, 2740 (1981).
204. M. Takami, *J. Chem. Phys.* **73**, 2665 (1980).
205. M. Takami, *J. Chem. Phys.* **76**, 1670 (1982).
206. M. Takami, *J. Mol. Spectrosc.* **93**, 250 (1982).
207. C. W. Patterson, R. S. McDowell, F. F. Moulton, and A. Mooradian, *Opt. Lett.* **6**, 93 (1981).
208. M. Dubs, D. Harradine, E. Schweitzer, J. I. Steinfeld, and C. Patterson, *J. Chem. Phys.* **77**, 3824 (1982).
209. C. Reiser, J. I. Steinfeld, and H. W. Galbraith, *J. Chem. Phys.* **74**, 2189 (1981).
210. W. H. Weber and R. W. Terhune, *Opt. Lett.* **6**, 455 (1981).
211. J. Orr and T. Oka, *Appl. Phys.* **21**, 293 (1980).
212. R. K. Hanson, *Appl. Opt.* **19**, 482 (1980).
213. R. K. Hanson, P. L. Varghese, S. M. Schoenung, and P. K. Falcone, in *Laser Probes for Combustion Chemistry*, D. R. Crosley, ed. (ACS Symposium Series No. 134, 1980), p. 413.
214. P. L. Varghese and R. K. Hanson, *J. Quant. Spectrosc. Rad. Transfer* **26**, 339 (1981).
215. S. M. Schoenung and R. K. Hanson, *Appl. Opt.* **21**, 1767 (1982).
216. D. Labrie and J. Reid, *Appl. Phys.* **24**, 381 (1981).
217. R. Schieder, K. H. Sorgalla, and W. Herr, *Radiochim. Acta* **28**, 109 (1981).
218. P. B. Davies, C. J. Kho, W. K. Leong, and W. Lewis-Bevan, *J. Chem. Soc. Chem. Comm.* **690** (1982).
219. B. A. Thrush and G. S. Tyndall, *J. Chem. Soc. Faraday Trans. 2*, **78**, 1469 (1982).
220. G. A. Laguna and S. L. Baughcum, *Chem. Phys. Lett.* **88**, 568 (1982).
221. K. C. Kim, M. J. Reisfeld, and W. B. Person, *J. Mol. Struct.* **60**, 205 (1980).
222. A. Ohsawa, K. Honda, S. Ohkawa, and R. Ueda, *Appl. Phys. Lett.* **36**, 147 (1980).
223. C. Rolland, J. Reid, B. K. Garside, P. E. Jessop, and H. D. Morrison, *Opt. Lett.* **8**, 36 (1983).
224. H. Takezoe, K. Kondo, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.* **21**, L627 (1982).
225. W. C. Gardiner Jr., in *Proceedings of the Tenth Materials Research Symposium on Characterization of High Temperature Vapors and Gases*, J. W. Hastie, ed. (NBS Special Publ. No. 561, 1979), p. 835.
226. C. G. Venkatesh, P. S. Eng, and A. W. Mantz, *Appl. Spectrosc.* **35**, 111 (1981).
227. R. S. McDowell, C. W. Patterson, and W. G. Harter, *Los Alamos Science* **3**(1), 38 (Winter/Spring 1982).
228. T. H. Vansteenkiste, F. R. Faxvog, and D. M. Roessler, *Appl. Spectrosc.* **35**, 194 (1981).
229. J. A. Mucha, *Appl. Spectrosc.* **36**, 393 (1982).
230. P. S. Connell, R. A. Perry, and C. J. Howard, *Geophys. Res. Lett.* **7**, 1093 (1980).
231. J. Reid, M. El-Sherbiny, B. K. Garside, & E. A. Ballik, *Appl. Opt.* **19**, 3149 (1980).
232. G. Forrest and G. Vilcins, *Appl. Spectrosc.* **34**, 418 (1980).
233. H. Sano, R. Koga, M. Kosaka, and K. Shinohara, *Jpn. J. Appl. Phys.* **30**, 2145 (1981).
234. D. T. Cassidy and J. Reid, *Appl. Opt.* **21**, 2527 (1982).
235. G. T. Forrest, *Appl. Opt.* **19**, 2094 (1980).
236. M. Endemann and R. L. Byer, *Opt. Lett.* **5**, 452 (1980); *Appl. Opt.* **20**, 3211 (1981).
237. D. J. Brassington, *Appl. Opt.* **21**, 4411 (1982).
238. B. M. Landsberg, D. Crocker, and R. J. Butcher, *J. Mol. Spectrosc.* **92**, 67 (1982).