Critique of Tunable Infrared Lasers [and Discussion]

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Critique of tunable infrared lasers

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The operating characteristics of tunable infrared semiconductor, spin-flip Raman, difference-frequency, colour centre and vibronic lasers are reviewed for application to spectroscopy at ultra-high resolution. Emphasis is placed on sub-Doppler molecular studies with these lasers.

INTRODUCTION

Since the initial tunable diode laser spectrum of the ν_3 band of SF_6 taken by Hinkley (1970) there has been an explosive growth in the development of tunable infrared lasers and in their application to molecular spectroscopy. In this paper I shall review the characteristics and relative merits of these lasers for high-resolution spectroscopy at the Doppler limit and beyond. In particular I shall emphasize techniques of sub-Doppler infrared spectroscopy using these tunable lasers.

Figure 1 shows the operational spectral ranges of various types of broad-coverage, continuous wave (c.w.) tunable infrared lasers. In the interest of clarity and brevity I have narrowed the scope of this figure and review to exclude pulsed lasers, such as optical parametric oscillators and pulsed mixers, pulsed spin-flip and dye lasers, high-pressure CO_2 lasers and free-electron lasers, which are not generally used for high-resolution studies. Also omitted, with less justification because of their rather extensive application to sub-Doppler spectroscopy, are the fixed- or quasi-tunable gas lasers such as the waveguide CO_2.

Semiconductor recombination lasers, both injection-(diode) and optically or electron-beam-pumped, were developed in the early 1960s but were not exploited for spectroscopy until 1970. The lead–salt semiconductors have been the most extensively used tunable infrared lasers so far. Several excellent comprehensive reviews of molecular studies with these and other tunable i.r. lasers have been published recently (Eng & Ku 1982; McDowell 1981; Schlossberg & Kelley 1981) whose material does not warrant repeating; so I shall confine my attention to newer developments and more limited aspects of the field. The quaternary semiconductor lasers of $In_xGa_{1-x}As_yP_{1-y}$ have been developed in the past 6 years in the near infrared for optical communications purposes and have not been used for spectroscopy; see Ettenberg & Olsen (1982) for a review.

The c.w. spin-flip laser was demonstrated by Mooradian *et al.* (1970) by taking advantage of resonant stimulated Raman scattering in InSb with a CO laser and it quickly found spectroscopic application (Patel 1971). The c.w. difference-frequency system was first demonstrated for spectroscopy by Pine (1974) by mixing visible argon ion and dye lasers in a $LiNbO_3$ nonlinear optical crystal. Many other nonlinear crystals and source laser combinations would be suitable for mixing in other portions of the infrared, but the only spectroscopic extension (to *ca.* 2100 cm^{-1}) reported so far has been with $LiIO_3$ (Zueva *et al.* 1980). Colour centre lasers were operated c.w. by Mollenauer & Olson (1974) several years before fine tuning control (Litfin *et al.* 1980) permitted their application to high-resolution spectroscopy. The vibronic lasers, which operate in the near infrared on vibronically broadened d-levels in divalent

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transition metals doped in various host crystals, shows much promise for application to spectroscopy both in their range shown and outside, by using nonlinear optical conversion methods (Moulton & Mooradian 1979). The semiconductor diode lasers, spin-flip laser and the $F_A II$ and $F_B II$ colour centre lasers shown in figure 1 have all been produced commercially and the $LiNbO_3$ difference-frequency system can be assembled from commercially available components. The newer $NaF:OH(F_2+)''$ (Mollenauer 1981) and $Tl:KBr(F_A III)$ (Gellermann *et al.*
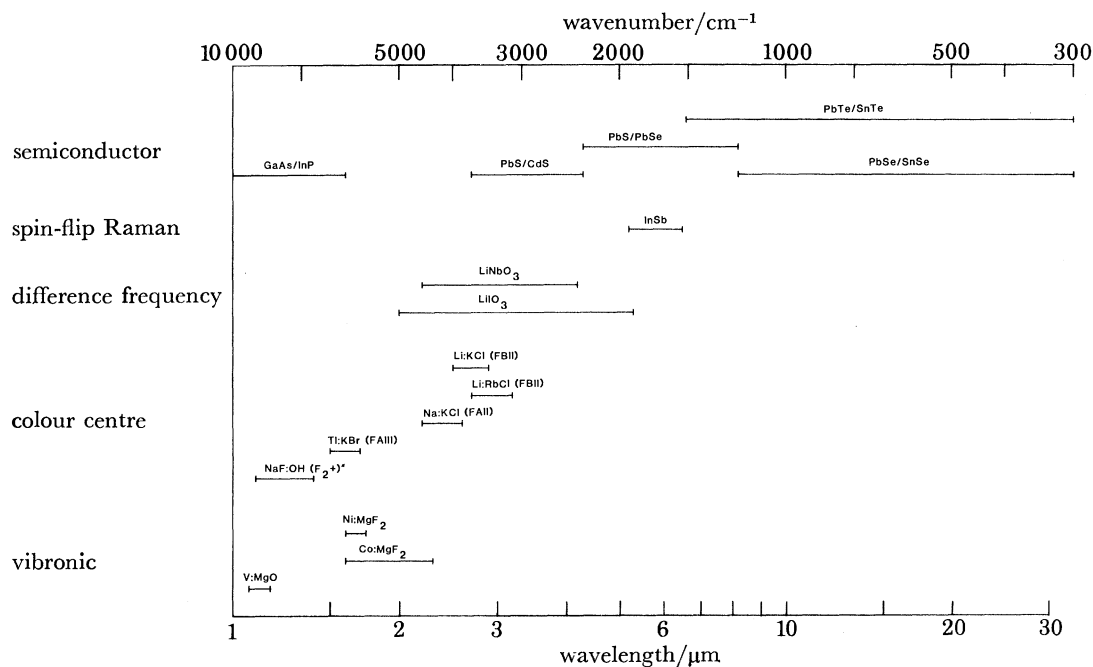

FIGURE 1. Spectral ranges of c.w. tunable infrared lasers for Doppler-limited spectroscopy.

1981) colour centre lasers and the vibronic lasers, all of which operate in the near infrared above the fundamental vibrational frequencies of any molecule, have not yet been refined for spectroscopic applications. However, the many vibrational overtone and combination bands and electronic transitions in this 'window' region should provide an incentive for spectroscopists to develop these lasers in the future.

OPERATING CHARACTERISTICS OF TUNABLE INFRARED LASERS

The lasers shown in figure 1 have a variety of spectral coverages, operating conditions, tuning characteristics, power outputs and amplitude and frequency instabilities. The semiconductor lasers can be compositionally tuned over the ranges indicated, with a given laser being thermally tunable from *ca.* 20 to *ca.* 100 cm^{-1}. The c.w. InSb spin-flip laser is confined to the near-resonant band gap region with magnetic field tuning of *ca.* 0.2 cm^{-1} T^{-1} about any CO pump laser line. The difference-frequency systems have complete coverage in the range indicated when pumped by various visible ion and dye lasers. Their long-wavelength limit is governed by the nonlinear crystal's transparency at the onset of multiphonon absorption. The colour centre and vibronic lasers are solid-state analogues of dye lasers with broad gain regions defined by the crystal field interaction with F-centre or impurity ion levels.

The Pb-salt semiconductor and the InSb spin-flip lasers operate best near liquid helium temperatures, with occasional diodes lasing c.w. up to 77 K. The colour centre and vibronic lasers work from liquid nitrogen temperatures to about dry ice temperatures in some cases; the difference-frequency systems operate at room temperature with the $LiNbO_3$ at elevated temperatures (175–450 °C) for phase-matching. Since the homogeneous gain bandwidth for these tunable lasers is on the order of kT, the higher temperature lasers, vibronic, colour centre and dye (used in the difference-frequency system) have a bandwidth greatly exceeding their cavity mode spacings; whereas the lower temperature lasers, diode and spin-flip, usually have a gain profile comparable with or sharper than the mode spacing for typical cavity lengths (less than about 1 mm for diodes, less than about 1 cm for spin-flip). Thus the higher temperature lasers use additional tuning elements in the cavity to achieve single-mode operation. Generally a coarse wavelength selecting element such as a prism, grating or birefringent filter, and one or more mode-selecting etalons are required – all of which need to be synchronously scanned with the cavity to provide continuous tunability. By contrast the low-temperature lasers use no extra selection and are simply scanned by varying a parameter such as temperature (by varying current), magnetic field or stress, which shifts both the gain peak and the cavity resonances. Unfortunately the gain and cavity often do not tune at the same rate, which results in mode-pulling, pushing and hopping, preventing smooth, linear, continuous coverage. Such mode-hops leave gaps in the coverage of typically 20–70 %. The low-temperature lasers have been operated in external cavities to eliminate the mode-hops at the expense of simplicity and convenience (Mozolowski et al. 1979).

The output power of the tunable i.r. lasers varies over a wide range even within a given category. The difference-frequency systems, when operated c.w., are very inefficient, yielding i.r. radiation of from 0.1 to 10 μW. This low power is adequate for linear absorption spectroscopy since standard detectors (e.g. InSb) have noise-equivalent powers of ca. 10^{-11} W. However, these c.w. mixing systems would not be adequate for such spectroscopic methods as fluorescence excitation, optoacoustic, saturation or heterodyne local oscillators. Diode lasers have from 10 μW to 10 mW output depending on their fabrication and mode idiosyncrasies. Colour centre lasers produce from 1 to 100 mW depending on the type of centre and crystal quality. The vibronic and spin-flip lasers can emit from 0.1 to 1 W and are therefore the best candidates for nonlinear effects.

Under most conditions the tunable lasers have vibration- or feedback-induced line widths from 0.1 to 10 MHz, which are well below the Doppler widths of most molecular species in the infrared. With special care sub-kilohertz line widths have been observed (Patel 1972). Scan calibration is usually accomplished by interpolation between known spectral absorption standards by using a Fabry–Perot interferometer. In limited scanning cases where higher precision is required, the tunable laser can be heterodyned with a known fixed gas laser in high-speed detectors (McDowell et al. 1976). Scan nonlinearities are often quite marked and lead to calibration inaccuracies unless some care is taken to control the scan rate (Coulombe & Pine 1979).

Sub-Doppler spectroscopy

The use of molecular beams or saturation spectroscopy is well known for reducing spectral widths due to random molecular motion. There have been many such applications using fixed laser coincidences in the infrared, and it is obvious that tunable lasers would relieve this
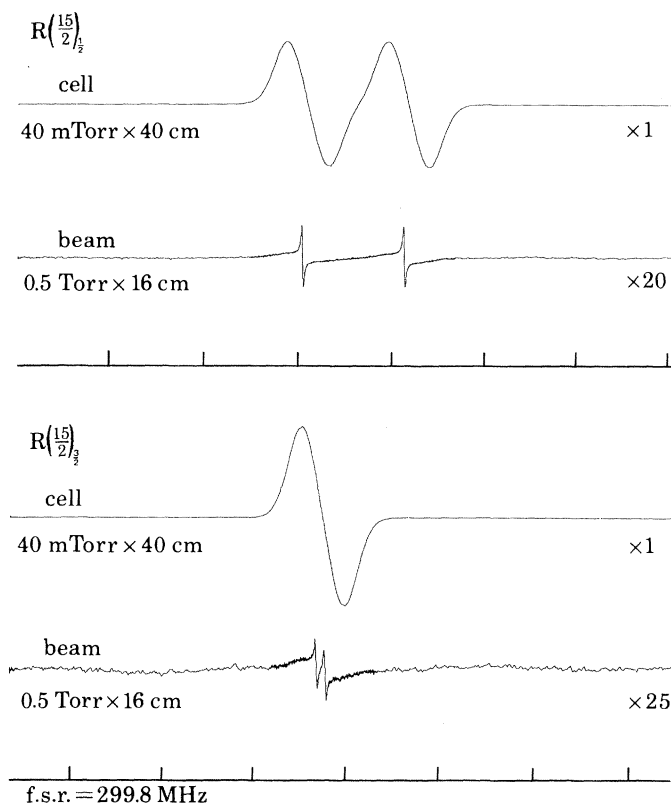
FIGURE 2. Effusive nozzle spectra of Λ-doublets of the $v = 1 \leftarrow 0$ band of NO. (1 Torr $\approx$ 133 Pa.)
(After Pine & Nill (1979).)

requirement for spectral coincidences. I shall therefore describe some sub-Doppler studies with tunable lasers with the use of molecular beams, saturation and double-resonance experiments and, less widely appreciated, numerical deconvolution.

Molecular beams

Both effusive and supersonic beams have been used for sub-Doppler spectroscopy. Figure 2 shows the derivative absorption spectra of two pairs of Λ-doublets for the NO fundamental obtained in an effusive beam from a multicapillary array by Pine & Nill (1979) using a tunable diode laser. Chu & Oka (1975) first demonstrated the use of such a multicapillary array for NH_3 and $^{13}CH_3F$ beams with N_2O and CO_2 lasers. The broad NO lines in figure 2 are Doppler-limited, and the Doppler reduction is a factor of 20 or 25 for the molecular beam – limited principally by the beam collimation, but also somewhat by the laser line width and unresolved hyperfine splitting. Eight Λ-doublets were observed in this study, where the $^2\Pi_\frac{3}{2}$ splittings had not been previously resolvable. The Λ-splittings agreed within experimental errors with those calculated from the constants obtained in a more extensive Doppler-limited spectrum of NO taken by Amiot *et al.* (1978) with a Fourier transform interferometer. There were, however, not enough transitions observed in the tunable diode–molecular beam study to improve upon the constants. The absorptions in this tenuous molecular beam were very weak (less than 1 %) even for this relatively strong fundamental band, so it required a laser with an exceptionally stable amplitude. Only one of five diode lasers tried was adequately noise-free, which accounts for the limited coverage.

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Higher resolution and sensitivity were achieved in a supersonic molecular beam by using an F-centre laser by Gough *et al.* (1981 *a*) as shown in figure 3 for the $R(\tfrac{1}{2})_{\tfrac{1}{2}}$ hyperfine-Λ-multiplet in the $v = 2 \leftarrow 0$ overtone of NO. The sensitivity was improved here by optothermal detection of the (higher power) laser-excited molecules impinging on a superconducting bolometer. This eliminates the noise constraints on the laser intensity present in absorption spectroscopy. The Doppler width reduction in this experiment was *ca.* 200 and was limited by a combination of beam collimation, laser line width and transit time considerations. The hyperfine splittings were not measured accurately owing to scan nonlinearities and drift; but apart from the
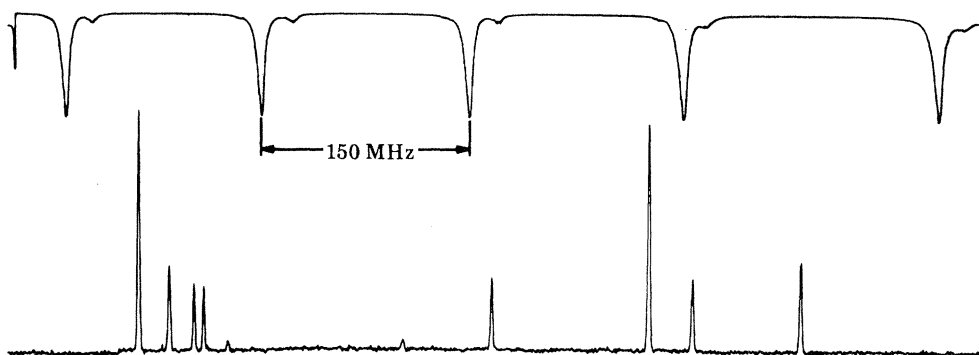

FIGURE 3. Supersonic nozzle spectra of the hyperfine-Λ-structure of the $R(\tfrac{1}{2})_{\tfrac{1}{2}}$ $v = 2 \leftarrow 0$ transition of NO. (After Gough *et al.* (1981 *a*).)

vibrational dependence, they are already known from microwave studies. Gough *et al.* (1977, 1978, 1981 *b*) have also studied the fundamentals of CO and NO in beams by using diode lasers and Stark splittings in HF beams with the F-centre laser. Supersonic nozzles are also known for their ability to cool the translational, rotational and (to a lesser extent) the vibrational motion of the molecule adiabatically, which can greatly simplify and sharpen the spectral structure of complex species. This feature had earlier been exploited with tunable diode lasers in beams of UF_6 (Jensen *et al.* 1976). For simple molecules, however, this cooling may be detrimental, as it prevents higher J transitions from being observed.

Nonlinear spectroscopy

Both saturation and double-resonance spectroscopy are used to sample particular velocity groups beneath the Doppler distribution. These techniques have been used with great success with fixed- or quasi-tunable gas lasers and tunable dye lasers for measurements at ultra-high resolution of hyperfine splittings and recoil effects, and for establishing frequency standards. Here I review the relatively few such experiments accomplished with tunable infrared lasers.

Saturation or Lamb-dip spectroscopy was first demonstrated for tunable infrared lasers by Patel (1970) in water vapour, using a spin-flip laser. Figure 4 illustrates the sharp Lamb dip of full width *ca.* 200 kHz observed with a nearly counterpropagating reflected probe beam, using 10 mW of spin-flip power. The sample was isolated from the laser by an attenuator (OD2) and the reflected beam was slightly tilted to avoid feedback instabilities. The laser was not actively stabilized and accounted for most of the observed width of the Lamb dip.

A similar Lamb dip was reported by Jennings (1978) for NH_3, using a tunable diode laser with a slightly detuned counterpropagating reflected probe beam. However the broad, un-symmetrical, uncentred appearance of the dip and its transient display may indicate some

experimental artefact such as a mode-hop instability. The low power, poor beam quality and notorious susceptibility to feedback instabilities of diode lasers make this singular result somewhat unconvincing. More recently Baer & Hall (1982) have observed the hyperfine structure of HF by using f.m. heterodyne saturation spectroscopy with an F-centre laser. Active electro-optic stabilization of the laser permitted them to observe hyperfine line widths of *ca.* 50 kHz with splittings of *ca.* 200 kHz and to study a marked vibrational influence on the hyperfine interaction. These are the narrowest spectral lines yet achieved for a tunable infrared laser.
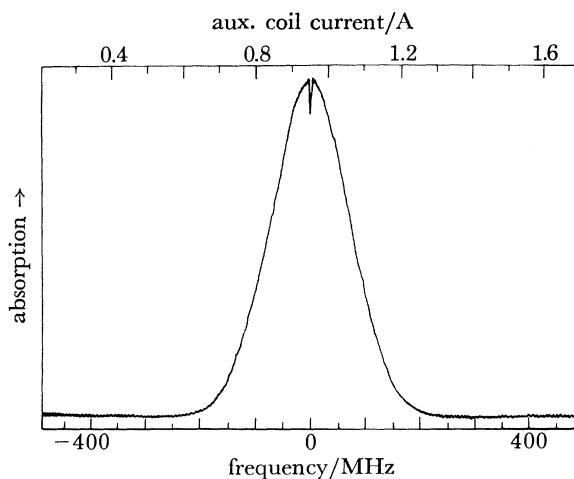

FIGURE 4. Lamb-dip spectrum of the $\nu_2(5_{3,2} \to 6_{4,3})$ transition of H_2O; $p_{H_2O} \approx 30$ mTorr; $l = 40$ cm. (After Patel (1974).)

Sub-Doppler double-resonance spectroscopy with a tunable infrared laser was recently reported by Weber & Terhune (1981). Their spectrum of Stark-split ν_2 band transitions of NH_3 taken with a diode laser is shown in figure 5. Here the lower levels of these transitions were simultaneously pumped intracavity with a CO laser in resonance with Stark-tuned ν_4 transitions. Two separate velocity groups are excited for $m'' = 9$ and $m'' = 8$ levels whose Doppler widths overlap and give rise to the two prominent sharp peaks when the CO pump and diode probe beams are copropagating. Subsidiary peaks arise from counterpropagation pump and probe and from velocity-conserving collisional transfers. The observed widths of *ca.* 2 MHz are due in part to pressure-broadening, Stark field inhomogeneities, and laser width; they are the narrowest yet achieved for a diode laser.

Previous double-resonance experiments with fixed and tunable lasers (see, for example, Moulton *et al.* 1977) have been concerned with rotational state labelling, not with sub-Doppler resolution. Consequently, resolution was limited by the transverse pump–probe geometry, power-broadening and pump pulse duration. I am not aware of any double resonance experiments with two tunable infrared lasers that would eliminate the constraints of spectral coincidences. Recent tunable diode laser–microwave resonance studies in CF_4 by Takami (1981), however, show the potential of such experiments.
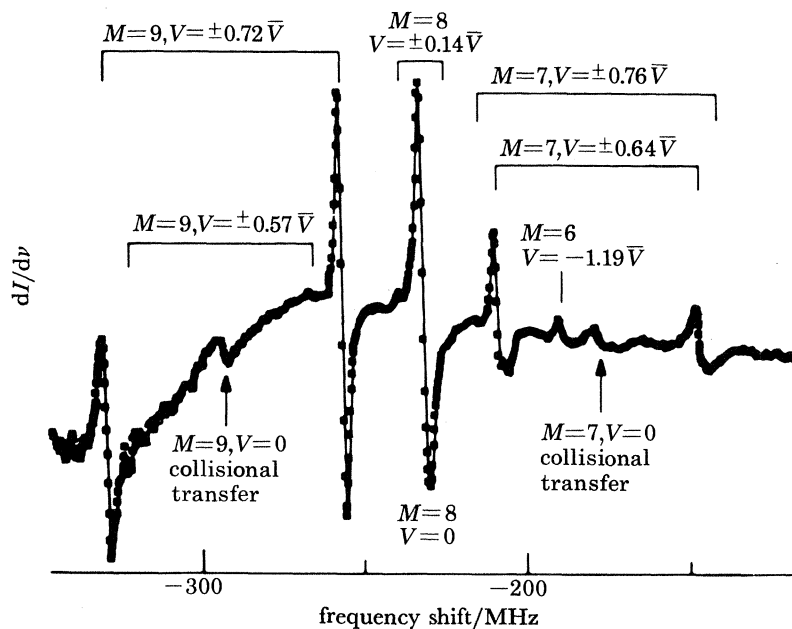
FIGURE 5. Stark-tuned double-resonance spectrum of the $m = 9$ and $m = 8$ levels of the $\nu_{2a}Q(9, 9)$ transition of NH$_3$; $p_{NH_3} = 20$ mTorr; $E = 4278$ V cm^{-1}. (After Weber & Terhune (1981).)
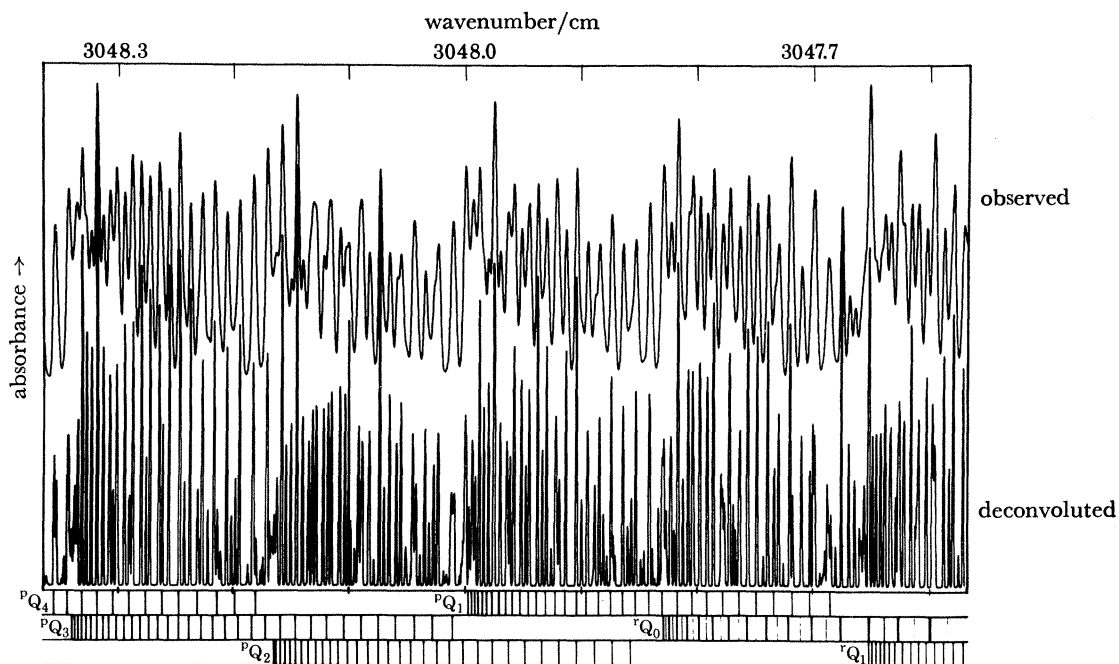
FIGURE 6. Deconvoluted spectra of the Q-branches of the ν_{12} band of C$_6$H$_6$. (After Pliva & Pine (1982).)

Deconvolution

A modest, but important, reduction in the Doppler width of spectral lines can be achieved with numerical deconvolution of high-quality Doppler-limited spectra (Pliva *et al.* 1980). An example is shown in figure 6 for the Q-branches of the ν_{12} C–H stretching band of benzene taken with a difference-frequency system by Pliva & Pine (1982). Here the deconvoluted structure of the dense and complex spectrum for this heavy molecule permitted a complete rotational assignment and analysis to be made. The iterative numerical deconvolution procedure can reduce the spectral widths by a factor of 3–4 for data with an experimental signal:noise ratio of *ca.* 1000. Deconvolution has also been used to fully resolve torsional splittings in diode laser spectra of the ν_9 band of ethane by Susskind *et al.* (1982). It is clear that such a procedure, while not spectacular in its resolution capabilities, can be crucial in many spectroscopic studies and helps to take advantage of the 'overqualified' tunable laser for Dopper-limited measurements.

Conclusions

The application of tunable infrared lasers to Doppler-limited spectroscopy has become almost commonplace in the past decade, but progress in the sub-Doppler régime with these lasers has been disappointingly slow and sporadic. As seen from this review, most sub-Doppler experiments so far have just been demonstrations rather than studies producing results that could not have been obtained otherwise. Only in the last year or so, with the deconvolution methods and with molecular beam and saturation techniques with F-centre lasers, have useful data emerged. Part of the difficulty in applying tunable lasers to sub-Doppler measurements is technological, e.g. the low power and unstable outputs of some of these devices, or the difficulties in controlling and calibrating them, or the complexity and expense of the systems. However, part of the problem is motivational since molecular spectroscopists traditionally have had lower interest in the hyperfine realm than in the fine-structure régime accessible at the Doppler limit.

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Discussion

J. P. CONNERADE (*Imperial College, London, U.K.*). Since the aim of the foregoing two papers was a survey of lasers for spectroscopy, could I ask the authors to comment on the possibilities offered by free-electron-laser systems? Admittedly, their resolving power is not high, but their potential wavelength coverage seems to be large.

A. S. PINE. Free-electron lasers have been proposed to operate from the far-infrared to the ultraviolet, though any particular design will be considerably more restricted in coverage. Oscillation has been achieved at the Stanford Linac in the mid-infrared, and gain has been observed in the visible at a storage ring facility in Orsay. Generally these are short-pulse high-power systems, and I am not aware of any spectroscopy yet demonstrated. The Proceedings of a Conference on Free-Electron Lasers held in Sun Valley, Idaho in June 1981 are to be published in volume 9 of *Physics of Quantum Electronics* by Addison-Wesley this year.

G. W. SERIES, F.R.S. (*University of Reading, U.K.*). Would Dr Pine kindly indicate for us the physical form of lasers based on colour-centre crystals?

A. S. PINE. Both colour-centre and vibronic lasers are configured similarly to dye lasers with the optically pumped crystals substituted for the dye cell or jet. Folded standing-wave cavities are most common, though some ring travelling-wave cavities have also been demonstrated.