Multiwavenumber linearized diode laser spectra by overlapping frequency scans

C. Brent Dane, Rudolf Brüggemann, Robert F. Curl, Jerome V. V. Kasper, and Frank K. Tittel

A method for producing diode laser spectroscopy scans which are several wavenumbers long, linear in frequency, and readily and accurately calibrated from reference spectra is described. The laser itself is current scanned under computer control over short segments (as is normally done) and such overlapping segments are linearized and pieced together to provide the final scan.

I. Introduction

The diode laser has become well established as a source of tunable infrared radiation for spectrometric applications. However, its usefulness in spectroscopy is still limited by a small continuous frequency tuning range (usually <1 cm^{-1}) and even these limited scans tend to be rather nonlinear in frequency. These tuning problems make many of the tasks involved in spectroscopy difficult, especially the recognition of patterns within collected spectra (such as rotational line series) and to a lesser extent the exact frequency calibration of spectral features. It is possible to partially solve this problem by choosing a reference gas with closely spaced calibration lines in order to calibrate from a short scan and then to replot the experimental spectrum as a stick diagram using computer graphics. However, this approach removes the raw data from working consideration during the analysis process and with it real information. For example, with some spectroscopic techniques, most notably magnetic rotation, spectral line shapes are a rich source of information aiding greatly the assignment process. Therefore, the ability to generate long range, linear spectral displays of the actual data acquired is of considerable value.

The conventional method of scanning has been simply to tune the laser current and then to change the diode temperature and scan another partially overlapping region.[1] Unfortunately, as has already been mentioned, single-mode current scans are limited to fractions of a cm^{-1}. In principle, longer scans are achievable with temperature tuning alone,[2] but so far controlled temperature tuning appears not to be technically feasible because of the inherently slow response time of the temperature servo loop. The recent development[3] of a scanning mode in which the diode is locked to a tunable external cavity permits accurate, if still somewhat nonlinear (because the external cavity is tuned by a Brewster plate), scanning over frequency regions approaching 1 cm^{-1}.

Although several papers have been written about computer-controlled diode laser spectrometers[1,4-6] and computer manipulation of the resulting spectral data, the problem of joining the intrinsically rather short scans into multiwavenumber scans appears not to have been specifically addressed. The purpose of this work is to describe our method for doing this which allows continuous and linear frequency scans to be routinely generated over 3 cm^{-1} in length. These scans can be readily and accurately calibrated from reference spectra.

II. Hardware

The infrared diode spectrometer consists of a Spectra-Physics diode laser source (SP-5150), an LSI-11 minicomputer, a 1-m multipass White cell, and diagnostic instrumentation configured as shown in Fig. 1. With our present collection of laser diodes and optical coatings the operating range spans 1750–2850 cm^{-1} but can be readily adapted for any region covered by lead salt diodes.

The laser output beam of the spectrometer is split by a ZnSe beam splitter and ~70% is directed into the multipass cell allowing up to an 80-m absorption path length for spectroscopic investigations. The remaining 30% of the radiation is divided among three diagnostic elements. These consist of two vacuum-spaced marker cavities and a reference gas absorption cell.

Rudolf Bruggemann is with Bonn University, Institute for Applied Physics, 5300 Bonn 1, Federal Republic of Germany; the other authors are with Rice University, Houston, Texas 77251.

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The marker cavities are constructed on an Invar frame kinematically positioned inside an evacuable chamber.[7] Their germanium optics have dielectric high-reflectivity coatings on the interior surfaces and antireflective coatings on the outer ones. The fine etalon is a semiconfocal cavity with a free spectral range (FSR) of 500 MHz. The second coarse etalon has a plane-parallel arrangement providing a continuously variable FSR, usually adjusted to around 3 GHz. The reference cell is 2.5 cm in diameter, 15 cm long, and employs CaF_2 windows that are tilted to prevent back-reflection into the laser. Liquid nitrogen cooled InSb detectors are used in conjunction with the three diagnostic elements and the White cell. Each detector is coupled via preamplifiers to separate lock-in amplifiers. Modulation is provided either by chopping the laser output at 400 Hz with the tuning fork chopper or by frequency modulating the laser in the range from 500 Hz to 10 kHz. However, most work involves free radicals and employs modulation of the absorption by concentration or Zeeman modulation.

III. Mode of Operation

The computer control of the diode laser and data acquisition follow standard methods. The current is scanned over $\sim 0.3\ \mathrm{cm}^{-1}$, then the temperature is adjusted (presently manually; in the future, it should be possible to execute this control function under computer control utilizing recent advances in high resolution D–A converters) to provide a new slightly overlapping current scan region, and the current scan is repeated. The mode selecting monochromator grating is adjusted under computer control. Incoming data from the experiment are buffered through operational amplifiers and are processed by a sixteen-channel A–D converter with differential inputs. The software used to scan the diode laser was adapted from a comprehensive program designed to operate tunable laser systems, in particular, a color center laser spectrometer.[7] A single program handles scanning as well as data collection, storage, and display to the terminal screen or to an X-Y plotter.

A given frequency scan consists of successive current scans between each of which the diode temperature is adjusted. During scanning, each time the end of the diode current lookup table is reached, the computer automatically halts the scan and enters a ramp mode in which the current is rapidly (200 Hz) ramped over the region just scanned. At this point the temperature must be adjusted in such a manner that, when scanning is resumed, a new region will be covered exhibiting an overlap with the previous region. This is accomplished by viewing the coarse marker cavity features (~3-GHz spacing) on the oscilloscope and carefully adjusting the temperature until the last peak on the high current side of the display is moved to the edge of the low current side. The user then signals the computer to continue the scan. This process can be repeated until either the laser mode being tuned loses its power or a mode hop occurs producing a discontinuity in the scan.

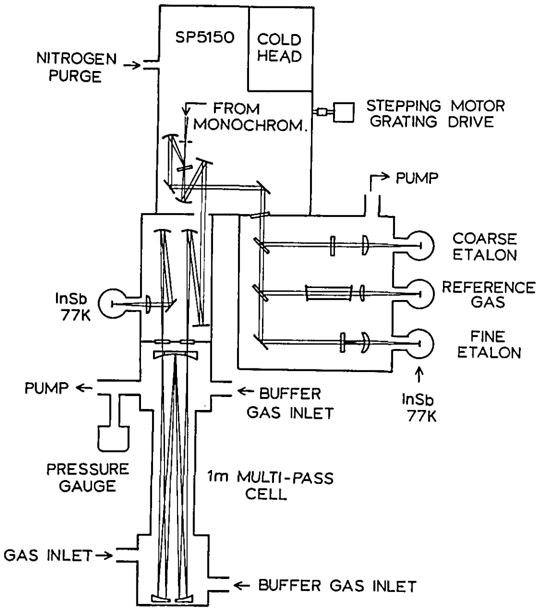

Fig. 1. Optical layout of the diode laser spectrometer and diagnostic instrumentation. The diagnostic box is evacuated during operation of the system.

IV. Overlap

The described scanning scheme results in a data set which covers many wavenumbers but has periodically spaced overlapping regions where current flybacks have occurred. To generate linear continuous frequency scans suitable for analysis and calibration, the individual segments must be linearized, overlaps must be removed, and the adjacent current scans accurately joined. A program has been developed to perform the tasks of linearization and overlap using high resolution screen graphics for data display and cross-hair input for the selection of spectral features.

To linearize the data in a given current ramp segment, the fine marker channel is examined for gross irregularities or discontinuities. If, as is normally the case, none is found, the program locates each marker peak using a centroid fit and determines the maximum spacing between successive peaks. All marker spacings are then normalized to this maximum spacing using a fourth-order polynomial fit to the marker positions and parallel corrections are made to each of the data channels. Aside from the considerable convenience to spectroscopic analysis of a linear frequency scale, the need for such linearization is shown in Fig. 2 where fine marker features are shown overlapped without and with linearization.

Once the individual segments have been linearized, the overlapping segments are joined. A spectral feature is identified as occurring on each side of the flyback and the two scans are aligned by superimposing these features. The relatively close spacing (500 MHz) of the fine marker peaks makes them the best choice as reference features for overlapping. However, since the size of the overlap is often such that more than one marker may be repeated after a current fly-

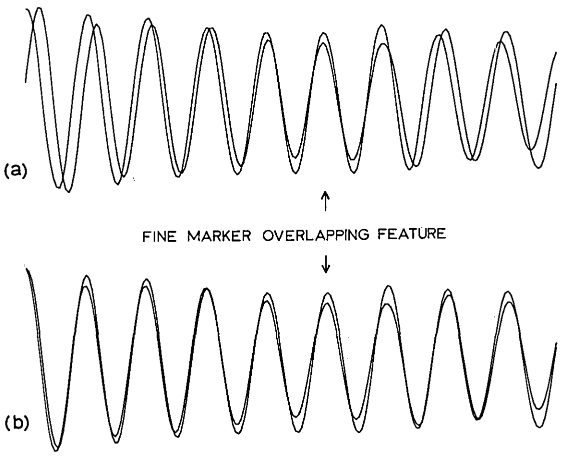

Fig. 2. Overlapping of two successive current scans showing the value of linearization of the spectrum: (a) the scans are not linearized before overlapping; (b) the two scans are linearized and then overlapped.

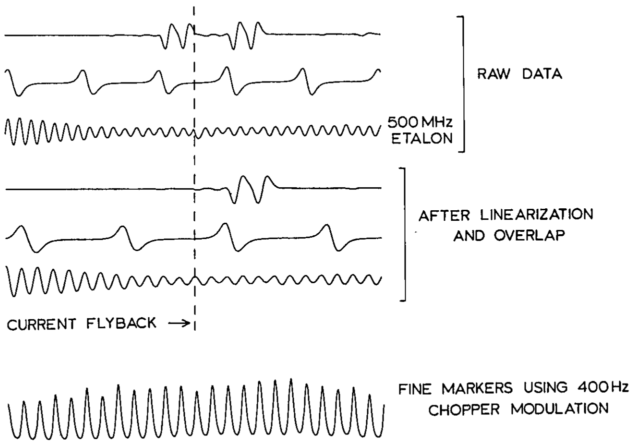

Fig. 3. Illustration of the overlapping procedure. Not all overlaps are as smooth as this one. However, any lack of smoothness results from variations in the vertical scale size in between scan segments and does not directly affect the frequency accuracy. These scans were taken using frequency modulation which washed out some of the fine etalon finesse. The bottom trace taken with the frequency modulation turned off shows the true fine etalon fringes.

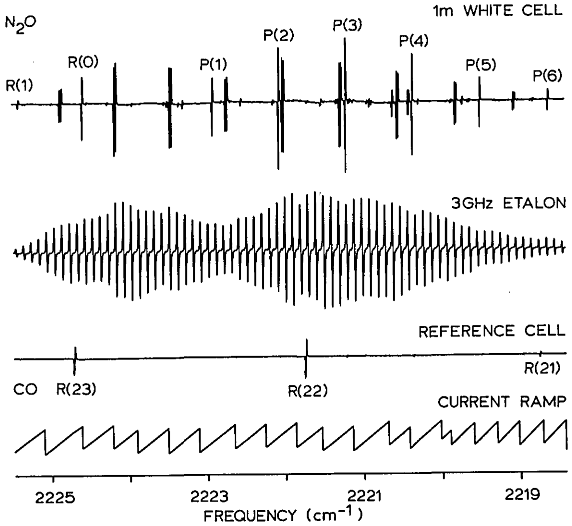

Fig. 4. A 7-cm^{-1} scan using frequency (current) modulation. The White cell contained a mixture of nitrogen oxides. The reference cell contained CO as a calibration gas. In the figure, the fine marker channel is not depicted as individual fringes are not resolvable on this scale. A refinement which can be readily added is to adjust the spectroscopic channels' vertical scale with the varying height of the coarse marker features across the scan. This has not been done as it was believed that the depiction of the diode power variations with frequency is more informative.

back, a second reference is required to make positive identification of two fine markers corresponding to the same frequency. The data from the coarse marker channel serves as this reference.

The software performs the overlapping of the current scans interactively with the user. The data channel from which overlapping features will be chosen is requested from the operator as well as the channel which will be used as a reference in order to insure that equivalent spectral features are selected. In the region of each current setback, the overlap channel is plotted on the lower half of the screen and the reference channel on the upper half with a vertical dashed line to indicate the position of the flyback. After the overlap features are chosen using the screen cross-hairs and the centroids have been determined, the data are replotted with the overlap features superimposed. The vertical cross-hair can then be used to select a cut point at which data from one current scan will stop and that of the next scan will continue in such a manner that a smooth transition occurs at the mend. Figure 3 illustrates such an overlap region. This procedure is repeated for each current flyback after which a continuous and linearized frequency scan is produced. Figure 4 illustrates one such scan covering a region of almost 7 cm^{-1}.

This spectrum can now be calibrated as one continuous scan by another set of calibration programs. Using the frequencies reported by Guelachvili[8] for the CO lines to calibrate the frequency scale of the traces shown in Fig. 4, the free spectral range of the fine etalon was determined to be 0.015433 cm^{-1}, and the N_2O frequencies were then measured using CO for calibration. The N_2O frequencies we obtain are systematically ~0.001 cm^{-1} higher than those measured by Amiot and Guelachvili.[9] The standard deviation of the differences is ~0.001 cm^{-1}.

V. Conclusion

In this work a system is described for producing multiwavenumber, frequency linear, readily calibrated single-mode diode laser spectroscopic scans to simplify the assignment and analysis of diode laser gas phase spectra. The recent report of the frequency stabilization of a diode laser to an external broadband cavity[3] provides the potential for acquiring frequency scans with increased spectral accuracy. The combination of that hardware with the overlapping methods presented here will significantly enhance laser spectroscopy in the infrared from 3 to 20 μm. New advances in diode laser technology hold great promise for the future application of diode lasers to spectroscopic investigations. Lasers capable of longer range current scans have already been produced,[10] and the quality and performance of commercially available diodes are expected to steadily improve. As diodes improve, the techniques described here can provide continuous, linearized spectra covering larger frequency regions.

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