

Elimination of Baseline Variations from a Recorded Spectrum by Ultra-low Frequency Filtering

AHMET K. ATAKAN,* W. E. BLASS, and D. E. JENNINGS

Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37916 (A.K.A., W.E.B.) and Infrared and Radio Astronomy Branch, Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771 (D.E.J.)

A technique for the elimination of baseline variation is discussed and illustrated. The method involves ultra-low frequency filtering in the frequency domain (transform space) and is illustrated by applying it to several diode laser spectra of C₂H₆ (ethane). In the examples presented, the technique eliminates the effects of diode laser output energy variations as a particular mode is scanned. This technique may be especially valuable for diode laser spectroscopy where a multipass cell is used and where the cell cannot readily be removed from the beam to obtain a background scan. The technique should be applicable to baseline variation problems in general.

Index Headings: Spectroscopic techniques; Computer applications; Lasers.

INTRODUCTION

Various recorded absorption spectra exhibit long period variations in the baseline signal. These variations may cause problems with interpretation of the spectrum and in some cases must be removed from the spectral record if further processing of the record is to be attempted (cf. for example, Blass and Halsey¹).

I. EXPERIMENTAL

It is productive to consider a spectrometric system as a series of linear transformations successively convoluted with the primary signal source.¹⁻⁴ For example, the output signal of a spectrometric system without a sample in the beam could be represented as:

$$S(t) = \int I(\nu) T(\nu' - \nu) G(t - \nu') d\nu d\nu' \quad (1)$$

where T is the transfer function of the optical system, G is the transfer function of the electronics system, and $I(\nu)$ is the energy density of the radiation source. Eq. (1) may be expressed as

$$S = I * T * G \quad (2)$$

where $*$ represents convolution.^{5,6} Eq. (1) implies that the recorded signal is a function of time, which is generally true and is clearly reasonable if one views time not as the driving variable of S but as the observation fiducial marker. That is, the recorded signal may profitably be viewed as a time series.^{1,4,7}

Ideally, one would prefer that the source energy density represented by $I(\nu)$ would have constant energy output as a function of frequency and time, but this is not generally the case. Although taking frequency and time variations into account is theoretically trivial, it

may in practice be difficult. The quantity I in Eqs. (1) and (2) may be replaced by

$$I * M$$

where I is assumed to be of constant output energy density and M is the frequency and time amplitude modulation function of the source (which usually is not known explicitly).

Additionally, the optical transfer function T also includes some efficiency variation as a function of frequency.³ This can be treated in an analogous manner to the source by replacing T by

$$E * T$$

where E is the frequency dependent optical efficiency function (which normally can be characterized). Eqs. (1) and (2) can be rewritten as

$$S(t) = \int I(\nu) M(t, \nu' - \nu) T(\nu'' - \nu') E(\nu''' - \nu'') \cdot G(t - \nu''') d\nu d\nu' d\nu'' d\nu''' \quad (3)$$

$$S = I * M * T * E * G \quad (4)$$

The modulation and efficiency function can be collected into one variable represented by

$$V = M * E \quad (5)$$

The unmodulated record which can be represented by

$$R = I * T * G \quad (6)$$

will become

$$S = R * V \quad (7)$$

in the more general case.

If V were analytically known or measurable, then the effects of V could be eliminated by taking the Fourier transform⁵ of the data, S , and the variation function V

$$\hat{s} = \hat{r} \cdot \hat{v} \quad (8)$$

and dividing by \hat{v} and retransforming to signal space

$$S^* = \left[\frac{\hat{s}}{\hat{v}} \right] = \left[\frac{\hat{r} \cdot \hat{v}}{\hat{v}} \right] = \hat{r} \quad (9)$$

where \hat{s} indicates the Fourier transform of S .

This procedure makes use of the convolution theorem,^{5,6} and the "corrected" spectral record is then represented by S^* .

Since V may not be known or measurable (viz. random long period source intensity variation), an alternate method for the elimination of the effects of V has been tested.

Received 12 November 1979.

* Permanent address: Physics Department, Boğaziçi University, Bebek, Istanbul, Turkey.

Long period (although not necessarily periodic) variations in the 100% transmission signal are represented in frequency (i.e., transform) space by the spectral frequency content very close to zero frequency. If the spectral frequency content (in transform space) of the desired spectrum lies principally at significantly higher frequencies, then a straightforward elimination procedure is possible. The major effects of V may be eliminated by simply attenuating the spectral frequencies of \hat{s} near zero frequency and retransforming to signal space.

The procedures that have been used are as follows:

1. Each observed scan was hand digitized at intervals of 0.5 mm which resulted in a total of 512 data points.
2. In order to maintain the resolution of the data after transformation it was necessary to add 766 data points to each end of the data file by means of linear extrapolation.
3. To prevent aliasing, the data files were then expanded to a final 4096 data points by quadratic interpolation.
4. A discrete Fourier transform was performed on S to yield \hat{s} .
5. The power spectral density and the phase transform of \hat{s} were calculated.
6. The power spectral density was multiplied by the ultra-low frequency filter function \hat{f} yielding $|\hat{s}|^2 \cdot \hat{f}$.
7. The phase transform of \hat{s} was retained.
8. An inverse discrete Fourier transform was performed on the retained phase angle information and $|\hat{s}|^2 \cdot \hat{f}$ which yielded the "filtered" spectrum.

II. RESULTS

The uppermost curve of Fig. 1 is a diode laser scan of a small section of the $5 \mu\text{m}$ $\nu_9 + \nu_{12}$ (E_u) band of C_2H_6 .⁸ The particular diode used here exhibited unusually large output intensity fluctuations when operated in the spec-

tral region shown ($5 \mu\text{m}$), which resulted in a relatively low signal/noise ratio.

The lower trace in Fig. 1 shows the filtered output. Fig. 2 presents four further examples using various filter function parameters as described below. The particular filter function \hat{f} used here was of the form

$$\hat{f} = \frac{1}{2} [1 + \tanh \{a(x - x_0)\}] \quad (10)$$

where x is the data point number. As the value of a becomes large this function provides a steep but smooth transition from high attenuation at zero frequency to minimum attenuation at very low frequencies. The parameter x_0 determines the 50% attenuation point. The filter function is mirrored at the "high end" of the discrete Fourier transform array. Any function that has the above properties should, in principle, satisfy the role of a filter function.

Some high-frequency noise filtering has been incorporated into the process as may be apparent in the lower

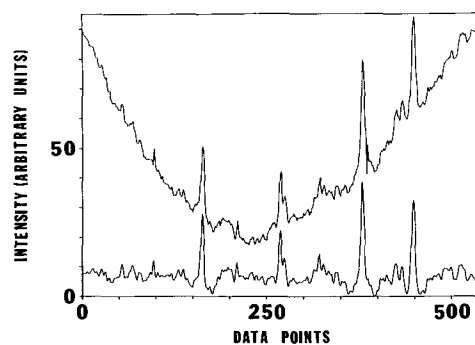


FIG. 1. Section of $\nu_9 + \nu_{12}$ spectrum of C_2H_6 from approximately 2051 to 2052 cm^{-1} with right-most strong transition ${}^{\text{R}}\text{R}_2(6)$.

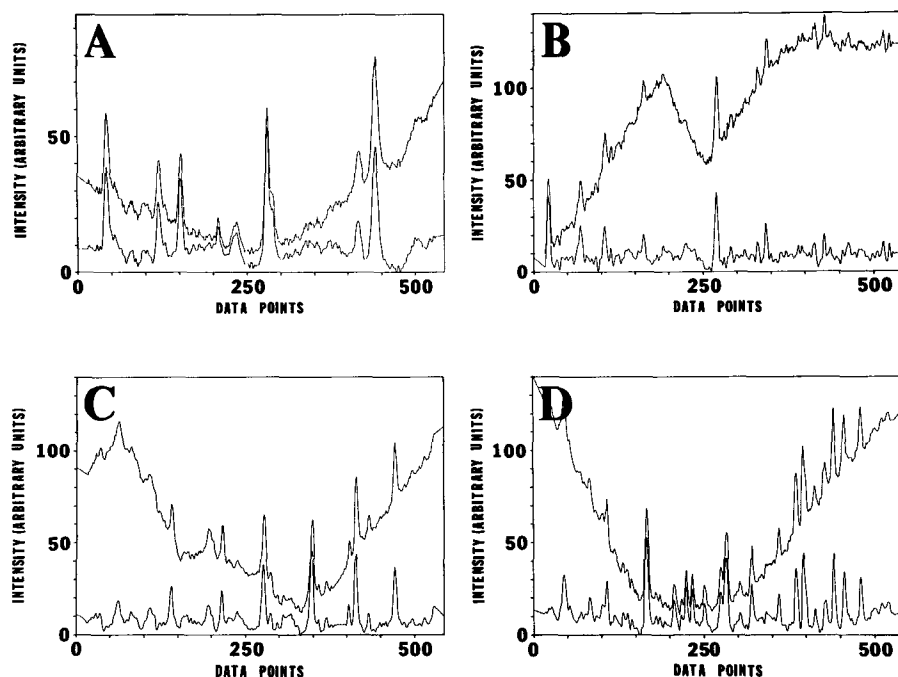


FIG. 2. A. Section of $\nu_9 + \nu_{12}$ spectrum of C_2H_6 from approximately 2052.5 to 2053.5 cm^{-1} with right-most strong transition ${}^{\text{R}}\text{R}_2(7)$. B to D. Various sections of the low frequency end of the ${}^{\text{R}}\text{Q}_3(\text{J})$ Q branch of the $\nu_9 + \nu_{12}$ spectrum of C_2H_6 between approximately 2048 to 2049 cm^{-1} .

traces of Figs. 1 and 2. This noise filtering is accomplished by setting the attenuation to high levels (actually infinite in the examples presented) in the high-frequency region of the discrete Fourier transform array. To accomplish this the filter function was set equal to zero for the values of x larger than some value of x called the "high filter cutoff", N_0 . The value of N_0 was determined by trial and error. As far as the actual power spectral density array in the discrete Fourier transform procedure is concerned the filter function \hat{f} is shown in Fig. 3 with x_0 and N_0 indicated. The parameters a , x_0 , and N_0 used in the calculations of Figs. 1 through 4 are given in Table I.

Fig. 4 is the Fourier transform of the filter function of \hat{f} . The total array length N_A is 2048.

In principal, convolution of the spectrum in signal space (the actual spectrum as recorded) with the transform of the filter function \hat{f} , i.e., F , should produce the same result and may well be more practical for long high resolution records typical of the most advanced spectrometers where an encoded (machine readable) spectrum may contain a quarter million data points or more.

III. CONCLUSION

A technique for the removal of baseline variations from recorded spectra has been demonstrated. The particular examples used here were diode laser spectra, but any spectrum with baseline variations could have been used. Although tests for positional stability were not performed, the superimposed plots indicate that the position

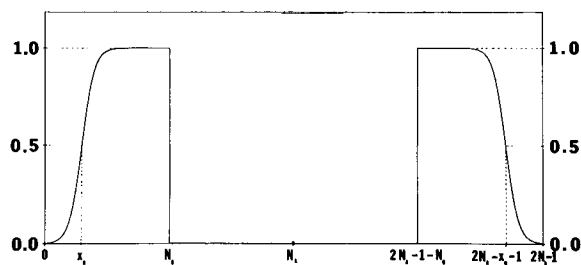


FIG. 3. Filter function $\hat{f} = \frac{1}{2}[1 + \tanh \{a(x - x_0)\}]$.

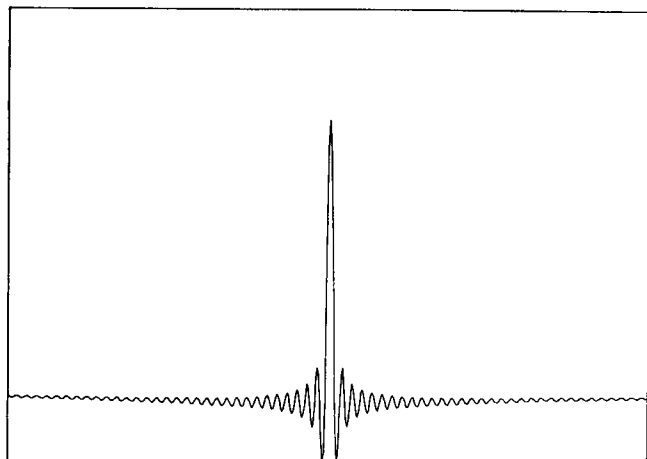


FIG. 4. Central portion of the inverse Fourier transform, F , of the filter function \hat{f} .

TABLE I. Filter function parameters.

Fig.	Value of constant a	% 50 attenuation point x_0	High filter cutoff N_0
1	0.1	30	512
2A	15.0	15	512
2B	1.2	30	512
2C	1.2	30	512
2D	0.1	20	512
3	0.01	300	1024
4	15.0	10	512
5	0.1	30	512

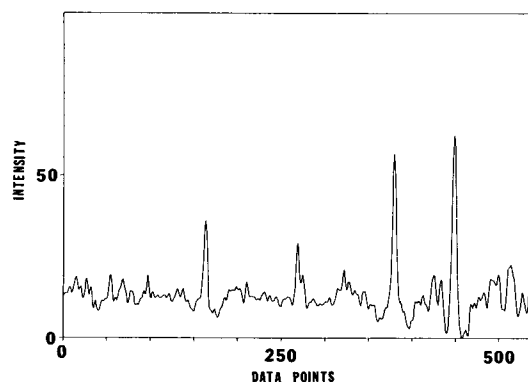


FIG. 5. Data contained in Fig. 1 processed so that the correct relative intensities appear in percent absorption.

information is invariant under this procedure. It should be noted that since the transform of the convoluting filter function F shown in Fig. 4 is symmetric, positional stability of the spectral features is to be expected. In addition, if the same filter is passed over a calibration scan, then any shifts incurred would affect both the data scan and the calibration scan in the same way.

Although it was not done in all the work reported here, one can obtain the correct relative intensities in the data by conversion to percent absorption. This can be accomplished by using the difference of the "raw" data with the "filtered" data as the baseline. The baseline so obtained is then ratioed with the filtered spectrum to correct to absorption. An example showing the correct relative intensities for the data in Fig. 1 is shown in Fig. 5.

Spectra that showed widely varying backgrounds were chosen in order to demonstrate the power of this technique. This filtering was applied to these spectra in their entirety. No partitioning was done on any of the scans, as is usually done in the technique of background subtraction.

Details of the technique and programs may be obtained from the authors.

ACKNOWLEDGMENTS

One of the authors (A.K.A.) would like to thank the Head of the University of Tennessee Department of Physics and Astronomy, Professor W. M. Bugg, for making available his departmental facilities. He is also grateful to Halil Ibrahim Sur of Boğaziçi University for painstakingly hand encoding the diode laser spectra. Another of the authors (D.E.J.) expresses appreciation to J. J. Hillman and J. L. Faris for laboratory cooperation and support. The authors would like to thank Dr. S. J. Daunt for his help in the preparation of this paper. We would also like to thank the Academic Affairs Office of the University of Tennessee for its policies which make the extensive computer facilities of the University available to us, and the Computer Center (UTCC) for its support and assistance.

This work was supported in part by the planetary atmospheres program of NASA under Grant NGL-43-006-001, and in part by NATO Grant NRG-1690.

1. W. E. Blass and G. W. Halsey, *Deconvolution of Infrared and Other Types of Spectra* (Academic Press, New York, in press).
2. W. E. Blass and A. H. Nielsen, in *Methods of Experimental Physics*, 2nd Ed., D. Williams, Ed. (Academic Press, New York, 1974), Vol. 3A, pp. 126-202.
3. J. E. Stewart, *Infrared Spectroscopy* (Dekker, New York, 1970).
4. W. E. Blass, *Appl. Spectrosc. Rev.* **11**, 57 (1976).
5. E. O. Brigham, *The Fast Fourier Transform* (Prentice Hall, Englewood Cliffs,

- NJ, 1974).
6. R. Bracewell, *The Fourier Transform and Its Applications* (McGraw-Hill, New York, 1965).
7. E. A. Robinson, *Multichannel Time Series Analysis with Digital Computer Programs* (Holden-Day, San Francisco, 1967).
8. K. F. Lin, W. E. Blass, and N. M. Gailar, *J. Mol. Spectrosc.* **79**, 151-157 (1980).

Application of Laser-excited Atomic Fluorescence Spectrometry to the Determination of Nickel and Tin

M. S. EPSTEIN,* J. BRADSHAW, S. BAYER, J. BOWER, E. VOIGTMAN, and J. D. WINEFORDNER†

Department of Chemistry, University of Florida, Gainesville, Florida 32611

The analytical determination of nickel and tin by laser-excited atomic fluorescence spectrometry (LEAFS) is studied. Non-resonance nickel fluorescence near 340 nm is excited at several nickel lines near 300 nm and direct-line tin fluorescence at 317.5 and 380.1 nm is excited at the 300.9 nm line in a nitrogen-separated air-acetylene flame. Factors which affect detection limits and methods which can be used to improve them are discussed. The application of LEAFS to the determination of nickel and tin in several standard reference materials (river water, unalloyed copper, and fly ash) is investigated, including problems related to iron spectral interference encountered for analysis in these matrices.

Index Headings: Flame atomic fluorescence spectroscopy; Lasers, pulsed dye.

INTRODUCTION

While laser-excited atomic fluorescence spectrometry (LEAFS) has been shown to be an extremely sensitive method of trace metal analysis,¹ its application to the analysis of real samples can be limited at resonance transitions or at close nonresonance transitions by the scatter of laser radiation into the detection system due to matrix constituents. Such scatter is not easily discernible from fluorescence, and, even when it can be, such as when scanning methods are employed,² the scatter signal increases the noise level of the measurement when its magnitude significantly exceeds that of the fluorescence signal. Since the ideal detection system in atomic fluorescence is a high optical speed (good throughput) spectral isolation device with a wide spectral bandpass, the most useful transitions for LEAFS should be those non-resonance transitions which are far enough away from the wavelength of excitation so that no scatter interference occurs. Furthermore, the use of nonresonance transitions extends the linearity of analytical growth curves

since postfilter effects are often not as significant as when resonance fluorescence is employed. The use of non-resonance transitions (which are separated by more than 15 nm from the excitation transition) for LEAFS has been reported for iron (296.7 nm excitation/373.5 nm emission),¹⁻³ lead (283.3 nm/405.8 nm; 405.8 nm/283.3 nm),^{1,4} thallium (377.6 nm/535.0 nm), vanadium (370.4 nm/411.2 nm), and indium (410.4 nm/451.1 nm).¹

This investigation is concerned specifically with the application of LEAFS to the determination of nickel and tin using a frequency-doubled, flashlamp-pumped, tunable dye laser to excite fluorescence in a nitrogen-separated air-acetylene flame. Since the most intense laser radiation from this system is generated using rhodamine 6G as a laser dye, we were specifically interested in the excitation of near ground-state transitions around 300 nm, which is the maximum of the dye's gain curve, and the measurement of nonresonance fluorescence induced by this excitation.

The analytical application of LEAFS to nickel and tin determination is evaluated using several National Bureau of Standards (NBS) Standard Reference Materials (SRM). These included a simulated river water (SRM 1643, 49 ng/g of Ni), unalloyed copper (SRM 394, 65 µg/g of Sn; SRM 396, 4.2 µg/g of Ni, 0.8 µg/g of Sn), and fly ash (SRM 1633, 98 µg/g of Ni).

I. EXPERIMENTAL

A. Instrumentation. The instrumentation used in this study is described in Table I and a diagram of the arrangement of experimental components is shown in Fig. 1. Radiation from a frequency-doubled, flashlamp-pumped tunable dye laser (with intracavity etalon for bandwidth narrowing) is directed into the flame cell through a 0.3 cm aperture in a planar mirror which can be used as part of a multipass arrangement by replacing the light trap opposite the planar mirror with a toroidal mirror.² The entrance slit of the 0.1 m monochromator, which is mounted on its side, has its long axis parallel to the direction of propagation of the laser beam for best

Received 12 July 1979.

* On leave from the Center for Analytical Chemistry, National Bureau of Standards, Washington, DC 20234.

† Author to whom correspondence should be addressed.