
7 Tunable infrared laser spectroscopy

R. F. Curl and F. K. Tittel

*Departments of Chemistry and Electrical and Computer Engineering,
Rice Quantum Institute, Rice University, Houston, TX 77005, USA*

1 Introduction and scope

The infrared region of the spectrum has been of great interest to researchers for many years with the mid- to far-IR frequency region from about 100 to 3800 cm^{-1} of particular interest. The vast majority of chemical substances have vibrational fundamentals in this region, and the absorption of light by these fundamentals provides a nearly universal means for their detection. For many years, work in this area with dispersive spectrometers was hampered by the low spectral brightness of blackbody sources. This situation has changed dramatically with the widespread use of Fourier transform infrared spectrometers with their multiplex advantage largely overcoming the low source intensity problem. To a lesser, but still very significant and growing extent, the development of tunable infrared laser sources is contributing to the development of infrared spectroscopy. The purpose of this review is to describe recent research in tunable infrared laser spectroscopy.

This review covers recent developments in three areas: tunable infrared laser sources, techniques for tunable laser infrared spectroscopy and applications of tunable infrared laser spectroscopy. The focus time period of this review is the years 1996 to 2001. There has not been a recent review that has attempted to be as general as to cover the topics listed above. However, there have been a number of recent reviews of various aspects of these subjects and several databases of interest to workers in the field. These reviews and databases will be referred to near the beginning of the appropriate topic. Generally, these reviews will provide the reader with a more in-depth discussion of that particular topic. The present review will focus primarily upon cw infrared lasers and will pay scant attention to most tunable pulsed infrared sources such as free electron lasers, pulsed OPOs, and Raman shifting IR sources. These are important and valuable sources for spectroscopy, but outside our personal areas of interest.

There is some ambiguity about what constitutes the infrared region of the spectrum. Generally we define the region as the range from 50 to 12 000 cm^{-1} . At the low frequency end of this region, we will not consider work done with electronic sources such as traveling wave tubes. At the high end, we will not consider electronic transitions directly excited and detected by fluorescence or the detection or manipulation of atoms. Nor will any LMR or Stark work involving fixed frequency IR

sources, where the transition is tuned into resonance with the laser by external fields, be considered.

2 Spectroscopic sources

A Diode lasers

The majority of current semiconductor lasers are constructed from n- and p-type layers of different semiconductor materials in Groups 13 and 15 of the periodic table. As research and development have progressed, many complicated lattice matched structures such as AlGaAs, InGaAs, GaAlAs and GaAlAsP have evolved. As the result of intense development efforts, extremely reliable, room temperature semiconductor lasers are now commercially available in the visible and near-infrared. To date the best monolithic diode laser sources are those with distributed feedback (DFB) structures. Mass produced 1.3 and 1.5 μm DFB lasers developed for communications technology provide high output powers of up to 25 mW, pure single frequency emission at high modulation frequencies, continuous wavelength tuning and a lifetime in excess of 10 years.

Soon after the first semiconductor diode laser was developed in 1962,¹ diode laser spectroscopy began to be used for the detection, identification, and measurement of molecular and atomic species in the gas phase. The applications of diode lasers to spectroscopy have grown greatly as has the quality and variety of diode lasers available (see reviews on diode lasers^{2,3}). The reasons for the wide acceptance of diode lasers in the spectroscopy community are threefold. First, lasers offer better wavelength resolution (linewidth) and spectral brightness (power emitted per unit linewidth) than conventional spectroscopic instrumentation. Second, among all lasers, diode lasers offer a unique combination of tunability, excellent power conversion efficiencies, small size with typical dimensions of less than 1 mm, and modulation capabilities. Third, they are simply excited by electric current and, further, the laser wavelength and the output power depend on the current. For small changes in the injection current that dependence is nearly linear and instantaneous, allowing predictable and fast wavelength control.

Diode laser spectroscopy can be divided into two categories according to spectral region. Mid-infrared spectroscopy corresponds to the "fingerprint" region from 3 μm to 25 μm where most molecular species exhibit fundamental absorptions. The lead salt cw diode lasers operating at mid-infrared wavelengths typically deliver output powers of about 100 μW and require cryogenic cooling (see Section 2.A.3). Near-infrared, or 'overtone', spectroscopy employs room-temperature, single frequency diode lasers primarily developed for optical telecommunications applications with output powers up to tens of mW at wavelengths below 2 μm . These lasers access molecular overtone transitions that are typically a factor of 30 to 300 weaker than the fundamental transitions of the mid-IR. In trace gas monitoring applications, mid-infrared spectroscopy offers higher sensitivity at the cost of complexity while overtone spectroscopy is the method of choice in applications where lower sensitivity can be tolerated, but where cost and room-temperature operation are paramount.

1 VCSEL diode lasers. A new development in diode lasers is the creation of low-power consumption, efficient vertical cavity surface emitting lasers (VCSELs). VCSELs provide a unique gain medium, which has led to compact, low cost, tunable, single frequency laser sources compatible with fiber-optics technology.⁴⁻¹¹ This is accomplished by employing a very thin gain region sandwiched between two highly reflecting Bragg mirrors consisting of tens of layers of $\lambda/4$ thickness. This results in a very short laser resonator that is inherently a single-wavelength structure.¹² Furthermore VCSELs emit a circular, relatively weakly diverging, and astigmatism-free beam, in contrast to the highly divergent rectangular beams of end-emitting diode laser designs.

2 Antimonide diode lasers. For reasons of sensitivity, laser sources in the mid-IR are of considerable interest. Continuous wave lasing at room temperature at wavelengths above 2 μm with output optical powers up to 20 mW facet⁻¹ has been achieved using structures grown by molecular beam epitaxy (MBE) on GaSb substrates and employing compressively strained GaInSbAs quantum wells (QWs) between Ga(Al)Sb(As) barriers in the active region. Narrow ridge Fabry-Perot GaInSbAs/GaSb type II electrically pumped QW lasers emitting at 2.35 μm have been reported.^{13,14} These lasers emit in the fundamental spatial mode and exhibit single frequency operation over a range of currents and temperatures. They emit in a spectral region where lower overtone and combination absorption lines of such gases as CO, CH₄, NH₃ and NO₂ can be accessed. In efforts to extend coverage to the fundamental region, several groups have reported the development of antimonide diode lasers in the 2 to 3 μm spectral region¹⁵ and InAsSb/InAs lasers between 3 to 5 μm .¹⁶⁻²⁰

3 Lead salt diode lasers. Lead-salt diode lasers have been developed for operation at wavelengths from 3 to 30 μm . These lasers typically deliver 100–500 μW of output power in a near-diffraction-limited beam and can be tuned by temperature or current control. They are based upon (typically ternary) material combinations of Pb, S, Sn, Se and Te and operate in the temperature range 15–80 K.²¹⁻²⁸ Therefore, a cryogenic refrigerator or liquid nitrogen is required, together with a temperature controller, in order to maintain the temperature of the diode within a few mK. Frequency jitter is of the order of 1–10 MHz although the jitter can be increased by refrigerator vibrations.

Mid-infrared spectrometers employing lead-salt diode lasers have demonstrated very high sensitivities. They have provided most impressive performances to date in terms of minimum detectable gas concentration in trace gas detection,^{19,24,29} and they are extensively employed in studies of transient species,³⁰ as well as a variety of other applications.³¹ There are four reasons for this high sensitivity. First is the high line strengths of fundamental molecular vibrational bands. For example, carbon dioxide at a 3.3 ppm concentration in air (which is roughly 100 times lower than its typical ambient level) will cause absorption of 15% at 4.23 μm over a 1 m path. Such macroscopic absorption signals can be easily measured, even without sophisticated signal processing techniques. Second, cryogenically cooled InSb or HgCdTe detectors with noise-equivalent powers in the range of 0.5–50 pW Hz^{-1/2} are used in lead-salt diode laser spectrometers. Although the lead-salt lasers produce less output power than their near-infrared counterparts, they still provide enough light to render the detector noise

negligible, allowing near quantum-noise-limited detection. Third, near-diffraction-limited beam characteristics of lead-salt diode lasers allow beam shaping and propagation over long distances. This makes possible the use of multipass cells or remote sampling in the open air. Fourth, lead-salt diode lasers have frequency-modulation (FM) capabilities similar to those of near-infrared diode lasers, allowing the use of harmonic detection and two-tone modulation techniques, which are efficient methods of noise bandwidth reduction (see Section 4.C.2.b). These characteristics add up to an impressive real-world instrument performance.

Lead-salt diode lasers have proved effective in scientific applications, but they are less often used in industrial applications, because of several important practical drawbacks. Perhaps the most serious is the difficulty in obtaining diodes at a specific frequency because of the large manufacturing spread. The situation is aggravated by the fact that each individual laser has a rather limited tuning range, typically 100 cm^{-1} with temperature control, and tuning in that range is almost never free of mode hops. Furthermore, the characteristics of the diode often change upon warming up to room temperature. Thus obtaining and maintaining a laser diode that tunes to a specific wavelength, as is required in applications in which there is a limited choice of absorption lines free from interference by other lines, *e.g.* detection of formaldehyde,^{24,32} is difficult.

Despite these technical difficulties, a number of spectrometers based on lead-salt diode lasers have been developed for molecular spectroscopy,^{31,33} trace gas monitoring (see Section 4.C.3), chemical diagnostics,³⁴ and other applications.³¹

4 Grating-tuned external-cavity and monolithic tunable semiconductor lasers. Many of the problems in tuning diode lasers can be enormously reduced by incorporating the diode into a grating-tuned external cavity (ECDL).³⁵ In an ECDL, one or both faces of the laser chip are antireflection-coated to eliminate optical feedback. Instead the feedback required for laser action is provided by a larger, external cavity. The cavity acts as a wavelength selector, picking a specific wavelength out of the usually broad gain spectrum of the semiconductor laser material. Several cavity configurations have been developed that differ in the method of tuning, component count, output beam characteristics, and output coupling efficiency. Mode-hop-free single frequency tuning ranges of over 1000 GHz have been demonstrated for an ECDL.³⁶⁻³⁸ Grating-tuned external cavity diode lasers with large tuning ranges have been commercialized in the near-infrared from 0.9 to 1.6 μm .

This approach is ideally suited to achieving mode-hop free tuning for Fabry-Perot type diodes and QC lasers (see Section 2.D) in the mid-IR. A grating-coupled external cavity has been used to obtain a wavelength tuning of hundreds of nanometres, or up to 8% of the central wavelength in the 3–4 μm region for InAs/InAsSb or GaSb/InAsSb heterostructure lasers with a few hundred mW peak power.³⁹ Fabry-Perot quantum cascade lasers at 4.5 and 5.1 μm have been tuned with an external cavity.⁴⁰ The principal technical issue is the need to deposit a low loss anti-reflection coating on one of the laser output facets.

A further potential future development will be broadly tunable monolithic integrated multi-section diode laser chips employing gain, filter and Bragg tuning elements.⁴¹ Unlike external grating controlled diode lasers these lasers⁴²⁻⁴⁴ would offer fast and versatile electronic wavelength tunability ($\sim 70\text{ nm}$ at 1.56 μm).

B Tunable solid state lasers

A large and important class of tunable lasers is based on the vibronically broadened transitions that can occur in certain gain media, such as color centers and certain transition metal or rare-earth ions in crystalline hosts.⁴⁵⁻⁴⁸ When such a medium is placed in a tunable cavity and pumped above the laser threshold, stimulated emission can be made to occur at any desired frequency within the emission band. Tunable laser media based on 3d-3d transitions of transition-metal ions and 4f-5d transitions of rare-earth ions cover almost the entire spectral range between 0.27 and 4.7 μm . Recent spectroscopic studies have demonstrated that chromium-doped zinc selenide ($\text{Cr}^{2+}:\text{ZnSe}$) has several favorable characteristics as a mid-infrared solid-state material near 2.5 μm .^{49,50} These include room-temperature operation, broad tunability, the possibility of direct diode-pumping and cw operation.

The Group II-VI host materials are generally characterized by high thermal conductivity, chemical and mechanical stability, but with a relatively high thermal lensing parameter. Cw output powers of 1.5 W, TEM_{00} polarized cw operation with 660 mW output power, and tunability over a 600 nm band have been demonstrated.^{48,51} The tuning range of such lasers can be widely varied by the choice of the impurities and by selecting different hosts to cover the red and near-infrared spectral range from 0.65 to 2.5 μm . Titanium-doped sapphire ($\text{Ti}^{3+}:\text{Al}_2\text{O}_3$) has become the most useful tunable solid-state laser material with a wide tuning range from 660-1100nm and a large gain cross-section in laser spectroscopy largely replacing dye lasers.² Near the border between the mid-infrared and the near-infrared region color center lasers⁵³ have also been used extensively in laser spectroscopy for the past two decades. However, in recent years color, alexandrite and dye lasers are being replaced by more robust titanium sapphire lasers, OPOs, diode, and rare-earth doped fiber lasers.⁵⁴

C Nonlinear optical frequency conversion devices

Difference-frequency generation (DFG) and optical parametric oscillators (OPOs) provide a convenient means of extending the frequency range of available near-infrared and visible robust laser sources to the mid-infrared.

1 Sources based on difference frequency generation (DFG). A number of IR DFG sources have been constructed and used for spectroscopy; here⁵⁵⁻⁶³ are some recent examples. In the case of DFG, two laser beams ('pump' and 'signal') at different frequencies combined in a nonlinear material with suitable dispersion characteristics generate a beam at the difference-frequency ('idler'). The narrow emission spectra of the 'pump' (highest frequency) and 'signal' (middle frequency) translate into a similarly narrow spectrum of the idler wave. Idler wavelength tuning is accomplished by tuning the pump laser, or signal laser, or both. In order that the idler wave continue to build up as the beams pass colinearly through the nonlinear material, the three waves must stay in phase (the 'phase matching condition'). This imposes a condition on the refractive indices of the three waves.

This condition can often be satisfied with a birefringent nonlinear crystal by having some of the three waves polarized along an ordinary axis and some polarized along a direction that includes the extraordinary axis. If the polarization direction that includes the extraordinary axis is not parallel to it (angle tuning), the three waves will not propagate in the same direction (double refraction) and the beams will separate as they pass through the crystal ('walk-off') limiting the overlap region and the DFG power. In order to satisfy phase-matching keeping all waves exactly parallel or perpendicular to the optic axis ('90° phase matching'), the refractive indices must be tuned as the difference frequency is tuned by varying the temperature of the crystal or by tuning pump and signal simultaneously.

In the early demonstration of the DFG method by Pine,⁶⁴ single mode argon-ion and dye laser outputs were combined in bulk lithium niobate crystal to produce narrow-band (15 MHz) radiation tunable from 2.2 to 4.2 μm by temperature tuning the crystal. Simultaneous tuning of both signal and idler has been used^{65,66} in AgGaS_2 to provide tunable single frequency radiation from 3.5 to 9 μm . For DFG radiation longer than 5 μm it is possible to use birefringent bulk nonlinear optical materials, such as AgGaS_2 ,^{67,68} AgGaSe_2 ⁶⁹ and GaSe .⁷⁰⁻⁷²

Another approach to phase matching is to introduce periodic short (about 10–30 μm wide) regions in which the sign of the third order susceptibility alternates, thus bringing the three waves back into the right phase relationship. This is called quasi-phase matching. It is most easily achieved in the ferroelectric material lithium niobate where the direction of the extraordinary axis can be reversed locally by the application of an external electric field at elevated temperatures. The resulting material is called periodically-poled lithium niobate (PPLN).

The development of PPLN now permits near-infrared diode or fiber lasers to be used^{61,62,73-78} instead of much bulkier cumbersome dye or Ti:sapphire lasers, making it feasible to construct compact mid-infrared spectrometers that operate at room temperature and can generate cw output powers up to 1 mW.⁷⁹ Thus the convenience and practicality of near-infrared diode laser and optical fiber technology are combined to achieve the analytical power of mid-infrared spectroscopy in a single instrument. Such an instrument inherits the single-frequency operation and high modulation speed capabilities of diode lasers, and takes advantage of their relatively wide tuning range. For example, a typical 780 nm diode laser can be grating tuned over 20 nm, or 2.6% in wavelength, without appreciable changes in output power. When the output of such a laser is down-converted by mixing with a 980 nm diode laser, the tuning range in frequency units remains the same, in this case a very significant spectral coverage: 3.6–4.1 μm , or 13% in wavelength.

The implementation of diode-pumped mid-infrared frequency conversion received a significant boost from the development of novel periodically poled nonlinear materials, such as lithium niobate (PPLN),⁸⁰ lithium tantalate (LiTaO_3), and potassium titanyl phosphate (KTiOPO_4 , or KTP) at wavelengths in the 2.5–5.2 μm spectral region.⁸¹⁻⁸³ The quasi-phase matching properties of each of these crystals can be engineered for interaction of any pump and signal wavelengths within the transparency range of the crystal, allowing significant flexibility in the choice of laser sources.⁸⁴⁻⁸⁶ In the future, quasi-phase matched GaAs,⁸⁷ should become available, greatly extending the long wavelength region covered by DFG.

A detailed quantitative theory of this nonlinear optical process is beyond the scope of this review chapter (see the paper by Zondy⁸⁸ and the references contained therein). Therefore, we will simply state that the maximum idler power generated in a given crystal is proportional to the product of crystal length, pump power, signal power, and the squared second-order nonlinear coefficient of the crystal. Maximum DFG output power is achieved by means of optimal focusing. There is an optimal focus because as the focus is tightened a point is reached at which any further increase in beam intensity through tighter focusing is offset by a decrease in interaction length due to diffraction, resulting in loss of output power. Although this type of source is routinely used for spectroscopy and gas detection, DFG in bulk nonlinear (either birefringent or quasi-phase matched) crystals is characterized by low conversion efficiency, typically⁸⁹ in the range 0.002–0.05 % $\text{W}^{-1} \text{cm}^{-1}$

The tradeoff between beam size and interaction length can be eliminated altogether in guided-wave DFG. Tight optical confinement of pump and signal radiation near the waveguide core creates a region of high intensity and good modal overlap that can be maintained throughout the length of the waveguide. Thus the interaction length at tight focusing is now limited by the length of the waveguide, and not by diffraction. Guided-wave parametric processes, such as OPO, SHG, and DFG, have been demonstrated⁹⁰ in periodically poled LiNbO_3 , LiTaO_3 , and KTP. In LiNbO_3 , for example, a waveguide can be formed by titanium in-diffusion, or by a $\text{Li}^+ - \text{H}^+$ ion exchange, typically followed by several hours of annealing at elevated temperature to create a graded index distribution.

A DFG waveguide designed to carry a single spatial mode at the idler wavelength is necessarily multimode at the shorter, pump and signal wavelengths. The presence of multiple spatial modes complicates waveguide phase matching characteristics. For example, a TM_{00} (fundamental) mode at the signal wavelength will interact with TM_{02} and TM_{10} modes at the pump wavelength, but not with TM_{01} or TM_{11} modes. Efficient and reproducible fundamental-mode excitation of a DFG waveguide was first achieved by Chou *et al.*,^{90,91} using a combination of a mode filter and an adiabatic taper. An improved device featuring separate inputs for the pump and signal beams followed by a directional coupler has also been demonstrated. DFG waveguides have been used to build viable sources of mid-infrared radiation for spectroscopic purposes.^{92–94}

2 Tunable optical parametric oscillators (OPO). Optical parametric oscillators (OPOs) are progressing as useful spectroscopic tools for the generation of coherent radiation that is continuously tunable over large spectral ranges.^{95–101} Unlike DFG the nonlinear crystal is placed in a cavity and is used to generate output beams at two new frequencies (signal and idler) ν_1 and ν_2 from a single pump beam at ν_3 . Energy conservation requires $\nu_1 + \nu_2 = \nu_3$. How the frequency is divided between the new waves, signal and idler is determined by the phase-matching condition. The development of pulsed OPOs is mature, and these devices are available commercially. On the other hand, cw OPOs still have some practical problems in terms of requiring high power pump sources, efficient and high quality nonlinear crystals, low loss broadband optics, and mode-hop-free-operation with good frequency stability in order to realize their potential as spectroscopic sources.

In order to have sufficient pumping power and/or sufficient feedback, the OPO is configured so that, in addition to the signal frequency being inside a resonant cavity, the pump frequency is also resonant (singly resonant) or in addition the idler can also be made resonant (doubly resonant). In principle, both doubly resonant and singly resonant OPO configurations can be used although as a practical matter doubly resonant OPOs are extremely difficult to construct and very hard to tune.

Quasi-phase matching in periodically poled ferroelectric crystals offers several distinct advantages for their use in cw OPOs, such as non-critical phase matching and a high effective nonlinear coefficient, d_{eff} . A particularly significant development was the demonstration of the use of PPLN as the parametric gain medium, in which case the oscillation threshold of externally pumped cw singly resonant OPOs can be reduced to the few watt level, hence making it feasible to use diode pumped solid-state pump lasers.^{100,102-107} Pump powers as low as 800 mW were used to pump a PPLN singly resonant OPO in which both the pump and signal were resonated.¹⁰⁸

The parametric process can also be used in optical parametric amplifiers (OPAs) to boost infrared output powers. Continuous wave OPOs amplified by pulsed OPAs offer a competitive alternative to other tunable lasers in the 1 to 5 μm spectral region in terms of linewidths, wavelength tunability and output powers.

D QC lasers

Quantum cascade (QC) lasers are unipolar semiconductor injection lasers based on intersubband transitions in a multiple quantum-well heterostructure. They are designed by means of band-structure engineering and grown by molecular beam epitaxy. The emission wavelength of a QC laser depends on the thickness of the quantum well and barrier layers of the active region rather than the band gap of diode lasers. These lasers operate either as cw or pulsed devices. There are several papers¹⁰⁹⁻¹¹² providing details of their design and operating characteristics.

Quantum cascade lasers grown in the InGaAs/AlInAs lattice matched to the InP material system have been fabricated for emission wavelength from 3.5 to 24 μm . Quantum cascade lasers have excellent spectroscopic properties in terms of power and linewidth, but their tuning range is limited and their beam divergence is large. Devices with 100 stages (quantum well gain regions in series) have peak powers of 0.6 W at room temperature. Until recently room temperature operation was only feasible for pulsed operation, but CW operation up to temperatures of 312 K was reported in 2001.¹¹³ Single frequency operation is achieved through the integration of a Bragg grating into the laser waveguide, resulting in a distributed feedback (DFB) laser.

The latest generation of QC-DFB lasers is based on a “top-grating” approach that takes advantage of the characteristics of a mid-infrared waveguide. For mid-infrared wavelengths below 15 μm , a dielectric waveguide built from low-doped semiconductor layers that have appropriate refractive index modulation is used.¹¹⁴ At longer wavelengths, the waveguide is overlaid with metal. In this case the radiation is guided not only by the dielectric but also by the surface plasmon mode.

Continuous wavelength tunability without mode hops is achieved through the temperature dependence of the waveguide parameters. The temperature can either be varied by a temperature change of the heat sink on which the device is mounted or

more rapidly by dissipative heating through changing the direct current through the device. Characteristic total tuning ranges per current sweep are typically around 0.4% of the emission wavelength. For many spectroscopic purposes, the spectral linewidth of the laser emission is as important as continuous tunability. The linewidth of cw QC lasers ranges from a few MHz through current stabilization to a few kHz with frequency stabilization, but exceeds 150 MHz in pulsed operation. Device reliability and long-term stability are excellent as a result of using robust materials, such as InP and GaAs based hetero-structures.

E Line tunable gas lasers

Line-tunable carbon dioxide and carbon monoxide lasers are available at wavelengths near 10 μm and 5–8 μm , respectively with output powers of several watts and linewidths of less than 100 MHz.¹¹⁵ Their laser transitions coincide with pressure-broadened absorption lines of numerous chemical compounds. The disadvantage of the limited number of available laser transitions can partly be compensated in the case of the CO₂ laser by selecting CO₂ isotopes that provide additional laser wavelengths. Laser emission can occur in the bands of 10.2–10.8 μm using a large number of rotational lines. Individual P and R branch lines can be selected using a Littrow-mounted grating. Fine tuning corresponding to the CO₂ Doppler width can be accomplished for ~50 MHz at every line. To avoid the tuning gaps between adjacent laser lines, pulsed continuously-tunable high pressure (at atmospheric and up to 10 atm) pulsed CO₂ lasers have been developed.¹¹⁶ At 10 atm. the pressure broadening is ~2 cm^{-1} and the individual rotational–vibrational lines, that are typically separated by 1–3 cm^{-1} , merge. Monochromatic cw laser action tunable over <1 GHz can be obtained in waveguide lasers operating near 1 atm.

For high resolution spectroscopy, a more satisfactory way^{117–122} to achieve tunability is to mix the output of a tunable microwave source with the CO₂ laser frequency in a non-linear medium, thereby adding microwave sidebands on the CO₂ laser carrier frequency.

Other useful line tunable molecular IR lasers include discharge excited CO lasers, which yield a large number of lines in the 5.1–5.6 μm region. However, in order to achieve efficient operation, the CO discharge tube must be cooled to low temperatures, which complicates their practical use. CO lasers can also be operated near 3 μm on CO overtone lines.^{123,124} The tunability of CO lasers can also be extended by introduction of microwave sidebands.^{125–127} Also significant are HF and DF chemical discharge lasers, which operate in the 2.8–4 μm spectral region.¹²⁸ Tunable far-IR radiation can be generated by mixing a fixed frequency far-IR laser with a microwave source.¹²⁹

F Free electron lasers

Free electron lasers¹³⁰ involve major facilities. They produce a rapid sequence of short, intense pulses useful for photolysis and spectroscopy where high resolution is not important.

3 Spectroscopic techniques

A Multipass cells for long optical pathlength spectroscopy

Sensitive laser absorption spectroscopy often requires a long effective pathlength of the probing laser beam in the media being analyzed. Traditionally, this requirement is satisfied using an optical multipass cell. There are three types of multipass cells in use: White cells,^{131,132} Herriott cells,¹³³ and astigmatic mirror cells.¹³⁵ For all three types of cells, focusing mirror curvature, applied to the beam at each reflection, keeps the beam from diverging, as if in a cavity.

The White cell^{131,132} is the oldest arrangement. It has two semicircular mirrors called the "D" mirrors closely spaced along a common diameter facing a third notched mirror in a nearly confocal arrangement. The probe beam enters through one notch and emerges through the other. The number of passes is varied by changing a D mirror angle.

The Herriott cell¹³³ has two identical spherical mirrors separated by slightly less than their diameter of curvature (a nearly concentric arrangement) facing each other. A probe beam, launched through a hole in one of the mirrors at an angle to the optical axis, completes a certain number of passes between the mirrors, and exits through the same hole (or a hole in the other mirror). The beam bounce pattern and pathlength are controlled by adjusting the mirror separation.

For both the White and the Herriott configurations, the number of passes, if not limited by attenuation of light, is limited by the overlapping of spots on the mirrors. Spot overlapping creates an etalon causing the base line to oscillate with optical interference fringes. Astigmatic mirror cells¹³⁴ are variations on the Herriott cell that spread the light spots over the mirror surfaces, greatly increasing the number of spots achievable without overlapping spots and therefore the number of passes. With this type of cell, the number of passes can routinely exceed 100, thus providing a commensurate improvement in signal strength. The three multipass arrangements can be enclosed in a vacuum housing, for measurement in static gas samples or controlled gas flows, or open to ambient air (for trace gas monitoring applications).

Certain design rules must be followed to ensure that the beam exits the cell after a controlled number of passes, especially in the case of astigmatic cells. It is important to recognize that mirrors are not perfect, and a small portion of the probe light is lost to absorption and scattering each time the beam bounces. Optical throughput of the cell and peak-to-peak absorption both decrease exponentially with the number of passes. In a system where sensitivity is limited by detector noise, for small absorptions and maximum sensitivity, the optimum number of reflections corresponds to the output light being 1/e times the input light. However, as long as the noise is determined by laser intensity fluctuations rather than by detector noise, additional passes will improve S/N.

Performance of long pathlength multipass cells, especially those with dense beam patterns, suffers from optical interference fringes caused by light scattering by the cell mirrors even in the absence of spot overlaps. The fringe magnitude is sensitive to optical alignment and is typically on the order of 0.01–0.1% full-scale transmission. Mirror drift and vibration can also become a problem, as they modulate the cell transmission. However, deliberate vibration of a mirror can reduce the effective

magnitude of interference fringes, as it scrambles the baseline variations caused by accidental etalons within the cell.

B Cavity enhanced spectroscopies

1 Cavity ring-down spectroscopy. Cavity ring-down spectroscopy (CRDS) is a direct absorption technique, which can be performed with pulsed or continuous light sources and has a significantly higher sensitivity than obtainable in conventional absorption spectroscopy.¹³⁵⁻¹⁴² The CRDS technique is based upon the measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined in an ultra-high finesse optical cavity consisting of two highly reflective concave mirrors. The advantage over traditional absorption spectroscopy results from intrinsic insensitivity to the probing laser intensity fluctuations and the extremely long effective pathlengths (up to many km can be achieved in cell lengths less than 1 m) that can be realized in stable optical cavities. CDRS spectroscopy has the additional advantage that the absorption is measured on an absolute scale compared to other absorption techniques, such as modulation techniques. CDRS is especially effective in gas-phase spectroscopy for measurements of weak absorptions of abundant species. Today, CDRS is used extensively in the visible and near-infrared. It is being investigated for use in the mid-infrared with progress being determined by the availability and cost of ultra-low loss cavity mirrors. Good mirrors give ring-down times exceeding 10 μ s. Although CDRS is significantly more sensitive than most absorption spectroscopies, it cannot compete with background free techniques such as laser induced fluorescence (LIF) or resonant enhanced multiphoton ionization (REMPI)

With pulsed lasers, CRDS requires that a short laser pulse be injected into a high finesse optical cavity to produce a sequence of pulses leaking out through the end mirror from consecutive traversals of the cavity by the pulse. The intensity of pulses in such a pulse train decays exponentially with a time constant

$$\tau = \frac{l}{c} \frac{1}{a l - \ln R} \quad (1)$$

where a is the absorption coefficient of the intracavity medium, l is the cavity length and R is the mirror reflectivity (both mirrors are assumed to have the same reflectivity). By measuring the ringdown time, τ , without and with the absorbing gas present, the value of a can be determined. This technique is simple and immune to laser power fluctuations. The energy of the first pulse transmitted in the ringdown sequence is $(1 - R)^2$ times smaller than the exciting laser pulse. The mirrors for CRDS experiments typically have $R > 99.95\%$. This makes the measurements with the ~ 1 nJ IR pulses ($P \sim 100$ mW, pulse length 10 ns) available from most cw IR sources practically impossible.

With narrow band low power cw sources, the laser and cavity can be slowly tuned into coincidence, filling the cavity with radiation on resonance. After the cavity is filled with radiation, the laser emission can be interrupted and the ringdown decay measured in the same manner as is done with a pulsed laser. This cw modification of CRDS

was first introduced by Romanini *et al.*^{143,144} using cw near-infrared DFB diode lasers. CH₄ and HF detection at 1.65 and 1.31 μm, respectively yielded a sensitivity of ~ 10⁻⁷ cm⁻¹ for atmospheric concentrations in the range 0.5 to 200 ppmv and HF concentrations from 0.1 to 50 ppmv.

The first work on CRDS measurements with a QC-DFB laser was published in 2000.¹⁴⁵ The authors used a cw laser generating 16 mW at 8.5 μm. The measured ringdown time of the empty three-mirror cavity was 0.93 μs. An acousto-optic modulator was used to interrupt the cavity injection for ringdown time measurements. The system was tested on dilute ammonia mixtures, and a noise-equivalent sensitivity of 0.25 ppbv achieved. An estimated 1.0 × 10⁻⁹ cm⁻¹ absorbance was reported as the limit of detection. Kosterev *et al.*¹⁴⁶ describe a spectroscopic gas sensor for NO detection based on a cavity ringdown technique. A cw QC-DFB laser operating at 5.2 μm was used as a tunable single-frequency light source. The technique used has the following features:

1. The laser frequency is slowly scanned across the absorption line of interest.
2. One of the cavity mirrors is dithered back and forth to ensure periodic, random coincidences of the laser frequency with a cavity mode.
3. Once such a resonance occurs and the cavity is filled, the laser beam entering the cavity is abruptly interrupted or set off-resonance, and the decay rate of the exiting light is measured.

The noise-equivalent sensitivity was estimated to be 0.7 ppbv for an 8 sec data acquisition time.

Interesting work¹⁴⁷ has been done combining a novel OPO with cavity ringdown spectroscopy.

2 Integrated cavity output spectroscopy. A simpler (as compared to CDRS) way to exploit a high finesse optical cavity for increasing the sensitivity to absorption has been developed¹⁴⁸⁻¹⁵³ called “integrated cavity output spectroscopy” (ICOS) or “cavity-enhanced absorption” (CEA spectroscopy). Here, laser light is coupled into the high finesse cavity *via* accidental coincidences of the light with the cavity eigenmodes. The time-integrated intensity radiation leaking out of such an optical cavity, averaged over many cavity modes, can then be used to characterize the absorption of the intracavity medium. Effectively this is equivalent to a time integration of the ringdown curve. Just as in cavity ringdown spectroscopy, an effective optical path-length of several km can be obtained in a very small volume. However, in its most naïve application, the noise levels are made quite high by the fact that the laser has many transverse modes that may be excited with poorer transmission than TEM₀₀. Further when the laser and cavity are running free, the peak transmission as the two resonances pass over each other varies radically.

Presently a variety of techniques exist to perform high-sensitivity absorption spectroscopy in a high finesse optical cavity.^{139,154-156} One of the most advanced is called the “noise-immune cavity-enhanced optical heterodyne spectroscopy” (NICE-OHMS) technique.^{157,158} In this technique, the laser frequency is locked to the frequency of a cavity mode. This method has the potential to provide shot-noise limited sensitivity with an effective pathlength determined by the cavity ring-down time. Ma *et al.*¹⁵⁷ reported a sensitivity of 10⁻¹⁴ cm⁻¹. This spectacular sensitivity is superior to that achieved with CRDS. The first implementation of this technique

using a QC-DFB laser has been reported.¹⁵⁹ However, this approach is technically highly sophisticated and probably is only suitable for very specific applications at the present time.

C Optothermal

Optothermal spectroscopy is a method invented by Gough *et al.* for obtaining very high resolution molecular beam spectra of molecules cooled to about 1 K by supersonic expansion.¹⁶⁰ In brief, a laser beam is crossed with a molecular beam at 90°. On a molecular absorption line, the molecule is excited. When the molecular beam impinges on a cryogenically cooled bolometer, the molecular excitation increases the bolometer temperature and this temperature rise is detected.

With typical linewidths of a few MHz and molecules cooled to a few K, optothermal spectroscopy is capable of providing very high resolution rotationally analyzable spectra of both fairly large molecules¹⁶¹ and smaller molecules with large amplitude motions.^{162,163} In a recent paper,¹⁶⁴ optothermal spectroscopy has been combined with Stark state mixing to obtain information about the normally invisible gerade levels of acetylene in the overtone region in the near-infrared.

Weakly bound complexes are readily formed in supersonic expansions of gas mixtures. Generally the rotational constants of such complexes are rather large because of the large internuclear separations of van der Waals bonds. Thus optothermal spectroscopy is a powerful means for investigating such complexes. There are several recent publications¹⁶⁵⁻¹⁷¹ where the spectra of complexes were obtained optothermally and rotationally analyzed.

Optothermal spectroscopy provides a means of investigating the dynamics of the infrared photodissociation of complexes. In the simplest experiment, mode specific line broadening of rotational components is observed. A better approach is to position the bolometer detector so that it is not detecting the main beam, but instead is detecting photofragments recoiling out of the beam.^{168,172} Miller has developed the method of studying the dissociation dynamics of complexes by translational spectroscopy extensively and has written a recent review¹⁷³ of this subject.

Optothermal spectroscopy is also useful for studying IVR in stable molecules through observation of the mode mixings.¹⁷⁴⁻¹⁷⁹ The energy region of greatest interest in this work is that where the spacing between states interacting with intensity bearing state is becoming comparable with the interaction matrix elements. For molecules with three to five atoms that are heavier than hydrogen, this typically is the region of XH stretching fundamentals (X=C,N,O,Si)^{175,177,178} or of the first overtone of the XH stretch.^{174,176,179}

Miller and Wight have developed a method for studying scattering of molecules by surfaces using optothermal spectroscopy and have used this to observe rainbow scattering of methane from a LiF surface.¹⁸⁰ They are able to label the molecules with vibrational excitation prior to their scattering from the surface, thereby being able to investigate the retention of vibrational excitation as a function of scattering angle. Since the molecules being scattered have very few rotational states populated after the supersonic expansion, they can investigate rotational excitation by the scattering

event, by labeling the molecules with vibrational energy with rotational resolution after they are scattered off the surface.

D Surfaces—sum frequency generation

Three-wave mixing processes such as sum frequency mixing, difference frequency mixing and second harmonic generation are forbidden by symmetry in isotropic media. Thus when a visible laser and an infrared laser impinge on an interface, any light generated at the sum frequency is a specific probe of the anisotropy introduced by the interface. This makes such a sum frequency technique a very valuable means for observing the vibrational spectra of molecules adsorbed at the interface. Because the nonlinear effect is proportional to the product of the two laser intensities and there are few molecules in a monolayer, intense laser sources are required. As very high resolution is not required, the tunable infrared sources employed are pulsed and high power. The main sources used are optical parametric oscillators, difference frequency generation, Raman shifting, or free electron lasers. The theory of this technique, its apparatus and methodologies, and its applications have been very recently reviewed by Buck and Himmelhaus.¹⁸¹

The investigation of molecules at interfaces by sum frequency generation is a vast subject. Since 1996 there have been at least fifteen reviews,¹⁸²⁻¹⁹⁶ in addition to the one cited above, of various aspects of this technique. The reader is referred to these reviews for further information on this subject.

E Photoacoustic spectroscopy

Photoacoustic spectroscopy (PAS) has found its principal uses in sensitive trace gas detection. It is based on the photoacoustic effect, in which acoustic waves result from the absorption of radiation. Its history goes back to the work of Alexander Graham Bell in 1880. In its application to laser spectroscopy, the laser beam impinges on a selected target gas in a specially designed cell.¹⁹⁷⁻²⁰⁶

In contrast with other mid-IR absorption techniques, PAS is an indirect technique in which the effect on the absorbing medium and not direct light absorption is detected. Light absorption results in a transient temperature rise in the absorbing medium *via* non-radiative relaxation processes, which then translates into a pressure rise or sound wave. This is detected with a sensitive microphone or microphones. There are two modes of operation for PAS, either the exciting light can be modulated at a frequency away from any cell resonance or it can be adjusted to coincide with an acoustic resonant frequency. The in-resonance mode is usually employed with the low-power pump lasers to provide larger signals. PAS is ideally a background-free technique: the absorbing gas generates the signal and, in the absence of an absorbing gas, there is no acoustic signal. In real PAS experiments background signals can originate from nonselective absorption by the gas cell windows (coherent noise) and from outside acoustic (incoherent) noise. PAS signals are proportional to the pump laser intensity and therefore PAS has mostly used high-power laser sources, in particular CO₂ and CO lasers. (see Section 2.E). In addition, diode lasers, solid-state lasers,

DFG and OPOs in the infrared have been applied to photoacoustic trace gas detection.

The key features of the photoacoustic technique include (1) excellent detection sensitivities down to sub-ppbv concentrations with powers in the watt range, (2) a large dynamic range, (3) PAS detector responsivity almost independent of the pump wavelength and (4) PAS signal usually directly proportional to the absorbed radiation intensity. However, in trace gas monitoring applications, PAS is limited to point monitoring due to the requirement of an absorption cell.

F Thermal lenses, gratings and deflection

The index of refraction of a material depends upon its temperature. The deposition of energy into a substance by laser irradiation at a vibrational transition results in heating. Consider an IR beam copropagating through a sample with a larger diameter visible laser. The local heating in the center of the visible laser beam creates a lens through the refractive index change that defocuses the visible beam. Thus thermal lensing can be used to detect molecular absorptions. Similarly, if the two beams are of about the same diameter and are crossed at a small angle, the heating by the IR laser on a molecular absorption, with its consequent refractive index change, can lead to a deflection of the visible beam. Or by creating a standing IR wave, a thermal grating can be created in the medium and a visible laser beam diffracted from it.

The thermal lensing methodology goes back to the middle 1970s in the work of Albrecht and co-workers, who used it to detect overtone transitions of aromatic compounds.²⁰⁷ This methodology has never become popular. Since 1996, there have appeared only two papers^{208,209} using mid-IR generated thermal gratings although the thermal grating method has been included in a review on the application of laser spectroscopy to combustion systems.²¹⁰

Thermal deflection spectroscopy^{211,212} is applied extensively to the study of thin films. In this technique, the thermal expansion of the sample upon light absorption is detected. This subject is rather remote from the main thrust of this review, and will not be covered. An interesting extension²¹³ is the use of thermal deflection spectroscopy to investigate electrochemical surfaces. In the gas phase, photothermal deflection has been used to monitor ethylene emission by fruit.²¹⁴ Photothermal changes in refractive index have been used to detect ammonia.²¹⁵

G Double resonance

Double resonance experiments were proposed²¹⁶ and carried out²¹⁷ by Bitter and Brossel. Over the intervening years, double resonance has blossomed into a variety of techniques of molecular spectroscopy and molecular dynamics. The introduction of a second photon provides enormous flexibility. In the following sentences, some of this flexibility will be described. Example papers using a tunable infrared photon as part of the double resonance scheme will be cited. Because of the choice to cite recent work, the primary inventors and original descriptions of the techniques to be outlined

are unfortunately likely to be slighted. Also here experiments using more than two photons are lumped into the category of double resonance.

Double resonance methods can be classified into several categories by: (1) the spectral regions of the two light sources (here at least one will be in the IR), (2) the number of energy levels involved (normally three, but with collisional energy transfer possibly four), (3) the method of detection, (4) the purpose of the experiment (*e.g.* access to spectroscopic information or investigation of dynamics), and (5) whether time resolved (pump-probe) or not.

With one light source fixed to be in the infrared, the other, in principle, could be anywhere in the electromagnetic spectrum. In practice, the other photon involved must be where reasonably powerful light sources are available. This in effect rules out the soft X-ray and shorter wavelength regions. All other regions are fair game with the proviso that if one wants to have a powerful tunable source in the far-IR access to a free electron laser is almost mandatory.

Although more photons and energy levels may be used to detect the spectroscopic signal, most double resonance schemes involve one intermediate level accessed by two photons of different frequencies and can thus be categorized as three level schemes. If the pump and probe photons belong to spectroscopic transitions with no common level, then collisional energy transfer is used to connect the two level schemes. Such four level schemes can be used to study collisional energy transfer,²¹⁸⁻²²⁷ a technique pioneered by Oka around 1970. A more unusual type of four level double resonance scheme uses a collision to transfer population to states not easily directly accessible, to permit spectroscopic study of transitions from these states. Either the molecule of interest may be laser excited and the population allowed to distribute by collision,²²⁸ or a different chemical species may be excited and energy levels of the molecule of interest may be then populated by near-resonant V-V energy transfer.²²⁹

A wide variety of detection schemes are used in double resonance experiments: (1) absorption of one of the frequencies,^{219,225,228-237} (2) LIF,^{218,220-223,227,238-253} (3) detection of fluorescence from photofragments,^{238,241-245} (4) detection of ions, either parent or product,^{247,254-263} and (5) optothermal detection.^{162,174,177,178,264-268} In addition to these methods a couple of specialized techniques have been developed: (1) detection by time of flight of a photofragment²⁶⁹ and (2) detection by deflection in a molecular beam through dressed states with optogalvanic detection.²⁷⁰ This last method is somewhat different from the relatively standard molecular double resonance method where the two focusing fields of molecular beam electric resonance are replaced by two laser beams that move populations with the C field being a microwave field (There appear to be no recent examples of the standard technique using tunable IR lasers). In the deflection experiment²⁷⁰ cited above both infrared and microwave are applied simultaneously and the effect of the double resonance is observed with a single focusing field. What is going on is too complex to describe here.

One purpose for carrying out double resonance experiments is to obtain spectroscopic information, *i.e.* assigned energy levels.^{162,177,178,231-235,237,239-241,247-250,252-255,258,259,261,263,264,267,270} This information can then be interpreted in terms of molecular structure. Or it can provide information about the molecular environment as, for example the environment inside a helium droplet.^{266,267} Or it can be interpreted in terms of intramolecular vibrational energy

redistribution (IVR) through analysis of the coupling of bright states to background levels.^{174,177,178,222,231,238,243,245,249,264,265}

Typical purposes of double resonance experiments carried out in a time resolved manner are to determine rates of collisional energy transfer^{218–227} or to determine state resolved rates of unimolecular decay.^{239,242,244} Most of these time resolved experiments have been done in the gas phase, but there is one recent example of vibrational energy transfer between O₃ molecules in rare gas matrices.²³⁶

Finally, double resonance can be used for analytical chemistry purposes. An example is the use of double resonance in determining OH concentrations in the troposphere.²⁵¹

H Miscellaneous methods

There is extensive work on laser IR multiphoton photolysis. This work is usually done with fixed frequency CO₂ lasers and will not be covered here. Sometimes tunable lasers are used. Thus silicon isotopes have been separated by tunable FEL photodissociation.²⁷¹

4 Applications

There are a wide variety of applications of tunable infrared laser spectroscopy. The principal categories of application are (1) obtaining information about molecular structure, (2) investigating dynamics and (3) analytical applications such as trace gas monitoring. Each of these applications will be taken up in turn.

A Spectroscopy and molecular structure

One of the traditional roles of molecular spectroscopy is to provide information about molecular structure through the determination of molecular geometries from the rotational constants obtained by rotational analysis and the force constant information obtained from vibrational frequencies. As a general purpose tool for high resolution spectroscopy, tunable laser infrared spectroscopy has severe competition from Fourier transform infrared spectroscopy (FTIR). A large FTIR instrument is capable of providing resolution at or very near the Doppler widths of individual gas phase molecular absorption lines while simultaneously providing wide spectral coverage and rather good sensitivity. Because lasers provide a higher spectral intensity at a given frequency than any practical blackbody sources and a very well collimated beam, the true advantage of tunable laser sources for spectroscopy is in providing high sensitivity and short response times. This leads naturally to the application of tunable infrared laser spectroscopy to highly reactive systems such as free radicals, carbon clusters, ions, various reactive metal compounds, and weakly bound complexes, or to situations where the laser power in a small frequency region is required by the detection scheme such as optothermal, photoacoustic, or helium droplet spectroscopies.

Table 1 Tunable mid-infrared laser investigations of stable molecules 1996–2001

Substance	Method	Laser source	Reference
PH ₃	Absorption	Sideband CO ₂	272
CH ₂ FCN	Absorption	Diode	273
CH ₂ BrF	Absorption	Diode	274
CH ₂ FCI	Absorption	Diode	275–277
CHBrCIF	Absorption+others	Diode	278
CS ₂	Absorption	Diode	279
CH ₃ I	Double resonance		235
HCCH	Absorption	Diode	280
ICN	Absorption	Diode	281,282
OCS	Abs, sub-Doppler	Sideband overtone CO	283–285
CH ₂ =(CHCl)	Absorption	Diode	286,287,298
C ₂ F ₆	Abs. jet-cooled	Diode	288
C ₆ H ₆	Abs. jet-cooled	Color center	289
SF ₆	Double resonance	Sideband CO ₂	290
NH ₃	Double resonance		233,234
H ₂ CCO	Double resonance jet-cooled		241
CHCl ₃	Abs. jet-cooled	Diode	291
C ₂ H ₆	Optothermal	Color center	163
H ₂ FCCH ₂ F	Optothermal electric resonance	Sideband CO ₂	161
HF ₂ CCH ₂ F	Optothermal electric resonance	Sideband CO ₂	161
HF ₂ CCHF ₂	Optothermal electric resonance	Sideband CO ₂	292
<i>Cis</i> -HCIC=CFH	Absorption	Diode	293–295
<i>Cis</i> -CHF=CHF	Absorption	Diode	296,297
CH ₃ OH	Double resonance	Sideband CO ₂	237
CH ₃ OH	Optothermal electric resonance		162
	double resonance		
	Absorption		
CD ₃ OD	Absorption	Waveguide CO ₂	299
F ₂ C=CHF	Absorption	Diode	300,301
NO	Abs, sub-Doppler	Sideband CO	302
CO	Absorption	Sideband CO	303

The discussion below is classified by the type of system being investigated. The categories are: (1) stable molecules, (2) radicals, (3) carbon clusters, (4) ions, (5) metal compounds, (6) complexes and (7) condensed phase systems.

1 Stable molecules. Most of the detection methods already considered have been used to obtain the high resolution spectra of stable molecules. It is hard to categorize the various purposes of high resolution investigations of stable molecules. These can range from the measurement of rotational constants, to obtaining data for understanding large amplitude motions, to finding suitable absorption lines for monitoring a substance, or to obtaining highly accurate transition frequencies for metrology purposes. Rather than listing the various investigations on stable molecules by method or purpose, we choose to list them by chemical substance with notes about method and laser source. Table 1 lists investigations of stable molecules by tunable lasers in the mid-IR.

There have been almost as many publications involving the investigation of vibrational overtones in the near-infrared as in the mid-IR. One reason for this is an

Table 2 Spectroscopic investigations of stable molecules in the near-infrared

Molecule	Method	Special aspects	Reference
HCCH	Optothermal	Stark effects	164
H ₃ SiD	Photoacoustic	Also FTIR	304
H ₃ CNO ₂ (Also D substituted)	Photoacoustic	Also FTIR	305–307
C ₆ H ₅ CH ₃ (D substituted species)	Photoacoustic	Also FTIR	308,309
H ₂ O (D substituted species)	Photoacoustic	³¹¹ D ₂ O; ³¹² HDO	310,311
CH ₂ CCH ₂ Cl	Photoacoustic	Also FTIR	312
HCCCN	Double resonance		231
C ₅ H ₅ N	Photoacoustic	Also liquid and non-laser	313
ClCN	Photoacoustic	Ti:sapphire source	314
HSiF ₃	Photoacoustic	Ti:sapphire source	315
HCN	Photoacoustic	Ti:sapphire source	316
SbH ₃	Photoacoustic	Ti:sapphire source	317
CH ₃ C ₅ H ₄ N	Photoacoustic	Also non-laser	318
CO ₂	Photoacoustic		319
OCS	Photoacoustic	Ti:sapphire source	320
2,6-Difluorotoluene	Photoacoustic	Ti:sapphire source	321

interest in IVR, which will be discussed later. Perhaps another is that the development of near-IR laser diodes is far more advanced than that of mid-IR laser diodes making work in the near-IR easier. In Table 2 are listed the publications in the near-IR on the overtone spectra of stable molecules not aimed specifically at obtaining information about IVR as IVR is a subject for later discussion.

2 Radicals. Molecular species that are highly reactive or ionic have always fascinated spectroscopists. Starting almost two hundred years ago, the electronic spectra of very many diatomic molecules have been investigated by their emission in the visible or ultraviolet. Because the excited electronic states of polyatomic molecules can usually find a way to dissociate, a much smaller number of polyatomics have been studied in emission. The electronic absorption spectra of quite a few polyatomic molecules have been studied, mostly in the UV or visible. However, absorption spectroscopies of vibrational or rotational transitions in the infrared and microwave offer a very significant advantage over spectroscopy of electronic transitions, because dissociation of the upper state is impossible energetically. Thus there has been much work in these spectral regions on the spectra of transient species: radicals, ions, and high temperature molecules.

There has been a recent (2000) general review of this area by Hirota³²² in this series. For constantly updated information, Jacox maintains a database *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules* online as part of the NIST Webbook (<http://webbook.nist.gov/>), This is based on her original monograph,³²³ which she also updates in print regularly.³²⁴ In Table 3, publications on radicals since Hirota's review are listed. The criteria for inclusion in Table 3 are much more restrictive than Hirota's review. To be listed in Table 3, a paper must be a tunable laser spectroscopic investigation of a nonmetallic radical and not be an ion or a carbon cluster.

Here we will focus primarily on methodologies for investigating free radical spectra, as the work of Hirota³²² has provided such excellent coverage of the literature through

Table 3 Infrared radical publications 2000–2001^a

Species	Production	Method	Laser source	Reference
D ₃	Discharge	Absorption	DFG	325
HOPO	Discharge	Absorption	Diode	326
CH ₃ CH ₂	Discharge	Jet abs	DFG	327
CIBO	Rxn with disch. prod.	Absorption	Diode	328
BO	Rxn with disch. prod.	Absorption	Diode	329
HCCN	Flash photolysis	Absorption	DFG	330
CN	Discharge	Absorption	Ti:sapphire	331
HCB _r	Flash photolysis	Absorption	Ti:sapphire	332
CCN	Discharge	Absorption	Diode	333
CH ₂	Flash photolysis	Absorption	Ti:sapphire	334
BBr	Discharge	Absorption	Diode	335

^a The year 2001 is incomplete.

1999. Generally there are four methods for the production of radicals for spectroscopic investigation:

1. passing an electrical discharge through a gaseous mixture of a buffer gas containing suitable precursors,
2. producing a flow of highly reactive species usually an atom (F is most used) by a microwave gaseous discharge, which is then mixed with a suitable precursor to produce the radical by a chemical reaction (typically hydrogen atom extraction),
3. flash photolyzing a suitable precursor causing bond rupture,
4. pyrolysis of more stable compounds.

As can be seen from Table 3, the first three methods are used almost exclusively for normal cell absorption spectroscopy. If pyrolysis is used in conjunction with an absorption cell, the pyrolysis is done outside the cell with a fast flow system carrying the pyrolysis products into the cell, since flash pyrolysis of large volumes is difficult. This restricts its use to longer-lived species. However, jet pyrolysis is proving to be a powerful technique.³³⁶

The production of radicals for spectroscopic study by electric discharge has been used effectively and extensively for many years. As a means for the production of radicals in cells, it remains very much a hit and miss proposition. While much is known about the nature of glow discharges in gases, the neutral chemistry in the discharge, which is driven most often by dissociative electron bombardment, is very rarely understood. In contrast, the production of ions for spectroscopic study tends to be better understood as a result of decades of investigations of ion–molecule reactions.

Discharge flow methods using F atom abstraction of hydrogen for radical production usually produce predictable radical products. The products of O atom reactions are somewhat less predictable, but this method for radical production is highly effective and was used in the investigations of CIBO³²⁹ and BO³²⁹ cited in Table 3.

The use of flash photolysis to produce radicals goes back to the pioneering work of Norrish and Porter³³⁷ in the late 1940s. The flash photolysis method, which we think is most appropriately called “kinetic spectroscopy” was used extensively by Herzberg,

Ramsay and their coworkers to investigate the electronic spectra of many small radical species in the decades of the 1950s through the 1980s. The adaptation of kinetic spectroscopy to use with tunable infrared lasers was first carried out by Kim *et al.*³³⁸ and Laguna and Baughcum³³⁹ at Los Alamos National Laboratory. Since we will be returning to this technique in conjunction with the use of tunable infrared laser spectroscopy for kinetics investigations (see Section 4.B.1), it seems appropriate to discuss it in somewhat more detail here.

In the original version of kinetic spectroscopy,³³⁷ the absorption spectrum of radicals was obtained on a photographic plate by firing a photographic flash at known time delay after the photolysis flash. Thus spectra at all relevant wavelengths at a single time after the flash were obtained in a single sequence of two flashes. To use a tunable monochromatic cw infrared laser as the spectroscopic probe, data at a single wavelength but all relevant times are collected with a transient digitizer in a single flash. The photolysis laser is usually an excimer laser permitting the repetition of the experiment at 10–100 Hz as the probe laser is slowly scanned for a spectroscopic investigation. Alternatively the probe laser may be fixed on the peak of an absorption line and the time behavior of the absorption signal may be acquired with averaging over repeated flashes for chemical kinetics studies. Radical chemical kinetics will be discussed in Section 4.B.1.

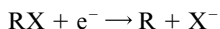
Instead of using excimer laser flash photolysis, mercury sensitized photolysis may be carried by introducing a small amount of mercury vapor into the absorption cell and flash photolyzing with a mercury flash lamp.³⁴⁰

a Spectroscopy of jet-cooled radicals. The observation and analysis of the high resolution mid-IR spectra of transient free radical molecules provides a powerful and nearly universal means for obtaining information about their molecular structure and a definitive means for monitoring their concentrations. However, the rotational assignment of the infrared spectra of free radicals becomes increasingly difficult as the size of the species increases. Typically, for rigid species at dry ice temperature, assignment is just feasible for molecules containing three first row atoms. If large amplitude motions such as low barrier internal rotations or tunnelings are present, even molecules with only two first row atoms, *e.g.* CH₃CH₂ or H₂COH, produce dry ice temperature mid-IR spectra that are complex and difficult to analyze. As is well known, the rotational congestion causing this problem can be greatly reduced by supersonic expansion cooling to a few K, thereby greatly reducing the number of rotational levels thermally populated.

Radicals can be produced in the nozzle of a slit jet, cooled by supersonic expansion, and their infrared spectra observed by absorption spectroscopy. Electric discharge,³⁴¹ flash photolysis,³⁴² or pyrolysis^{336,343} may be used to produce the radicals. The radical of interest is produced in relatively high concentration ($\sim 10^{15}$ cm⁻³) at or just inside the nozzle of a slit jet expansion. Only a moderate loss of the radicals by chemical reaction typically takes place during the expansion process. Expansion greatly reduces the concentration of the radicals, but the adiabatic cooling of the supersonic expansion process is simultaneously reducing the number of rotational states populated. For small quantities of radicals and precursor seeded into a rare gas expansion, the temperature is proportional to $n^{-2/3}$ (where n is the number density) by the thermodynamics of reversible adiabatic expansion. For a nonlinear polyatomic radical, the rotational partition function is proportional to $T^{3/2}$. Therefore, the number of radicals

in the lowest rotational state is unchanged by the expansion. Reasonable signals can be expected and are indeed observed. With an absorption pathlength of 50 cm obtained by using a slit 2 cm in length and 25 passes with a Herriott cell, an absorption of 5% has been observed³⁴⁴ for CH₃ produced by flash photolysis of CH₃I.

Each of the production methods has advantages and disadvantages. The work of Nesbitt^{327,341,345-347} uses a very short discharge region (~1 mm) just prior to the expansion so that the gas is subjected to the hostile environment of the discharge for only 1–2 μs. Nesbitt has often been able to find an I- or Br-substituted precursor where the radical formation is likely to be the result of dissociative electron attachment in the discharge.



where X = Br or I. The duty cycle of the system is relatively high with the discharge being on for ~1 ms per gas pulse and a repetition rate of ~10 Hz. The radical concentration may be AC modulated at up to 100 kHz, greatly increasing sensitivity.³⁴⁷

The principal advantage of flash photolysis radical preparation over the electrical discharge is that the photolysis process is usually well understood and can be rather reliably tailored to produce the species of interest. Excimer laser flash photolysis typically produces a somewhat higher signal than electric discharge.³⁴⁴ However, the duty cycle is quite low as the radical is present for only about 3 μs for each gas pulse. However, because the detector level just before the absorption signal appears is subtracted from the detector level when the signal is present, low frequency noise is effectively eliminated.

Pyrolysis can also be a very clean source of the species of interest.³⁴³ As a radical preparation method, it has been developed to a very high degree by Chen³⁴⁸ for mass spectrometric investigations. Because the final jet temperature is proportional to the pre-expansion temperature, the temperature in the probe region tends to be higher, e.g. 45 K for a nozzle temperature of 1500 K, as compared with 15–20 K for discharge preparation and as low as 8 K for flash photolysis preparation.

At present there are only a few publications from the time period after the Hirota review, most of which are concerned with technique and all of which have already been cited. There are only three radicals that have been extensively investigated: allyl,³⁴⁶ chloroketene³⁴³ (if chloroketene can be counted as a radical), and ethyl.³²⁷ However, carbon clusters have been produced and observed with jet cooling and will now be discussed.

3 Carbon clusters. The spectra of carbon clusters, carbon cluster ions, and slightly hydrogenated carbon clusters have been the subject of intense investigations for more than a decade. Much of this work has been in the visible and UV (John Maier) or in the microwave (Gottlieb, Thaddeus, and McCarthy) and therefore is not covered by the present review. Saykally, who has been at the forefront of this research in the IR, has recently reviewed the field.³⁴⁹ Subsequent to this review by Vanorden and Saykally, there has been only one IR gas phase carbon cluster paper³⁵⁰ on linear C₁₀.

4 Ions. The vibrational spectra of ions are covered by the Hirota review³²² and the Jacox database. If we exclude ions in clusters or complexes with neutral molecules,

only a few papers on ions have been published since 1999. Several are on H_3^+ , including a review.³⁵¹ There is a paper on combination bands of H_3^+ ,³⁵² and two on H_3^+ kinetics in the discharge.^{353,354} There is one paper³⁵⁵ on the near-IR electronic transition of CS^+ studied in absorption with a Ti:sapphire laser source. There are two papers^{263,356} on special spectroscopic techniques for investigating ions. In one,³⁵⁶ ions of the aromatic compounds, naphthalene, phenanthrene, anthracene, and pyrene, are created by excimer laser ionization and stored in a quadrupole ion trap. They are then irradiated with a free electron laser and undergo multiphoton fragmentation. The fragment ions are detected by mass spectrometry, thereby producing the infrared spectrum of the parent ions. In the second paper,²⁶³ high Rydberg states are produced by two color excitation. These are then vibrationally excited with an infrared laser and the IR absorption detected by the consequent autoionization.

A number of papers on clusters or complexes between ions and neutrals have been published. These will be discussed in the sections on complexes.

5 Metal compounds. Five experimental spectroscopy papers using tunable infrared lasers on metal compounds have been published in the period 2000 to 2001. The first is a diode laser absorption investigation at 1000 K of the vibrational spectrum of $RbCl$ ³⁵⁷ in which vibrational states up to $\nu''=8$ and $J''=160$ have been observed and assigned. Two^{358,359} are jet cooled spectra of transition metal carbonyl compounds from the Davies group: iron pentacarbonyl³⁵⁸ and tungsten hexacarbonyl.³⁵⁹ The final papers describe spectra observed through thermionic emission produced by multiphoton excitation of nanocrystals with a free electron laser. In one, the spectra of zirconium oxide nanocrystals were observed.³⁶⁰ In the other, vanadium carbide nanocrystals from $V_{14}C_{12}$ to $V_{32}C_{32}$, were observed.³⁶¹ In addition to spectroscopic investigations, reaction kinetics of metal compounds can also be investigated using infrared kinetic spectroscopy (see Section 4.B.1).

6 Complexes. For the reader deeply interested in complexes, in late 2000 an entire issue of *Chemical Reviews* (vol. 100, Issue 11, November 2000) was devoted to van der Waals molecules. Two species can be bound together by forces weaker than a normal chemical bond. The energy of the bonding can range from those of very weak van der Waals attractions of a few cm^{-1} to nearly the strength of a chemical bond from the interaction between a Lewis acid and a Lewis base. The types of forces can be enumerated as (1) van der Waals, (2) Lewis acid–base, (3) ion–molecule interactions, (4) charge transfer interactions, (5) multipole interactions and (6) H-bonded interactions. The criteria used for a van der Waals molecule in the special issue of *Chemical Reviews* appears to include most of these interactions.

a Van der Waals, multipole, and Lewis acid–base bonding complexes. The field of complexes bound by van der Waals, multipole (e.g. dipole–dipole) or Lewis acid–base bonding remains active. Table 4 gives the titles and references to tunable infrared laser studies in this area.

b H-bonded. In Table 5 publications from 1996 to 2001 on neutral hydrogen bonding complexes are listed. Of particular interest is Saykally's mammoth project, which accounts for about half of Table 5, to determine the potential function for liquid water through studying water clusters.³⁷⁸ Most of his work has used tunable

Table 4 Tunable infrared laser studies of van der Waals molecules

Article title	Reference
Near-infrared laser spectroscopy of the Ar-C ₂ HD complex—Fermi resonance assisted vibrational predissociation	362
Infrared spectra of the Kr-CO and Xe-CO van der Waals complexes	363
Slit jet infrared absorption spectroscopy of N ₂ -HCl complexes	364
Vibrational predissociation of an inert gas cluster containing an active molecule—the ν_3 spectrum of Ar ₃ -HF	365
A study of the intermolecular ν_5^1 vibration in OC-(HCl)-Cl-35 based on near-infrared spectroscopy	366
High-resolution infrared diode laser spectroscopy of Ne-N ₂ O, Kr-N ₂ O, and Xe-N ₂ O	367
Pulsed molecular beam infrared absorption spectroscopy of HCCH-CO	368
Gentle recoil synthesis of free-radical clusters <i>via</i> unimolecular photolysis of closed shell complexes	369
Identification of the OC-IH isomer based on near-infrared diode laser spectroscopy	370
Isotopic probing of very weak intermolecular forces: Microwave and infrared spectra of CO-He isotopomers	371
Rovibrational spectroscopy of the C ₂ H ₂ -Ar van der waals complex, using a fluorescence depletion infrared-ultraviolet double resonance technique	239
The infrared spectrum and internal rotation barrier in HF-BF ₃	166
High resolution infrared spectroscopy and structure of CO-N ₂ O	372
Spectroscopy and structure of the open-shell complex O ₂ -N ₂ O	373
Intermolecular state dependence of the vibrational predissociation of N ₂ HF	374
Free-jet IR spectroscopy of SiF ₄ -N ₂ and SiF ₄ -CO complexes in the 10 μ m region	376
High resolution mid-infrared spectroscopy of Ar-H ₂ O—the ν_2 bend region of H ₂ O	377
The infrared spectrum of the Ar-CO complex—comprehensive analysis including van der Waals stretching and bending states	377

far-infrared radiation obtained by mixing a tunable microwave source with a fixed frequency far-IR laser.

c Ion-molecule clusters. High resolution investigations of clusters containing ions have been reviewed in 2000 by Hirota³²² and by Bieske and Dopfer.⁴⁰⁴ Publications in this area in 2000 that may have been published too late for the review of Bieske and Dopfer⁴⁰⁴ and 2001 publications are listed in Table 6.

In addition to the high resolution investigations included in these two reviews, lower resolution studies of ion complexes are also carried out. In 1997, Lisy reviewed the work on solvated alkali metal ions.⁴⁰⁶ Table 7 lists lower resolution tunable infrared laser publications on ion complexes.

7 Condensed phase systems. Typically, condensed phase systems have phonon broadened lines. Tunable IR lasers therefore offer no advantages in terms of resolution over FTIR. Normally very high sensitivity is not required for condensed systems so that the potentially higher sensitivity of laser methods is unimportant. However, there are a few special circumstances where tunable infrared lasers prove valuable.

a Hole burning and isomerization spectroscopies. In the solid phase, infrared lasers may be used to burn holes in heterogeneously broadened lines. Strauss has used such hole burning to investigate various types of orientational isomerization in a number

Table 5 Tunable infrared laser publications of hydrogen bonded non-ionic complexes

Title	Reference
Probing hydrogen bond potentials <i>via</i> combination band spectroscopy—a near-infrared study of the geared bend van der waals stretch intermolecular modes in (HF) ₂	379
Electronic and infrared spectra of jet-cooled 4-aminobenzonitrile–H ₂ O. Change of NH ₂ from proton acceptor to proton donor by CN substitution	380
Far-infrared laser vibration–rotation–tunneling spectroscopy of water clusters in the librational band region of liquid water	381
High symmetry effects on hydrogen bond rearrangement: The 4.1 THz vibrational band of (D ₂ O) ₄	382
Vibrational spectroscopy of single methanol molecules attached to liquid water clusters	383
Infrared spectrum of the water–carbon monoxide complex in the CO stretching region	385
Characterization of the (D ₂ O) ₂ hydrogen-bond-acceptor antisymmetric stretch by IR cavity ringdown laser absorption spectroscopy	386
4.5 μm diode laser spectrum of (HI) ₂	386
The infrared spectroscopy and dynamics of OCO–HCl and SCO–HCl—an example of mode specific intermolecular energy transfer	168
The far-infrared vibration–rotation–tunneling spectrum of the water tetramer-d ₈	387
Quantifying hydrogen bond cooperativity in water—VRT spectroscopy of the water tetramer	388
Far-infrared VRT spectroscopy of two water trimer isotopomers—vibrationally averaged structures and rearrangement dynamics	389
Characterization of a cage form of the water hexamer	390
Vibration-rotation tunneling spectra of the water pentamer—structure and dynamics	391
Terahertz laser vibration–rotation–tunneling spectroscopy of the water tetramer	392
Terahertz laser vibration–rotation–tunneling spectroscopy and dipole moment of a cage form of the water hexamer	393
Direct measurement of water cluster concentrations by infrared cavity ringdown laser absorption spectroscopy	394
Pseudorotation in water trimer isotopomers using terahertz laser spectroscopy	395
Terahertz laser vibration–rotation–tunneling spectrum of the water pentamer-d ₁₀ —constraints on the bifurcation tunneling dynamics	396
Infrared cavity ringdown spectroscopy of water clusters: O–D stretching bands	397
Quantitative characterization of the water trimer torsional manifold by terahertz laser spectroscopy and theoretical analysis. II. (H ₂ O) ₃	398
Infrared cavity ringdown spectroscopy of the water cluster bending vibrations	399
Quantitative characterization of the (D ₂ O) ₃ torsional manifold by terahertz laser spectroscopy and theoretical analysis	400
Terahertz laser spectroscopy of the water dimer intermolecular vibrations. I. (D ₂ O) ₂	401
Terahertz laser spectroscopy of the water dimer intermolecular vibrations. II. (H ₂ O) ₂	402
Terahertz vibration–rotation–tunneling spectroscopy of water clusters in the translational band region of liquid water	403
Far-infrared laser vibration–rotation–tunneling spectroscopy of water clusters in the librational band region of liquid water	382

salts and polymers.^{428–441} A different kind of experiment with a similar flavor has been carried out by Roubin *et al.*⁴⁴² Here the rotational isomerization induced by free electron laser irradiation of CH₂D–CH₂D isolated in rare gas matrices was investigated.

Table 6 High resolution studies of ion–molecule clusters in 2000 and 2001

Title	Reference
Microsolvation of the water cation in argon: II. Infrared photodissociation spectra of $\text{H}_2\text{O}^+-\text{Ar}_n$ ($n = 1-14$)	406
Observation of the infrared spectrum of the ν_3 band of the argon–ammonium ionic complex	407
Potential energy surface and infrared spectrum of the $\text{Ar}-\text{H}_2\text{Cl}^+$ ionic complex	408
The intermolecular potential of NH_4^+-Ar II. Calculations and experimental measurements for the rotational structure of the ν_3 band	409
Linear and centrosymmetric $\text{N}_2\cdot\text{Ar}^+\cdot\text{N}_2$	410
High resolution infrared direct absorption spectroscopy of ionic complexes	411
Infrared spectrum and ab initio calculations of the HNH^+Ne open-shell ionic dimer	412
Intermolecular potential energy surface of the proton-bound $\text{H}_2\text{O}^+-\text{He}$ dimer: <i>Ab initio</i> calculations and IR spectra of the O–H stretch vibrations	413
Microsolvation of the water cation in neon: Infrared spectra and potential energy surface of the $\text{H}_2\text{O}^+-\text{Ne}$ open-shell ionic complex	414
Spectroscopic and theoretical characterisation of the ν_2 band of $\text{Ar}\cdot\text{DN}_2^+$	415

Table 7 Lower resolution studies of ion–molecule clusters 1996-2001

Title	Reference
Infrared spectroscopy of $\text{NH}_4^+(\text{NH}_3)_{n-1}$ ($n = 6-9$)—shell structures and collective ν_2 vibrations	416
Electronic structures of cobalt cluster cations—photodissociation spectroscopy of $\text{Co}_n^+ \text{Ar}$ ($n = 3-5$) in the visible to near-infrared range	417
Pump–probe photodepletion spectroscopy of $(\text{C}_6\text{H}_6)_2^+$ —identification of spectrum in the charge resonance band region	418
Characterization of the hydrogen-bonded cluster ions	419
Hydrogen bonding in metal ion solvation—vibrational spectroscopy of $\text{Cs}+(\text{CH}_3\text{OH})_{(1-6)}$ in the 2.8 μm region	420
Vibrational predissociation spectroscopy of $\text{Cs}^+(\text{H}_2\text{O})_{(1-5)}$	421
Microsolvation of the ammonium ion in argon—infrared spectra of $\text{NH}_4^+-\text{Ar}_n$ complexes ($n = 1-7$)	422
Energy partitioning following the infrared photofragmentation of $\text{SF}_6\cdot(\text{C}_6\text{H}_6)^+$ cluster ions	423
Structures and isomeric transitions of $\text{NH}_4^+(\text{H}_2\text{O})_{(3-6)}$ —from single to double rings	424
Infrared spectroscopy of resonantly ionized $(\text{Phenol})(\text{H}_2\text{O})_n^+$	425
Infrared spectroscopy of jet-cooled neutral and ionized aniline–Ar	260
The infrared spectrum of the benzene–Ar cation	426
Charge transfer interaction in the acetic acid–benzene cation complex	427

b Para-H₂ matrix isolation. In recent years Oka and Momose have developed the field of matrix isolation spectroscopy using para-H₂ as the matrix. Momose has published a review of some of this work.⁴⁴³ This extremely soft matrix permits rotation of the isolated molecules for larger species than the harder rare gas matrices traditionally used. Usually FTIR is used for these investigations, but often the resolution provided by FTIR is insufficient. The papers published since 1996 in this area using tunable IR lasers are given in Table 8.

Table 8 Papers using tunable infrared lasers and *para*-H₂ matrices since 1996

Title	Reference
High-resolution infrared spectroscopy of isotopic impurity Q ₁ (0) transitions in solid parahydrogen	444
Infrared spectroscopic study of rovibrational states of methane trapped in parahydrogen crystal	445
High-resolution laser spectroscopy of methane clusters trapped in solid parahydrogen	446
Impurity molecules in parahydrogen crystal—high resolution infrared spectroscopy	447
Tunneling chemical reactions in solid parahydrogen—a case of CD ₃ +H ₂ →CD ₃ H+H at 5 K	448
High-resolution infrared spectroscopy of the <i>J</i> = 1 H ₂ pair in parahydrogen crystals	449
High-resolution spectroscopy of ions in gamma-ray irradiated solid parahydrogen	450
Observation of the high-resolution infrared absorption spectrum of CO ₂ molecules isolated in solid parahydrogen	451
Sharp spectral lines observed in gamma-ray ionized parahydrogen crystals	452

c Helium droplets. Another sort of matrix medium is nanodroplets of helium formed into a molecular beam and probed optothermally. The probing radiation can be in any part of the electromagnetic spectrum. Thus only part of the research in the area of helium nanodroplets also involves tunable infrared laser spectroscopy. There is much work, for example, in electronic spectroscopy. A special topics section of *The Journal of Chemical Physics* has just appeared (vol. 115, Issue 22, December 8, 2001) containing several minireview articles about the general subject. One⁴⁵³ of these reviews is directly concerned with tunable infrared laser spectroscopy of helium droplets. There are also several rather recent reviews of the general area.^{454–458} A fascinating aspect of these systems is that often the impurity species in the droplet being probed exhibits rotational structure, but with smaller rotational constants, which are 70% (or more) of those of the free molecule for hydrides, but otherwise often much smaller than those of the free molecule. Because this subject has been covered so extensively so recently, it will not be considered further here.

d Surfaces. Tunable infrared lasers are used in a variety of ways to probe surfaces and interfaces. By far the most important methodology is sum frequency generation at the surface. The basis for this method has been described and references to fifteen reviews related to this subject have been given in a previous Section on techniques (3.D). As the subject is so vast that it demands an entire review to itself, no further discussion of the general area will be given here. However, a promising development⁴⁵⁹ in surface imaging by near-field microscopy combined with sum frequency generation demands to be mentioned.

Apart from the area of sum frequency generation, there are other interesting applications of tunable infrared laser spectroscopy to surface science. These can be broken down into experiments probing the surface itself or experiments probing gas phase molecules. The gas phase molecules can be either scattering from the surface,¹⁸⁰ desorbing from the surface after chemical reaction⁴⁶⁰ or subliming from the surface without chemical reaction.⁴⁶¹ Alternatively the sticking coefficients of gas phase molecules, laser excited vibrationally, may be explored.⁴⁶² The vibrational spectra of molecules on the surface may be investigated using various non-sum frequency laser techniques.^{463–466}

B Dynamics

Tunable infrared laser spectroscopy can be applied to the study of various dynamic processes. These can either be the chemical kinetics studies of overall rates or various types of state-to-state dynamics.

1 Chemical kinetics. The kinetics of chemical reactions can be probed with infrared kinetic spectroscopy (IRKS) as described briefly in the techniques section. This topic has been the subject of a quite recent (2001) review.⁴⁶⁷ Some additional articles⁴⁶⁸⁻⁴⁷¹ in the area appeared in 2001. The Taatjes and Hershberger review⁴⁶⁷ does not cover kinetics work on metal compounds.⁴⁷²⁻⁴⁷⁹

2 State-to-state dynamics. For the past thirty-five years, many physical chemists have been fascinated with unraveling the dynamical behavior of molecules at the level of individual quantum states or at least of a fairly restrictive collection of quantum states. These processes can take the form of dynamical processes taking place in a single isolated molecule or they can result from collisions between molecules. For the single molecule the processes are (a) the closely related processes of intramolecular vibrational redistribution (IVR) and unimolecular decomposition and (b) photolysis. Collisional processes include (i) pressure effects on spectroscopic lines, (ii) energy transfer and (iii) its competition with unimolecular decay, and (iv) reactive collisions.

a IVR and unimolecular decomposition. In its most simplistic form, the normal means for applying spectroscopy to IVR is through the Fourier transform theorem. By taking high resolution infrared spectra of a polyatomic molecule, the energy eigenstates that couple with the radiation field can be observed and their intensity measured. For small molecules or low photon energies, the density of states at the level of the upper state of the spectroscopic transition is small and the observed transitions can be readily characterized by the usual language of normal modes, fundamentals, overtones, combination bands, and the semirigid rotor. However, at higher energies, where the density of states is large, the 'bright' spectroscopic states that carry the oscillator strength begin to interact with the 'dark' states that carry negligible oscillator strength through anharmonic terms in the Hamiltonian and Coriolis interactions. By characterizing the frequency spread over which a bright state shares its intensity and, statistically, the number of new transitions observed, information can be garnered about the strength of the coupling of the bright states to a subset of the background states and the number of actively coupling background states. Through the Fourier transform theorem coupling frequency behavior to time behavior, this provides information about the initial flow of energy from the vibrational state excited into other nearby states, and thus about IVR.

In reality the subject is far more complicated than the simple description given above and there has been considerable progress in it. Although there are a number of recent reviews of various aspects of the area, the most recent reviews⁴⁸⁰⁻⁴⁸² that appear to be fairly directly related to infrared laser spectroscopy date back several years.

In the area relating IVR to unimolecular decomposition, there is a very recent review by Callegari and Rizzo⁴⁸³ that describes a method for using a near-infrared laser to select a state that is then further pumped up by a second laser to a vibrational

Table 9 Publications in IVR and unimolecular decomposition relevant to tunable IR laser spectroscopy since 1996

Title	Reference
Molecular-beam infrared–infrared double-resonance spectroscopy study of the vibrational dynamics of the acetylenic C–H stretch of propargyl amine	177
Transient electronic absorption of vibrationally excited CH ₂ I ₂ : Watching energy flow in solution	484
Secondary time scales of intramolecular vibrational energy redistribution in CF ₃ H studied by vibrational overtone spectroscopy	238
Intramolecular energy transfer in highly vibrationally excited methanol. I. Ultrafast dynamics	485
Intramolecular energy transfer in highly vibrationally excited methanol. II. Multiple time scales of energy redistribution	243
Intramolecular energy transfer in highly vibrationally excited methanol. III. Rotational and torsional analysis	486
Eigenstate resolved infrared–infrared double-resonance study of intramolecular vibrational relaxation in benzene—first overtone of the CH stretch	264
The spectroscopy and intramolecular vibrational energy redistribution dynamics of HOCl in the $\nu(\text{OH}) = 6$ region, probed by infrared-visible double resonance overtone excitation	245
Intramolecular vibrational redistribution in aromatic molecules. I. Eigenstate resolved CH stretch first overtone spectra of benzene	265
Doorway state enhanced intramolecular vibrational energy redistribution in the asymmetric =CH ₂ hydride stretch of methyl vinyl ether	178
Chromophore dependence of intramolecular vibrational relaxation—Si–H stretch second overtone <i>versus</i> C–H stretch first overtone in methylsilane	179
Vibrational relaxation of OH and OD stretching vibrations of phenol and its clusters studied by IR–UV pump–probe spectroscopy	487
High-resolution spectrum of the $3\nu_1$ band of cyanoacetylene obtained <i>via</i> infrared/infrared double resonance	231
Molecular beam infrared spectrum of nitromethane in the region of the first C–H stretching overtone	176
Relaxation within and from the (3 ¹ 2 ⁴ 5) and (3 ¹ 4 ¹ 2 ⁴ 5 ¹) Fermi dyads in acetylene—vibrational energy transfer in collisions with C ₂ H ₂ , N ₂ and H ₂	222
State-to-state studies of intramolecular energy transfer in highly excited HOOH(D): Dependencies on vibrational and rotational excitation	249
Intramolecular vibrational dynamics of the asymmetric =CH ₂ hydride stretch of isobutene	175
Eigenstate resolved infrared and millimeter-wave–infrared double resonance spectroscopy of methylamine in the N–H stretch first overtone region	174
Sub-doppler infrared spectra and torsion–rotation energy manifold of methanol in the CH-stretch fundamental region	162
Sub-doppler infrared spectra of the OH-stretch fundamental of C-13-methanol	488
State-to-state studies of intramolecular dynamics and unimolecular reactions	489
Hydrogen bond breaking dynamics of the water trimer in the translational and librational band region of liquid water	490

state above the dissociation threshold with the OH reaction products observed and probed by state by pumping them in the UV and observing the fluorescence.

There are a number of papers in the area that are listed in Table 9.

The rate of unimolecular decay can be measured by measuring linewidths. An example is the investigation of the decay of CH₄-OH complexes by an infrared–

UV double resonance method.²⁵² As mentioned previously, the optothermal method may be used to investigate unimolecular dissociation of complexes.^{173,491}

b States produced by photolysis. Individual states produced by photolysis can be investigated by infrared absorption spectroscopy. A recent example is the determination of the branching ratio into O(¹D) in the photolysis of NO₂ at 193 nm.⁴⁹² Zhang and Hossenlopp⁴⁹³ have observed the bending excitation of CO₂ when anhydrides are photolyzed using IR diode laser probing. The vibrational excitation of CD₃ from the flash photolysis of d₆-acetone has been estimated.⁴⁹⁴ with IR diode laser probing. Alternatively, a particular rovibrational state of a molecule^{269,495} or cluster⁴⁹⁶ can be prepared with IR laser pumping, the system UV photodissociated and final products probed by LIF.

c Collisional processes. There are several processes that result from molecular collisions: pressure effects on spectroscopic lines (e.g. line broadening or narrowing), intermolecular vibrational energy transfer, rotational energy transfers, and chemical reaction. Tunable infrared laser spectroscopy has been used to investigate all of these processes.

i Pressure effects on spectroscopic lines. There have been several recent investigations of pressure effects on lineshapes.^{497–510} Some investigate pressure broadening of individual lines^{505,508,510} including, in some cases,^{508,510} theoretical treatments. There is also a recent study showing collisional line narrowing⁵⁰⁹ and several investigations of line mixing phenomena have been reported.^{506,507,510} Finally there is a report²³⁷ of pressure effects on the microwave line shape in microwave optical double resonance investigations of methanol using, as the IR source, microwave sidebands of a CO₂ laser.

ii Vibrational and rotational energy transfer. There is a not very recent (1996) review in this area.⁵¹¹ Vibrational energy transfer of small molecules in the gas phase has been investigated⁵¹² for very highly excited OH ($\nu=9$). Vibrational relaxation can also be investigated in matrix isolation by pump–probe methods as has been done for ozone in rare gas matrices.²³⁶ There have been several studies, by two different groups, of vibrational energy transfer including rotational state changes in acetylene using IR–UV double resonance.^{220–224,227,513} Infrared–UV double resonance has also been employed to investigate rotational changes in vibrational energy transfer in NO.^{218,226} Infrared–infrared double resonance has been used to investigate vibrational and rotational energy transfer in ozone.²²⁵ Nesbitt has developed a method for studying rotational energy transfer in a time and frequency resolved manner.^{514–516} He has extended the method to resolution of translational energies using the Doppler effect.^{517,518} Several other ingenious methods for investigating collisional energy transfer have been developed: Hermans *et al.* use light-induced drift,⁵¹⁹ Millot and Roche populate a particular state by SEP and then follow the population shifts upon collision with IR laser absorption spectroscopy;⁵²⁰ Kalinin *et al.* investigate cooling in a jet by diode laser absorption spectroscopy.⁵²¹

Flynn has developed a method for investigating collisional energy transfer between large molecules and small marker or probe molecules.^{522–525} He excites the large molecule electronically by a UV laser pulse and then observes the excitation of the probe molecule, typically CO₂, using a tunable diode laser to observe the rotationally resolved spectrum of the probe. This approach can yield the collision probability

function, $P(E, E')$, for transitions from energy E to energy E' .⁵²² This method is used by other groups.⁵²⁶

iii States produced by photodissociation. The competition between vibrational deactivation and photodissociation can also be studied by the method of Flynn and co-workers.⁵²⁷⁻⁵³⁰ He excites pyrazine and diazabenzenes in the UV and observes both the photoproduct, HCN, and vibrational excitation of the CO₂ bath gas with a tunable diode laser.

iv Reactive collisions. Nesbitt has used crossed supersonic jets to investigate the state distributions of the products of the reaction⁵³¹⁻⁵³⁴ $F + H_2 \rightarrow HF + H$ and the reaction^{535,536} $F + CH_4 \rightarrow CH_3 + HF$. The rovibrational energy distribution of the HF was obtained by probing HF with a single frequency laser. For the latter reaction, the HF Doppler profiles provided information on the angular distribution and the HF kinetic energy distribution.⁵³⁶

MacDonald *et al.*^{537,538} have investigated the nascent rovibrational distribution of HCN from the reaction of CN with H₂.

C Analytical applications

The analytical applications of infrared spectroscopy constitute a huge field. Some recent general texts on the subject are the book edited by Stuart and Ando⁵³⁹ and the handbook on near-IR spectroscopy edited by Burns and Ciurczak.⁵⁴⁰ There have been a number of recent collected conference proceedings on atmospheric monitoring⁵⁴¹⁻⁵⁴⁷ and on industrial applications⁵⁴⁸ and process control.⁵⁴⁹ These books are by no means limited to tunable laser spectroscopies, but are cited to provide a general background.

1 Principles of quantitative gas phase absorption spectroscopy. All analytical applications share a common background. The substance to be analyzed is typically a mixture of several to a number of substances. For all linear spectroscopy, the Beer–Lambert law is expected to hold so that the base e absorbance of a substance can be expressed as

$$A(\nu) = (\sigma_1(\nu) N_1 + \sigma_2(\nu) N_2 + \dots)L$$

where A is the absorbance at frequency ν , $\sigma_i(\nu)$ is the absorption cross-section of substance i at frequency ν , N_i is the concentration of i in molecules per unit volume, and L is the pathlength. The simplest case is for one $\sigma_i(\nu)N_i$ to be much larger than any other term in the expression so that the absorbance at frequency ν is effectively determined by a single substance. This simple case is rarely realized except in high resolution gas phase spectroscopy of small molecules on carefully selected absorption lines. If the simple case is not realized, it is still possible to determine the concentration of all species present by measuring the absorbance at a number of frequencies and inverting the resulting system of equations, provided that the $\sigma_i(\nu)$ are all known at each frequency.

In the gas phase, the absorption cross-section lineshape for a single rovibrational line depends upon the pressure, but the integral of the cross-section over the line profile does not. The lineshape is usually rather well approximated by the Voigt

function, a transcendental function (identical with the imaginary part of the plasma dispersion function) obtained from the convolution of a Gaussian with a Lorentzian function. In order to compute the absorption cross-section $\sigma(\nu)$ at frequency ν for a single line of a single substance, one must know the values of ν_0 (the line center frequency), S (the integrated line strength) and γ (the pressure broadening coefficient). These parameters have been determined for many lightweight gas molecules across the infrared spectrum, and compiled into extensive databases such as HITRAN⁵⁵⁰ and GEISA.⁵⁵¹ Numerically accurate absorption spectra can be computed based on these tabulated data, not only for single gas species but also for gas mixtures.

In trace gas sensing applications, self-broadening and broadening against other trace gases can be neglected in calculations, and dry air-broadening alone will suffice. At atmospheric pressure, $\gamma P \gg \Delta\nu_D$, so that the Doppler contribution to the overall linewidth can often be neglected, and the line shape be treated as pure Lorentzian. Likewise, at pressures low enough to ensure $\gamma P \ll \Delta\nu_D$, the line shape can be treated as pure Gaussian. In either case, calculation of the line profile is simplified considerably. At intermediate total pressures where $\gamma P \sim \Delta\nu_D$, which for most lightweight gases is in the range from 5 to 200 Torr, calculation of the Voigt profile is necessary to obtain numerically accurate absorption spectra. Methods for approximate calculation of the Voigt profile, and the related plasma dispersion function, are now a well-developed subject. The approximations published by Humlicek⁵⁵² are particularly useful for this purpose.

2 Detection Techniques. *a Balanced and balanced-ratiometric detection.* Laser intensity noise and drift may limit the sensitivity of absorption measurement. In this situation, balanced detection may be used to recover small absorption signals. The detected noise of an equal-intensity replica of the probe beam, such as that created by a variable-ratio beamsplitter, is subtracted from noise detected in the probe beam, thus leaving only the uncompensated weak absorption signals of interest. The variable-ratio beamsplitter can be made by placing a polarization rotator (a half-wave plate) in series with a polarizing beamsplitter cube. With the input polarization rotated about 45°, the beams emerging from the beamsplitter cube carry equal amounts of power P , and power noise ΔP . In the absence of absorption, the photo-currents generated by the (identical) signal and reference detectors can be subtracted to cancel laser amplitude fluctuations. When one of the beams is attenuated due to small absorption a , by a gas, the balance of photo-currents is disturbed, and a signal is seen at the output of the amplifier. Adjustment of the beam splitting ratio ('zeroing') is obviously necessary, as the signal and reference detectors will have unequal responses, and there are inevitably differences in the optical transmissions of the signal and reference arms. Furthermore, the detectors must have essentially identical frequency response characteristics at all relevant frequencies in order to cancel noise.

An implementation of this method that avoids the need for exact balancing the signal and reference light was proposed by Hobbs⁵⁵³ and commercialized by New Focus and Physical Sciences, Inc. It is known as balanced ratiometric detection (BRD). It employs electronic circuitry to compute a log ratio of photo-currents, rather than their difference, *and* to cancel noise currents at the same time. This analog divider uses logarithmic conformance and tight symmetry of base-emitter curves of a matched transistor pair. This scheme provides nearly perfect cancellation of noise

currents, even when the reference beam carries twice the power of the signal beam. Since the signal *versus* reference current balancing is performed by means of electronic feedback, no physical adjustment of the beam splitting ratio is necessary. The BRD differential response to absorption signals depends on the ratio of the signal and reference currents, which changes when the signal beam is partially absorbed. It also depends on temperature because the transistor base-emitter voltage does, and additional compensation circuitry is needed to produce a useful output voltage V_{out} that is linearly proportional to the absorbance. Noise-equivalent absorbances as low as $2 \times 10^{-7} \text{ Hz}^{-1/2}$ have been demonstrated by Allen and co-workers,⁵⁵⁴ close to the limit imposed by shot noise.

b Frequency- and wavelength-modulation spectroscopy. The ability of a diode laser to change its emission wavelength with injection current, and to do so very rapidly, permits frequency modulation spectroscopy.⁵⁵⁵ The diode tuning response depends on the modulation rate and ranges from 2–3 GHz mA^{-1} at low frequencies to under 300 MHz mA^{-1} at high frequencies. Frequency modulation is always accompanied by amplitude modulation, as the injection current also controls the laser output power. Sine-wave modulation of the diode laser has the effect of creating multiple side-bands in its otherwise nearly monochromatic emission spectrum. Each side-band is separated from the carrier by an integer multiple of the modulation frequency Ω .

In *frequency-modulation spectroscopy* Ω significantly exceeds both the laser linewidth that is typically several tens of MHz and is comparable to the absorption linewidth. Only the two first-order side-bands of the laser frequency ω , $\omega + \Omega$ and $\omega - \Omega$, have appreciable magnitude.^{556,557} After frequency independent attenuation, such as is encountered in non-resonant optical systems or media (*e.g.* imaging optics or vacuum), the side-bands upon detection combine coherently with the carrier and balance each other to produce an unmodulated output signal. If the attenuation strongly depends on frequency, however, as is the case with most gases, one of the side-bands will be absorbed to a greater extent than the other leading to the appearance of Ω (and its harmonics) in the detected laser signal. The strength of absorption determines the magnitude of these harmonics, which may be measured separately and with high noise immunity, by using a lock-in amplifier for example.

This detection technique was first applied by Bjorklund to a cw dye laser.⁵⁵⁸ It proved extremely powerful and is widely used in diode laser spectroscopy today, sometimes in modified form such as two-tone frequency-modulation (TTFM),⁵⁵⁹ or amplitude-modulated phase-modulation (AMP) spectroscopy.⁵⁶⁰

Wavelength modulation (WM) is really another form of FM spectroscopy, in which the modulation frequency Ω is smaller than the laser linewidth, and the modulation indices are large.⁵⁶¹ The aforementioned side-bands are then present to a very high order and, by virtue of their small separation from each other, merge into a continuous spectrum. Detection is again performed at the first, second, or higher harmonics of Ω as the laser carrier frequency ω is scanned in the vicinity of a gas absorption line. WM spectroscopy dominates applications that rely on relatively low-speed detectors, and its sensitivity is usually limited by the laser amplitude $1/f$ noise.⁵⁶²

3 Trace gas monitoring. Mid-IR and near-IR absorption spectroscopy methods for monitoring trace gases are making important contributions in several areas. The monitoring of urban air pollution, investigations of the stratosphere, medical

applications and industrial process monitoring are the most often cited. Tunable infrared laser spectroscopy is improving the sensitivity and speed of monitoring in all these areas.

The principal alternative methods employed for these purposes generally use sampling, followed by either a general analytical method such as gas chromatography-mass spectroscopy or by chemical processing to create species that can be detected by chemiluminescence or fluorescence, but if remote sensing is required only spectroscopic methods are suitable. Spectroscopy in the infrared offers the possibility of detecting a wide range of species as most molecules have infrared absorption bands. Infrared spectroscopic monitoring can be done either by laser methods or by Fourier transform infrared spectroscopy (FTIR). The latter offers broad spectral coverage at the expense of some selectivity because of the poorer spectral resolution of small instruments and also generally at the expense of sensitivity.

A general problem faced by both infrared spectroscopic methods (laser or FTIR) is interference by absorptions of water vapor and other constituents of the atmosphere. Long pathlengths do not help here as they increase not only the signal of interest but the interfering absorption as well. Multi-component spectral fitting algorithms have been developed that can resolve weak absorption lines of interest in the presence of heavy interference by a *known* gas. The problem becomes far more severe, however, when the identity of the interfering species is unknown.

a Laser remote sensing. Two major kinds of optical techniques applicable in active remote-sensing of the atmosphere, long path differential optical absorption spectroscopy (DOAS) and LIDAR, are well developed and the topic will not be treated in detail in this review (see the book chapters by Platt⁵⁶³ and by Svanberg¹²⁸). DOAS allows the quantitative determination of atmospheric trace gas concentration by making use of the characteristic absorption structures of trace gas molecules along a path of known length in the atmosphere. As a spectroscopic technique DOAS has the merits of inherent calibration, high sensitivity (sub-ppb to ppt) and precision (1–10%), good specificity and the capability for remote measurements. The DOAS principle can be applied in a wide variety of optical configurations. The most basic arrangement consists of a telescope looking into the light beam emitted from a light source (laser or incoherent light source coupled to a dispersive device) followed by a detector. A variation of this design uses a corner-cube retroreflector to return the light from a source located next to the detector. DOAS applications include studies in urban and rural air, observations of the troposphere, volcanic plume emissions as well as investigations of the distribution of stratospheric ozone and species leading to its destruction.^{546,565–569}

Atmospheric sensing by infrared LIDAR relies on two key factors: the strength of infrared nonresonant and resonant scattering from aerosols and industrial particulate emissions and the ease with which many molecular species can be monitored by means of their absorption spectra. IR LIDAR is a mature technological field with many excellent literature resources (see for example the book chapter by Orr⁵⁷⁰). Examples can be found in the work of Saito *et al.*⁵⁷¹ in forest measurements and Quagliano *et al.*⁵⁷² Meteorology drives much of the interest in LIDAR, as LIDAR is able to provide information on aerosols, atmospheric chemistry, clouds, winds and pollution. In the case of aerosols, LIDAR can be used to measure and map their characteristic spatial,

size and shape distributions, as well as their chemical and physical composition. The temperature-inversion mixing layer that often traps urban pollution can be monitored by ground based LIDAR, as can localized plumes of particulates and chemicals from industrial sites. Airborne and space-borne LIDAR platforms can provide coverage of large areas quickly.^{573,574}

b Architectures and examples of point measurement trace gas sensors. Point sensing may be done by sampling into a multipass cell (see Section 3.A). Five types of laser based spectroscopic sensors, which currently embody state-of-the-art technology will be described.

i Overtone band detection with near-infrared diode lasers. Near-infrared diode lasers, because of their excellent characteristics, are ideal light sources for spectroscopic gas analysis. Diode lasers, as reported in Sections 2.A.1 and 2.A.4, have distinct advantages in terms of output power, beam quality, linewidth, tunability, size, cost and lifetime. Near-infrared diode laser based analyzers can achieve detection limits comparable to that of FTIR systems. A number of near-infrared spectrometers employing commercially available diode lasers with emission wavelengths from 780 nm to 2 μm have been described in the literature.^{18,19,575-587}

Gas detection at near-IR wavelengths is based on the molecular vibration overtone and combination-overtone bands that are significantly less intense than the fundamental bands. For example, the lines of the first overtone of the CH stretching vibration of methane centered at 1.6 μm is roughly 160 times weaker than the fundamental. Ambient methane would cause a 0.005% absorption over a 1 m pathlength at this wavelength at room temperature.⁵⁵⁰ Reliable measurement of such low absorption is difficult, so that long optical pathlengths or special measurement techniques are necessary to obtain satisfactory signal-to-noise ratios for trace level monitoring applications.

Near-IR radiation can be detected with a silicon photo-diode. The near-IR diode laser source-Si detector combination is very fast, with modulation bandwidths of over 1 GHz, allowing rapid scanning, fast frequency modulation, and leading to gas detection in real time. Near-infrared diode lasers often come in compact sealed packages that include a convenient fiber-coupled output. Thus the probe light can be delivered from a single source to several sampling locations. Likewise, the radiation passing through the sample can be returned to a detector *via* a fiber, sometimes even the *same* fiber. Overtone spectrometers usually have adequate optical probe power. Near-infrared diode lasers emit anywhere from 1 to 100 mW of single-frequency radiation with low excess noise: 15 to 35 dB over the shot noise limit is typical.

High output power levels have two important benefits. First, detector noise can be neglected and the measurement of absorption can be performed near the optical shot-noise limit. For example, Allen *et al.*⁵⁵⁴ report a detection sensitivity of $2 \times 10^{-7} \text{ Hz}^{-1/2}$ absorption units with the use of a 1.3 μm diode laser and a balanced ratiometric detector. Second, with high initial power available in a beam, one can employ a multipass cell to propagate the beam back and forth through a gas sample, achieving long effective pathlengths and thus increasing the observed absorption signal. Although the throughput of such a cell decreases exponentially as the number of passes increases (see Section 3.A), there is sufficient light after many passes to permit measurements that are not limited by detector noise.

Near-infrared overtone spectrometers, such as that developed by Uehara and Tai,⁵⁸⁸ are usually built to detect one or a few specific gases, for two reasons. First, the near-infrared wavelength region is not covered completely. Diode lasers are only available at some wavelengths, and each diode has a limited tuning range when operated without an external cavity. Second, these near-infrared diodes are relatively inexpensive, making it economical to have several dedicated lasers, each detecting one gas species, in a single instrument. This configuration is also attractive because different gas species can be measured in parallel. For example, several groups have developed a gas sensor that is capable of monitoring several substances using one common beam path through the sample and one detector.⁵⁸⁹

Alternatively, a single external-cavity diode laser (ECDL) with a large tuning range can be used (see Section 2.A.4). A spectrometer based on such a widely tunable laser is a very useful tool in that it can acquire spectra of an entire molecular band in a single electronically-controlled scan in a matter of seconds. Oh and Hovde,⁵⁹⁰ for example, used a widely tunable 1.5 μm ECDL to record a spectrum of the $\nu_1 + \nu_3$ stretch-vibration combination band of acetylene.

ii Gas sensors based on lead salt mid-IR diodes. In recent years air monitoring employing lead salt lasers in tunable diode laser absorption spectroscopy (TDLAS) has met the major requirements for atmospheric trace gas monitoring; sub-ppb sensitivity, high detection speed and the potential for simultaneous measurements of several species. A number of groups have reported excellent performance of such sensors.^{19,24,27,28,29,582,591–593} For example, Fried *et al.*²⁴ achieved a CH_2O detection limit of 31 ppt for integration times of 25 s. This sensitivity corresponds to a minimum detectable absorbance of 1.0×10^{-6} and this is within a factor of two of that reported by Werle *et al.*⁵⁹² Scott *et al.*⁵⁹⁴ describe the design and operation of a fully automatic sensor for the measurement of five trace gases in the lower stratosphere on board an airplane. Their instrument houses four lasers and four detectors mounted on the same liquid-nitrogen-cooled platform, beam shaping optics, a compact multi-pass absorption cell with 80 m pathlength, analog electronics, and a computer-controlled data storage system. The instrument employs wavelength modulation and second harmonic detection to achieve high sensitivity. It is capable of detecting optical absorption as small as 10^{-5} . This sensitivity provides detection limits in the range of several tens of ppt for species such as HCl, NO_2 , HNO_3 , CH_4 , and N_2O .

iii Gas sensors based on difference frequency generation absorption spectroscopy. Further to our discussion in Section 2.C.1, it is possible to utilize various DFG architectures based on birefringent and quasi-matched nonlinear optical materials pumped by various pump sources such as Ti:sapphire lasers, diode and fiber amplified diode lasers and fiber lasers. Several groups worldwide have reported^{56,57,59,61,71,75,86,595} different architectures and applications (See Section 2.C.1).

For example Rehle *et al.*⁵⁹⁶ have used a laser spectrometer based on difference frequency generation in periodically poled LiNbO_3 (PPLN) to quantify atmospheric formaldehyde with a detection limit of 0.32 ppbv. To achieve this sensitivity, specifically developed data processing techniques and high power Yb and Er/Yb fiber amplifiers were used. With state-of-the-art fiber coupled diode laser pump sources at 1083 nm and 1561 nm, tunable narrow-linewidth (<60 MHz) difference frequency radiation can be generated in the 3.53 μm (2832 cm^{-1}) spectral region at power

levels of greater than 0.5 mW. This significantly higher power capability allows the use of an optical-noise-reducing dual-beam absorption configuration that employs two DC-coupled Peltier-cooled HgCdTe (MCT) detectors and a 100 m absorption pathlength in a low-volume (3.3 l) astigmatically compensated Herriott gas cell.

With this device, formaldehyde in ambient air in the 1 to 10 ppbv range has been detected continuously for nine and five days at two separate field sites in the Greater Houston area operated by the Texas Natural Resource Conservation Commission (TNRCC) and the Houston Regional Monitoring Corporation (HRM). The acquired spectroscopic data were compared with results obtained by a well-established wet-chemical *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) technique with good agreement. While the accuracy of the determined concentrations is comparable with results from conventional wet-chemical techniques, the described DFG sensor offers a time response of a few seconds and permits unattended continuous operation for long periods of time. The inherent maintenance-free design of a tunable infrared DFG based diode laser spectrometer and the capability of remotely controllable computerized operation makes such instrumentation a convenient, robust tool for mobile trace gas detection.

Further reduction in size, cost and performance improvements can be realized by utilizing the latest developments of optical fiber and amplifier technology and surface mounted electronics. For example, Richter *et al.*⁷⁹ describe a compact modular mid-infrared DFG source at the 0.1mW-level.

iv Detection of trace gases with cw QC-DFB lasers. Gas sensing with a cw QC-DFB laser was first reported by Sharpe *et al.*⁵⁹⁷ The laser was scanned *via* a sawtooth current ramp (5–11 kHz) and the absorbance of the sample was measured directly. The laser could be swept rapidly over a frequency range of up to 2.5 cm⁻¹. Absorption spectra of pure NO and NH₃ gases at low pressure were acquired at 5.2 μm and 8.5 μm, respectively.

The direct absorption approach with cw QC-DFB lasers has been further developed⁵⁹⁸ and the first successful application of a single-frequency QC-DFB laser to the analysis of trace gases in ambient air was reported in 2000.⁵⁹⁹ This work was later extended to higher sensitivity.⁶⁰⁰ A QC-DFB laser designed for cw operation at cryogenic temperatures in the 7.9 μm spectral region was used. Absorption in air was detected in a 100 m multipass cell at a reduced pressure of 20–40 Torr. A “zero-air” background subtraction technique²⁵ was used in order to suppress the influence of interfering effects. Spectra of ambient air and pollutant-free “zero air” were acquired alternatively. The zero-air signal (as a function of a datapoint number) was subtracted from the ambient air sample signal and normalized to the zero-air signal.

Detection of more complex organic molecules with congested unresolved ro-vibrational spectra sets a challenge to QC-DFB laser based chemical sensors. Traditionally, the spectral recognition of such species is performed by acquiring medium-resolution absorption spectra in a wide spectral region (thousands of wavenumbers) identifying absorption bands rather than isolated lines. This approach cannot be realized with QC-DFB lasers because of their limited tunability. The maximum demonstrated spectral range covered by a single-frequency QC-DFB laser is ~ 30 cm⁻¹, achieved in pulsed operation when the heat sink temperature varied from

50 K to 300 K.¹⁰⁹ In practice the tunability of a QC-DFB laser in a chemical sensor is usually limited to 1–3 cm^{-1} .

The feasibility of detecting and quantifying volatile organic compounds (VOCs) with cw QC-DFB lasers has been explored⁶⁰⁰ using ethanol ($\text{C}_2\text{H}_5\text{OH}$) as an example. The ethanol vapor absorption spectra (ethanol at 1 Torr pressure with ambient air added to a total pressure of 36.6 Torr) was acquired with the QC-DFB laser in a 0.43 m long gas cell. The rovibrational structure is reasonably well resolved in this spectrum, in contrast with the spectrum in the C–H and O–H stretch spectral regions ($\sim 3 \mu\text{m}$). The resolved spectral features clearly distinguish the absorption of ethanol from other species. However, the high density of the pressure-broadened spectral lines makes the technique of individual line fitting with a Voigt profile (local approach) inapplicable. Instead, some kind of global approach should be used in order to take advantage of the whole spectral fingerprint. The technique used⁶⁰⁰ is principally based on finding the correlation between previously acquired *reference* spectra and a sample spectrum (*test* spectrum) under the same line-broadening conditions (*i.e.* same air pressure and temperature). The test spectrum was considered as a linear combination of four reference spectra of the absorbing species. The resulting concentrations were found to be mutually consistent and in agreement with the concentrations of H_2O , N_2O and CH_4 extracted from the spectra by the traditional single-line fitting approach. This work establishes that, for one case at least, high-resolution IR absorption data acquired in a limited 1–3 cm^{-1} range with a QC-DFB laser can be successfully used for quantification of complex organic compounds as trace gas components.

Non-DFB multimode QC lasers (Fabry-Pérot devices) may find application in differential absorption lidar (DIAL) systems.⁶⁰¹ There is a wide-ranging interest in extending DIAL-based chemical sensing from the detection and quantification of major species to the characterization of dilute contaminants, *e.g.*, organic chemical vapors that do not possess spectrally resolved vibrational transitions. In general, the 8–12 μm wavelength spectral region is the most desirable wavelength range for performing sensitive, selective detection of organic species, but it is not yet known whether the weak absorptions by water vapor and other atmospheric species in this region will limit the DIAL range too severely.

Several QC lasers could be simultaneously used in a DIAL system to probe the broad absorption features at selected wavelengths. A pseudo-random code modulation scheme has been proposed to distinguish signals produced by different lasers.⁶⁰¹

v Gas sensors based on pulsed QC lasers. One of the most attractive features of QC lasers is that they can be operated near room temperature. This option is presently restricted primarily to pulsed QC-DFB devices. Pulsed operation poses a number of specific performance issues. The most fundamental limitations are reduced average power (peak power is essentially the same as in a cw mode, but the duty cycle is $<1\%$) and laser line broadening caused by the frequency chirping during the pump current pulse. The first work on spectroscopic chemical sensing with a pulsed QC-DFB laser was reported in 1998 by Namjou *et al.*⁶⁰² preceding the first cw QC-DFB laser based publication.⁵⁹⁷ In this work, a technique for fast-tuning the optical frequency of the laser pulses by applying a subthreshold current (STC) ramp was introduced. Wavelength modulation (WM) spectra of diluted N_2O and CH_4 samples were acquired near $\lambda = 8 \mu\text{m}$. The laser was excited by a 1 MHz train of 11 ns wide current pulses. The laser linewidth was estimated to be 720 MHz. Detection was performed using a slow

HgCdTe detector in essentially the same manner as in cw experiments. A similar approach to detection was used by Sonnenfroh *et al.*⁶⁰³ and is referred to as 'quasi-cw'.

An alternative approach to data acquisition with pulsed QC-DFB lasers is to use a fast detector and individually measure the peak power of every pulse with gated electronics. In this mode of measurement the detected signal is much higher than the detector noise and does not depend on the repetition rate. Time-gating permits suppression of the light that occurs earlier or later than the informative signal. This approach was utilized in the first successful application of a pulsed QC-DFB laser to the trace gas detection in ambient air.^{599,600} The flexibility provided by the digital frequency control employed in this study was utilized for linearization of the wavelength scan and for wavelength modulation. The sensor was used to measure CH₄, N₂O and HDO concentrations in ambient air and a precision of 9 ppbv, 4 ppbv and 120 ppbv was achieved for each of these species, respectively.

High sensitivity detection of NH₃ is also of interest in the control of deNO_x chemistry, industrial safety and medical diagnostics of kidney related diseases. A compact mobile ammonia sensor based on a thermoelectrically cooled pulsed QC-DFB laser operating at ~10 μm was described by Kosterev *et al.*⁶⁰⁴ The optical configuration of this sensor was similar to that described earlier,⁵⁹⁹ but the multipass cell was replaced with a simple 50 cm long double pass gas cell, and no zero air was employed. This sensor was applied to real-world measurements at NASA-JSC, namely the continuous monitoring of NH₃ concentration levels present in bioreactor vent gases. A sensitivity of better than 0.3 ppmv was estimated which was sufficient to quantify expected ammonia levels of 1 to 10 ppmv.

Multimode pulsed Fabry-Pérot QC lasers can be used in analytical applications that do not require or would not benefit from high spectral resolution.⁴⁰ One example is a spectroscopic analysis of liquids, where the spectral lines are broad. Such an application was demonstrated by Lendl *et al.*⁶⁰⁵ to quantify phosphate in Coke samples. A fiber-coupled injection cell with a pathlength of ~100 μm in the aqueous sample was used. The results were in a good agreement with the values found by ion chromatography.

vi Photoacoustic detection of trace gases. Trace gas detection by photoacoustic spectroscopy (PAS) has found wide ranging applications in environmental science, industry and medicine (see Section 3.E). As the photoacoustic signal is proportional to the intensity of the light sent through the sample, this method was, until recently, used in conjunction with intense infrared gas lasers. Diode laser based PAS is a very promising new development.^{204,606-608} A sensitivity of 8 ppmv was demonstrated⁶⁰⁸ with only 2 mW of modulated diode laser power in CH₄ overtone region.

Implementation of a QC-DFB laser in the fundamental absorption region has a potential for considerably improved sensitivity. Ammonia and water vapor photoacoustic spectra were obtained using a cw cryogenically cooled QC-DFB laser with a 16 mW power output at 8.5 μm as reported by Paldus *et al.*⁶⁰⁹ A PAS cell resonant at 1.66 kHz was used. The QC-DFB was used for frequency scans using temperature tuning and for real-time concentration measurements with a fixed laser temperature. Measured concentrations ranged from 2200 ppmv to 100 ppbv. A detection limit of 100 ppbv ammonia (~10⁻⁵ noise-equivalent absorbance) at standard temperature and pressure was obtained for a 1Hz bandwidth and a measurement interval of 10 min.

Recently, Hofstetter *et al.*⁶¹⁰ reported PAS measurements of ammonia, methanol and carbon dioxide using a pulsed 10.4 μm QC-DFB laser operated at 3–4% duty cycle with 25 ns long current pulses (2 mW average power) and close to room temperature with Peltier cooling. Temperature tuning resulted in a wavelength range of 3 cm^{-1} at a linewidth of 0.2 cm^{-1} . This sensor used a 42 cm long PAS cell with a radial 16 microphone array for increased detection sensitivity. In addition the cell was placed between two concave reflectors resulting in 36 passes through the cell (with an effective pathlength of 15 m). The laser beam was mechanically chopped at a resonant cell frequency of 1.25 KHz, which resulted in PAS signal enhancement by a Q factor of 70. A pyroelectric detector recorded the QC laser power to normalize the PAS signal. Detection of ammonia concentrations at the 300 ppbv level with a SNR of 3 was achieved at a pressure of 400 mbar.

c Laser spectroscopy in medicine. Laser spectroscopy is finding increasing applications in medicine and biology.^{611–614} A particular role for spectroscopy is in monitoring simple small molecules that have been shown to be important. The role of simple molecules such as nitric oxide (NO) in physiological processes has received considerable attention in recent years and was a subject of the 1998 Nobel Prize in Medicine.

One application is the measurement of NO in human breath samples, since exhaled air is an indicator of several processes taking place in the human body. To observe NO in breath, a cavity enhanced absorption spectroscopy (CES) sensor¹⁵³ with a cw QC-DFB laser operating at 5.2 μm with an output power of 80 mW was used. A direct performance comparison was carried out between a sensor configuration where the CES optical cavity was replaced with a 100 m pathlength multipass cell. It was found that, in spite of having an effective pathlength of 670 m, CES had a lower absorption sensitivity because of baseline noise of $\sim 1\%$ (averaging 10^4 QC laser scans). These baseline fluctuations are intrinsic to CES and result from the mode structure of the cavity transmission spectrum. Some improvement in CES baseline noise can be achieved with a recently developed off-axis technique.¹⁵¹

Recent work indicates that other gases, such as carbon monoxide (CO), can play also a very significant physiological role. CO is produced from heme catabolism by the enzyme heme oxygenase. Previous work has shown that CO promotes blood flow by inhibiting vascular tone and platelet aggregation and that neuronal CO production may modulate the NO-cGMP (guanosine 3',5'-cyclic monophosphate) signaling system, demonstrating important biochemical interactions between the two diatomic gases. The extremely low levels of gas production in living cells and the relatively short lifetime of cell cultures have complicated the detailed understanding of the kinetic, or time-dependent processes responsible for their generation. A typical production rate of CO, for example from vascular smooth muscle cells (VSMCs), is 1 to 10 pmol min^{-1} per 10^7 cells. Instrumentation for *in vivo* measurement of gas production should have sensitivities on the parts per billion (ppb) level in order that the dynamics of gas production can be followed with laboratory-scale cell sample populations.⁶¹⁵ Because of low CO production rates from biological tissues, measurements of CO concentrations have been limited to gas chromatography and radioisotope counting techniques. Although these methods are highly sensitive, they cannot measure CO directly, requiring several time-consuming intermediate steps requiring ~ 15 min, and may be affected by interferences from water, oxygen, and carbon dioxide.

Infrared laser absorption spectroscopy is an attractive alternative approach for the detection of biological CO at the ppb level in real time.^{616,617} Morimoto *et al.*⁶¹⁶ measured endogenous CO production from vascular cells using a mid-IR laser based on difference frequency generation (DFG) of two near-IR lasers as a spectroscopic source. The CO absorption was detected in the fundamental vibration band near 4.6 μm . In this work, an extractive technique was used with gas samples taken from the flask containing the cell culture to an 18 m pathlength optical multipass cell so that the measurements could be performed at a reduced pressure of 100 Torr.

Kosterev *et al.*⁶¹⁷ reported improved design and performance of an optical mid-IR CO sensor intended for continuous monitoring of cell culture activity at ambient atmospheric pressure. The same fundamental absorption band region was used for CO detection, but a quantum cascade laser with a distributed feedback structure (QC-DFB)¹⁰⁹ was employed instead of the DFG source. The high output power of the QC-DFB laser and an advanced data analysis approach made it possible to detect biological CO and CO production rates with ~ 1 m optical pathlength folded above a standard culture flask of VSMCs.

A further improvement of the pulsed QC-DFB based sensor was reported by Kosterev *et al.*⁶¹⁸ The laser beam was split into two channels, one being used to probe the gas absorption and the other as a reference to measure the laser pulse energy. The subsequent normalization eliminated pulse-to-pulse energy fluctuations as an error source, which was the predominant cause of error previously.⁶¹⁷ This automated sensor was also used for continuous monitoring of CO in ambient air detected by its R(3) absorption line at 2158.300 cm^{-1} ($\lambda=4.6$ μm). A noise-equivalent detection limit of 12 ppbv was experimentally demonstrated with a 1 m optical pathlength. This sensitivity corresponds to a standard error in fractional absorbance of 3×10^{-5} .

All the measurements were carried out at atmospheric pressure, and hence it was not possible to periodically acquire a baseline with an evacuated sample container. In order to keep the baseline (which included weak unwanted interference fringes from optical elements) stable during multi-hour measurements, the slow drifts of the laser frequency were actively compensated by computer-controlled corrections to the sub-threshold current. A constant CO production rate of 44 ppbv h^{-1} was observed, taking into account the 0.5 l volume of the cell culture container. This corresponds to a net CO production rate of 0.9 nmol per 10^7 cells h^{-1} , which is in agreement with previous measurements⁶¹⁶ obtained with similar cells and treatment regimes

d Isotope ratio composition measurements. The accurate measurement of isotopic abundance ratios is an extremely important research tool in a wide variety of scientific fields. Isotopic signatures have been successfully used to analyze the biochemical cycles of materials, in particular greenhouse gases and other areas of applications, such as in non-invasive medical diagnostics. In the environmental sciences it is well known that most naturally occurring compounds are isotopically labeled by isotopic fractionation effects. Hence, the isotopic signature can often be used as an indication of the compound's formation pathway under the prevailing environmental conditions. Laser spectroscopy is being developed as a new methodology for precision isotopic ratio measurements of gases. This technique joins other available tools such as traditional high precision isotopic ratio mass spectrometers (IRMS),⁶¹⁹ FTIR and NMR.⁶²⁰

The isotope abundance ratio in an environmental compound depends on the area where the sample was collected, thereby reflecting different production processes of the compound and different transportation histories in the atmosphere and ocean. For instance, the $^{13}\text{C}/^{12}\text{C}$ ratio ($\sim 1/100$) in CH_4 differs by up to a few percent from one production process to another⁶²¹ and the $^{15}\text{N}/^{14}\text{N}$ ratio in N_2O dissolved in oceans varies depending on the region and depth.

The standard means for measuring isotope ratios is mass spectrometry. Very high mass resolution is required for discrimination of species with small difference, such as $^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$ and it is impossible to separate $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, which have the same mass. In laser absorption spectroscopy, however, different isotopic molecular species can be distinguished easily irrespective of their masses if appropriate absorption lines are selected.

In absorption spectroscopy, the abundance ratio is determined by comparing the ratio of the absorbances for the selected absorption lines in a sample gas with that in the standard gas of known isotopic composition. There have been many demonstrations or proposals of isotopic analyses by absorption-spectroscopic methods, using lead-salt semiconductor lasers in the mid-infrared region,^{622–624} a DFB diode laser in the near-infrared,^{621,625} a color center laser,⁶²⁶ and a quantum cascade laser in the $8\ \mu\text{m}$ region.⁵⁹⁸ In these methods, the absorbances of adjacent lines of different isotopic species were compared by scanning the wavelength of a spectroscopic source. Usually a weaker line was selected for the more abundant species or the laser beams are made to travel different distances in an absorption cell in order to compensate the large abundance difference in order to balance the signal levels. Uehara *et al.*⁶²¹ demonstrated a precision of isotopic analysis of $\pm 3 \times 10^{-4}$ ($\pm 0.3\ \text{ml}^{-1}$) for $^{13}\text{CH}_4/^{12}\text{CH}_4$. Hence laser spectroscopy can complement mass spectrometry and is potentially an important tool for precise analysis of biogeochemical cycles of environmental substances.

In another field, a precise measurement of the ratio of the two stable carbon isotopes of CO_2 ($^{13}\text{CO}_2$ and $^{12}\text{CO}_2$) can provide valuable information about CO_2 exchange processes in the volcanic plume.⁶²⁷ Changes in the isotopic ratio can be explained either in terms of variations in the volcanic source, mixing with or anthropogenic sources (*e.g.*, agricultural or industrial) as well as photosynthesis,⁶²⁸ or could manifest global and local changes. The strong vibrational–rotational absorption bands of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ centered at 4.28 and $4.37\ \mu\text{m}$, respectively, also provide several line pairs that are suitable for isotope ratio determination by direct absorption spectroscopy for this species.

Acknowledgements

This work was supported by the Robert A. Welch Foundation and the National Science Foundation under Grant CHE-0111125 and Texas Advanced Technology Program.

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