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CONCERNING THE EFFECTS OF NOISE ON THE MEASUREMENT OF LINE STRENGTHS

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Abstract—The effects of shot and detector noise on well-resolved measurements of line strength are investigated. Simple analysis, computer simulation and numerical analysis are applied to determine optimum absorber quantities for both conventional and Fourier transform spectrometers. The sensitivity of these optimum absorber quantities to line shape, noise level and spectral resolution are investigated and shown to be small. Inherent bias in line strength measurements is explained and shown to be resolution sensitive. Consequences for experimental strategy are discussed. Copyright © 1996 Elsevier Science Ltd

1. INTRODUCTION

1.1. The problem

There is considerable interest in the measurement of spectral absorption coefficients (k_σ) and line strengths $\mathscr{S}$ (defined as the integral of k_σ across and absorption line), principally as a result of the need to calibrate remote gas detection systems and atmospheric models. Although there remains a real need to conduct laboratory measurements, large databases such as HITRAN[1] are available in PC-readable form. These data may not necessarily have been acquired using optimum conditions of path-concentration product, and may not be accompanied by error bounds. The determination of what constitutes optimum conditions, and the nature of the errors are addressed below.

Imagine a "simple" experiment in which the spectral absorption properties of a gas are to be measured using a light source, a gas cell and a spectrometer. The experimenter must choose the conditions within the gas cell with some care since the temperature, the pressure and the presence of any diluent "carrier" gas may all affect the breadth and shape of the spectral absorption lines and bands. Having set these physical parameters, it remains to choose the path length or, equivalently, the overall path-concentration product (or column density) for the cell. In cases where the absorption is not so weak as to demand all the available path and then some, the experimenter may ask if, given the characteristics of his equipment, there exists an optimum path-concentration product (and therefore an optimum peak absorption for the cell). The term "optimum" refers to those conditions which yield minimum uncertainty on the result, or perhaps minimum bias. It is common to employ a short path with small absorption in order to remain "in the linear region"; it will be shown that this strategem is inadequate, and that under some conditions it can be advantageous to use very large peak absorptions—up to 98%. The experimenter must also consider carefully the amount and type of noise present in his equipment as well as the resolution attainable before filling the cell.

The primary purpose of the study set out below is to illustrate the effect of noise on the choice of conditions; it is therefore assumed initially that the experimenter's equipment is more than capable of resolving the absorption profiles, with about 20 samples per Full Width at Half Maximum (FWHM). There has been considerable study devoted to the effects of marginal resolution on the measurement of line strengths (see, for example, Ref. 2), but not much with reference to noise. Subsequently, in order better to address the realms of practical measurement where only three or four samples per FWHM might be aspired to, the effects of resolution degradation are investigated. It is shown that whilst the optimum path-concentration product is not significantly affected by resolution, bias in the recovered line strengths is.

1.2. *Instrumental considerations*

It will be assumed that the experimenter is possessed of a stable light source, but that he is afflicted[4] by a combination of shot noise and detector noise. Both these noise types have Gaussian amplitude distributions, and "white" (uniform) electrical power spectra. Both may be reduced by signal averaging, albeit at the expense of observation time (their r.m.s. levels scale with the square-root of the effective electrical bandwidth). It is assumed that sufficient time is allowed between samples that the noise associated with successive measurements is truly uncorrelated.

In cases where shot noise predominates ("shot-limited" operation), the r.m.s. level scales with the square-root of the average signal level. For "detector-limited" operation however, the r.m.s. level is constant. Although the seasoned experimenter will be aware that there is never enough light in his system,[4] increasing the light level gives a better return in the detector-limited rather than the shot-limited situation.

Two types of spectrometer are considered: a conventional dispersive spectrometer (CDS) and a Fourier transform spectrometer (FTS). It is assumed that the dispersive system (utilising a grating) is fitted with an array detector for greater measurement efficiency (compared to a scanning monochromator with a single detector). The FTS system is attractive in that it offers greater optical throughput (the "Jaquinot advantage") and, since its single detector is presented with a relatively high light level at all times, the effects of detector noise are reduced (the "multiplex advantage" often quoted in the infra-red). The two types of instrument are included not in an attempt to compare them for overall merit, but rather because they are affected differently by noise. Each element in the array of a dispersive system receives light from a small element of optical bandwidth and yields a signal with a constant detector noise component and a shot component which scales with the square-root of the signal in that bandwidth element. The overall noise variance is simply the sum of the shot and detector variances. In a FTS the situation is different: a pre-filter is fitted to limit the bandwidth, and the detector is presented with an interferogram whose average level is proportional to the total amount of light entering the instrument. The shot noise contribution is therefore much larger (offsetting, relatively, the effects of detector noise), and it scales with the broad-band light level rather than the light associated with any given optical frequency. When the interferogram is subjected to Fourier transformation, the noise power is redistributed uniformly into all the resulting spectral samples, including those at the centre of a deep absorption. The signal-to-noise ratio (SNR) performance, comparing line centre to line wings, thus appears poorer than that of a dispersive system; on an absolute scale however, and especially when detector noise is a problem, the FTS may yield better overall SNR due to its throughput advantage (the multiplex advantage does not, of course, apply when comparing an FTS with an array-fitted CDS). It will be assumed henceforward that both a CDS fitted with an array and a FTS are available, and that both have the same resolving power.

1.3. *Outline*

The study commences with first-order analysis applied to the problem of determining a single frequency spectral absorption coefficient k_σ using a CDS, and optimum path-concentration products are derived for different noise regimes assuming small overall noise levels and unlimited resolution. The behaviour of the optimum path-concentration product as the relative importance of shot and detector noises changes is demonstrated.

Similar analysis is then applied to the measurement of line strength $\mathscr{S}$, and the results are checked by means of a statistical simulation of a typical experiment; results are given for both dispersive and FTS systems, and the shortcomings of the first-order analysis are exposed. Definite optimum absorber quantities are given for each system; it is shown that these conditions depend strongly upon the relative contributions of shot and detector noise in a CDS, but that for the FTS case they are less dependent upon the source of the noise.

It is shown that any noise-affected measurement of line strength is inherently biased due to the non-linearity of the relationship between irradiance and absorption coefficient, and a method is presented whereby error limits may be assigned to any measurement given a knowledge of the system noise. The effects of reduced resolution are investigated; it is found that there is little effect upon the optimum absorber quantities, but that the bias in recovered line strengths is affected significantly.

Some discussion is presented on the optimum choice of experimental strategy, and it is concluded that best results are obtained by obtaining a single high-quality irradiance spectrum rather than by averaging multiple measurements of line strength. Problems arising from inaccurate knowledge of the path-concentration product are also discussed.

The study concentrates on absorption spectroscopy, since the determination of an absorption coefficient from an emission spectrum requires more careful calibration. Furthermore, the optimum conditions are presented for particular line strengths, and several different measurements may be required should there exist a wide range of line strengths in a particular spectrum.

2. UNCERTAINTY IN THE SPECTRAL ABSORPTION COEFFICIENT k_σ

A useful insight can be gained by finding the fractional error in a single-frequency measurement of absorption coefficient as a function of total absorber quantity; the analytic approach which follows is applicable to a conventional spectrometer. Referring again to the notional absorption experiment, the irradiance I_m measured after the absorption cell at a particular optical frequency σ is determined by Beer's law (assuming the medium to behave linearly):

$$I_m = I_0\,e^{-qk_\sigma} \tag{1}$$

where I_0 is the source irradiance and q represents the total amount of absorber expressed as a path-concentration product. This formula may be inverted to obtain the spectral absorption coefficient k_σ explicitly:

$$k_\sigma = \frac{1}{q}(\ln I_0 - \ln I_m). \tag{2}$$

The quantity qk may be thought of as an optical depth in natural logarithmic units.

It is assumed that the measurements of I_0 and I_m are both noisy, with noise variances s_0^2 and s_m^2 respectively, and that the noise signals associated with each measurement are independent (uncorrelated). If the noise components are small compared to the average intensity levels, one can apply the standard first-order formulae for combining uncertain measurements[5] to obtain the variance s_k^2 of the inferred absorption coefficient:

$$s_k^2 = \frac{1}{q^2}\left(\frac{s_0^2}{I_0^2} + \frac{s_m^2}{I_m^2}\right). \tag{3}$$

Notice that, due to the logarithmic transformations, the errors appear in fractional form. This expression may be rendered entirely in terms of k by substituting for I_m from Beer's law to obtain

$$s_k^2 = \frac{1}{q^2 I_0^2}(s_0^2 + s_m^2 e^{2kq}). \tag{4}$$

This expression gives the absolute error on a measurement of k (as a variance); in order to determine the fractional error, it must be divided on both sides by k^2. This will not introduce any further factors of q, so that Eq. (4) may be used to determine the value of q which minimizes the fractional error also.

It is now necessary to make some assumptions regarding the noise variances; it will be assumed that both are made up of a combination of independent (Gaussian distributed) shot and detector contributions, and that the variances due to each contribution may be added together directly to arrive at the overall variances. Thus

$$s_0^2 = s_D^2 + \alpha I_0 \tag{5}$$

$$s_m^2 = s_D^2 + \alpha I_m \tag{6}$$

where s_D^2 is the variance of the constant detector noise component, and α scales the shot noise component, whose variance varies with the measured irradiance in each case. The quantity αI_0 is the shot noise variance observed when there is no absorber present. Substituting these expressions into Eq. (4) and dividing by k^2, a general formula for the fractional variance in k is obtained:

$$\frac{s_k^2}{k^2} = \frac{1}{(kq)^2 I_0^2}\{s_d^2(1 + e^{2kq}) + \alpha I_0(1 + e^{kq})\}. \tag{7}$$

It is apparent that as the total quantity q of absorber is increased, deepening the absorption and reducing the measured irradiance I_m, the variance in the recovered k value at first decreases (due to the $1/q^2$ factor) and then increases exponentially. If detector noise dominates, this increase is rapid since the signal-to-noise ratio of the measured irradiance I_m deteriorates rapidly. Conversely, in a shot-limited regime, the increase is delayed since the irradiance signal-to-noise ratio does not fall so rapidly. This behaviour is illustrated in Fig. 1 where the I_0 has been set to unity and normalized variances of 10^{-4} have been assigned to either α (shot noise) or s_D^2 (detector noise) in Eq. (7).

In order to determine the optimum gas quantity q to use for a given combination of detector and shot noise contributions, Eq. (7) may be differentiated. Figure 2 shows the optimum optical depth (kq) plotted against the ratio of shot noise to detector noise normalized r.m.s. levels (again assuming unit I_0). In producing this data, the total noise variances have been limited in order that the assumptions inherent in the analysis should remain valid even at the centre of the absorption line where I_m is minimum. Given this restriction, the graph is insensitive to the absolute values of noise standard deviation. In the shot-limited extreme, the optimum spectral transmission for the gas cell is given by $e^{-2.2177} = 0.11$ whereas for the detector-limited case it is only $e^{-1.1089} = 0.33$. The difference between the two regimes reflects the balance between fixed detector noise and variable shot noise for different values of the qk product. As shot noise begins to dominate, qk may be increased since the shot noise at the line centre will still be small. Eventually, the logarithmic transformation between irradiance and absorption coefficient begins to increase the variance in k.

3. UNCERTAINTY IN LINE STRENGTH $\mathscr{S}$

The line strength is defined as the integral of the absorption coefficient over frequency σ, carried out across the line width:

$$\mathscr{S} = \int_{\text{line}} k_\sigma \, \mathrm{d}\sigma. \tag{8}$$

The analysis of the previous section may be extended to cover the estimation of the uncertainty in $\mathscr{S}$ given the (different) uncertainties in the values of k at each frequency through the absorption

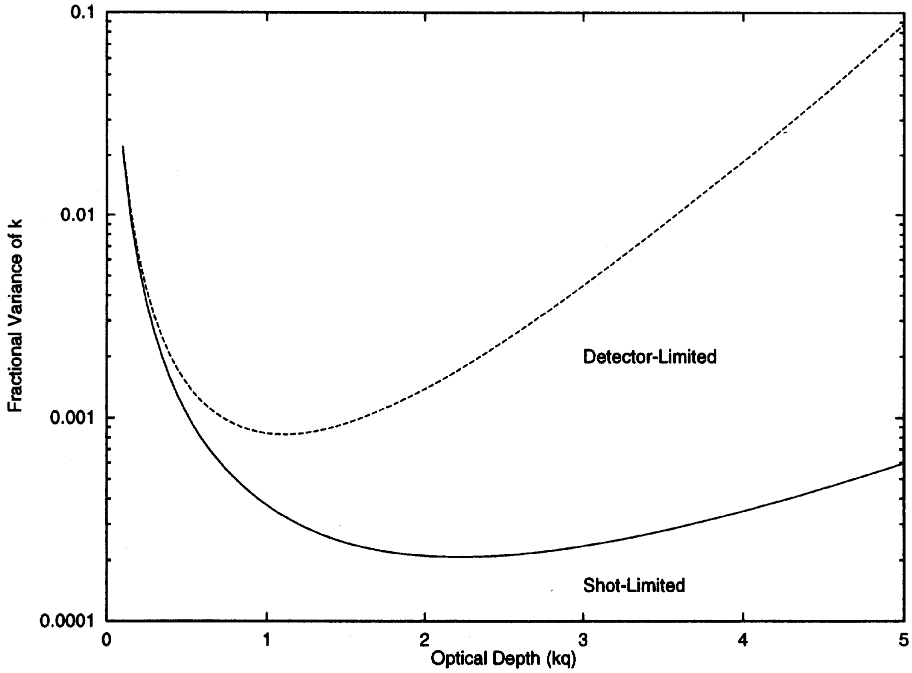

Fig. 1. Fractional variance in computed absorption coefficient as a function of "optical depth" (kq). Minima occur at $(kq) = 1.1089$ for the detector-limited case and at $(kq) = 2.2177$ for the shot-limited case.

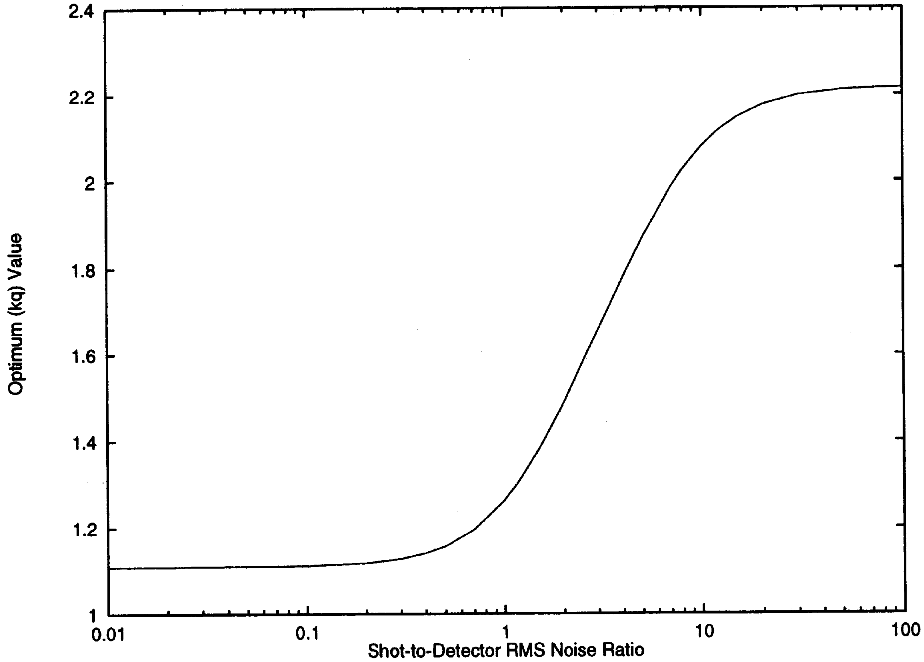

Fig. 2. The optimum "optical depth" (qk) as a function of shot-to-detector r.m.s. noise ratio in a dispersive spectrometer. The fractional uncertainty in the k value recovered in each situation will depend upon the absolute noise level, which is assumed to be small compared with the measured irradiances.

line. It is first necessary to assume a functional form for the absorption coefficient; a good general model is a Voigt profile $V(\sigma)$, which may be synthesized by convolving a Gaussian and a Lorentzian function together. This profile embodies both Doppler and pressure broadening, and the relative importance of each is characterized by the *damping factor*, which is defined as the ratio of the FWHMs of each component. Zero damping indicates a purely Gaussian profile with quickly-dropping wings, whereas a highly-damped profile resembles a Lorentzian function and has much more prominent wings.

Retaining the assumption of noise levels which are small compared to the measured intensities at all points across the absorption, the variance of $\mathscr{S}$ may be thought of as being the sum of the variances of each of the k values (corresponding to spectral bins of width $d\sigma$). The assumption may break down in the centre of a very deep absorption (when the absorber quantity q is high) since the individual measurements of k_σ will begin to show different, skewed probability distributions.

If a conventional spectrometer is employed for the measurements, the variance for each spectral measurement of k_σ is given by Eq. (7) above. The variance of $\mathscr{S}$ is found by integrating that expression over frequency, having first substituted the functional form of k explicitly:

$$s_{\mathscr{S}}^2 = \frac{1}{q^2 I_0^2} \int \{s_D^2[1 + e^{2qV(\sigma)}] + \alpha I_0[1 + e^{qV(\sigma)}]\}\, d\sigma. \tag{9}$$

If the spectrum is generated using a FTS, then a slightly different noise model is required as noted previously. If the interferometer is presented with a total bandwidth $\Delta\sigma$, the average measured irradiance is given by integrating Beer's law:

$$\langle I \rangle = \frac{1}{\Delta\sigma} \int_{\Delta\sigma} I_0\, e^{-qV(\sigma)}\, d\sigma \tag{10}$$

and the total noise variance per spectral irradiance sample will be

$$s_m^2 = s_D^2 + \alpha \langle I \rangle \tag{11}$$

where α is a scaling constant as before. Since, for a given gas quantity q, this variance will remain constant, the variance of the inferred absorption coefficients can be found by analogy to Eq. (7):

$$s_k^2 = \frac{1}{q^2 I_0^2}\{(s_D^2 + \alpha\langle I\rangle)[1 + e^{2qV(\sigma)}]\}. \quad (12)$$

The variance of $\mathscr{S}$ may then be found as previously by integrating this expression over frequency:

$$s_{\mathscr{S}}^2 = \frac{(s_D^2 + \alpha\langle I\rangle)}{q^2 I_0^2}\int [1 + e^{2qV(\sigma)}]\, d\sigma. \quad (13)$$

A numerical solution of both Eqs. (9) and (13) was implemented as follows: sampled versions of normalized Voigt profiles were generated numerically. The FWHM of the narrowest (Gaussian) profile was approximately 20 samples and each profile was normalized to have a unit maximum absorption coefficient. Next, the absorption strength $\mathscr{S}$ was computed by integrating the profiles numerically. As noted above, unit input irradiance is assumed and both shot and detector noise variances are normalized accordingly. The integrals of Eqs. (9) and (13) were evaluated over a frequency range extending to ± 3 times the FWHM of the particular profile $V(\sigma)$ chosen. The output is delivered in terms of a crude signal-to-noise ratio for $\mathscr{S}$ computed by dividing $\mathscr{S}$ by its standard deviation; this quantity was then plotted as a function of absorber quantity q. All results are referred to the "true" value of $\mathscr{S}$ computed within the specific limits in order to avoid truncation error.

In order to test the above analysis and its assumptions, a statistical simulation of the experiment was constructed: noise-free spectral transmission curves for different absorber quantities were generated using the same pre-computed, sampled Voigt profiles used previously. These profiles were then contaminated with Gaussian-distributed pseudo-random noise whose standard deviation was scaled according to user-defined shot and detector noise contributions. Each noisy profile, simulating a real measurement, was then used to compute an "experimental" $\mathscr{S}$ value by inverting Beer's law at each frequency [Eq. (2)] and integrating the recovered k values. The computations were carried out for frequencies within ± 3 times the FWHM of the profile, and it was assumed that an absorption-free region of the same width was available from which to measure the background irradiance I_0 (for which the same noise conditions were applied). This process was then repeated typically 10,000 times for each value of absorber quantity so that basic statistics could be accumulated on the recovered line strength—principally the mean and variance. The effective signal-to-noise ratio was then computed by dividing the mean line strength by its standard deviation. Results were compared to "true" line strengths evaluated within the same limits.

Some caution must be exercised when using pseudo-random generators in case they introduce bias into the results; to this end both congruential[6] and subtractive[7] algorithms (with shuffles) were used to generate uniform pseudo-random deviates with long periods. The Gaussian distribution was obtained by the transformation method.[8] No differences were noted between the two types of generator.

Since the irradiances generated in this experimental method are noisy, it is possible for values to arise which are either greater than illuminating irradiance or, more problematically, less than zero at the centre of a deep absorption. The former case simply generates a negative k value, but the latter cannot be treated with Beer's law, and has to be trapped by the software. The range of noise levels and absorber quantities considered was restricted so that this problem did not occur frequently, but it does constitute a real problem experimentally (usually attributed to stray light).

Both the analysis and the simulation were applied to line profiles with differing damping coefficients in the presence of differing proportional of shot and detector noise. The effects of variable absolute noise level were also investigated.

3.1. Results for a conventional spectrometer

Figure 3 shows the results obtained for a normalized r.m.s. irradiance noise level of 0.01 using a purely Gaussian normalized profile over a range of absorber quantity extending up to 4; the minimum transmission at the line centre would thus be $e^{-4} = 0.018$.

The uppermost SNR curve in Fig. 3, which corresponds to a shot noise limited regime, shows excellent agreement between analysis and simulation. In this case, the shot-noise r.m.s. level quoted corresponds to that which would be observed in the absence of any absorption. The SNR of the measured irradiance remains relatively large even in the centre of the absorption because of the way shot noise scales with irradiance. An optimum absorber quantity q of approximately 3.55 is indicated, corresponding to minimum transmission at line centre of only 3%. This value is much higher than that obtained for a single-frequency measurement of k_σ ($qk = 2.22$), and it reflects the balance between contributions to $\mathscr{S}$ from the line wings and the line centre which is set by the line profile. The "cleanest" contributions come from those narrow parts of the line for which qk is indeed around 2.2.

The remaining curves of Fig. 3 show the effect of increasing the proportion of detector noise (whilst maintaining the overall normalized r.m.s. noise level in the absence of absorption constant

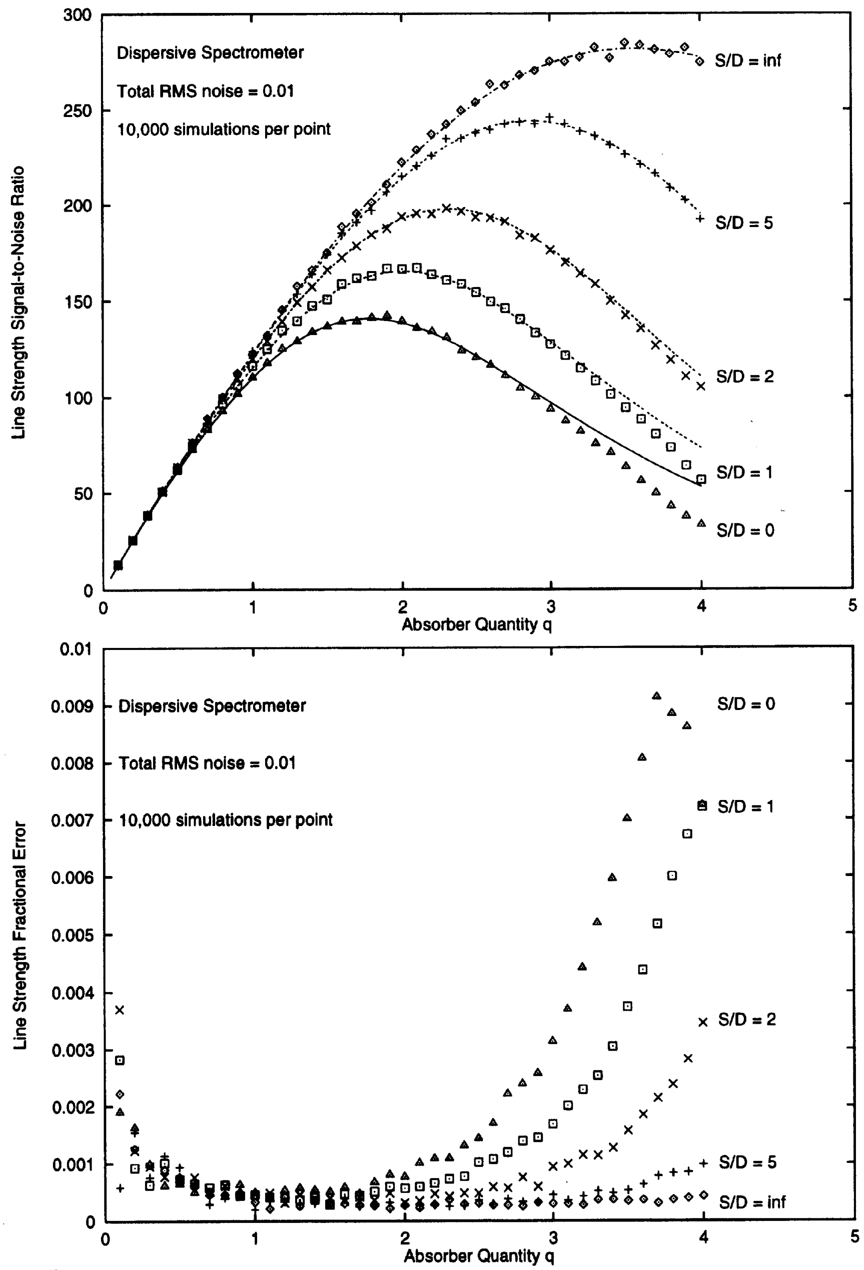

Fig. 3. Uncertainty in $\mathscr{S}$ for a CDS. The total normalized r.m.s. irradiance noise level is 0.01 (mixed shot and detector noise) and a Gaussian line profile is assumed. The lower graph plots fractional deviation of measured $\mathscr{S}$ from its true value.

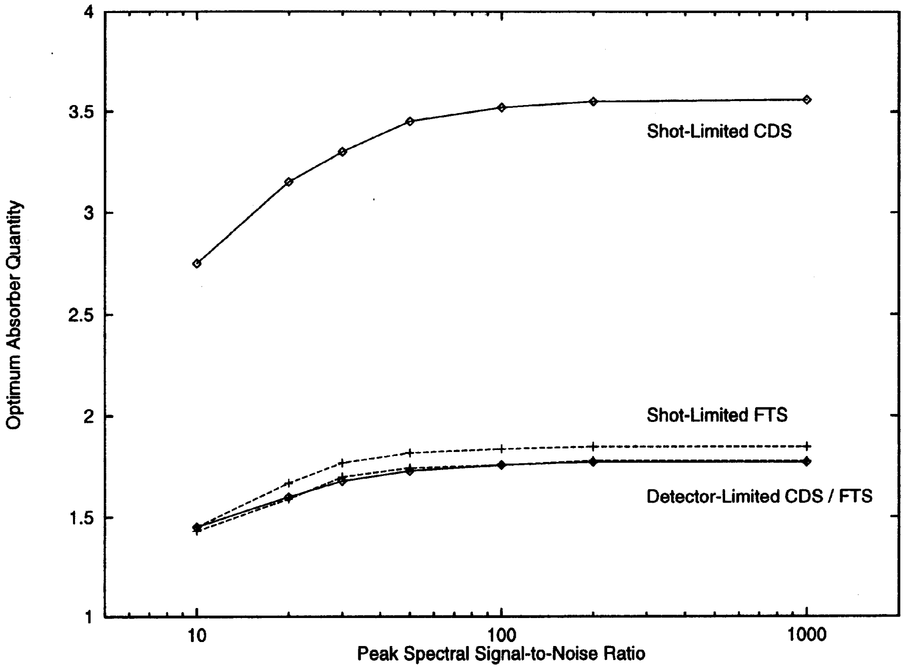

Fig. 4. Variation of optimum absorber quantity with spectral SNR outside the "small noise" regime. A Gaussian profile is assumed. These data are drawn from the simulation.

at 0.01). It is evident that even a small contribution from detector noise is sufficient to reduce the optimum value of q: when detector noise dominates, the best value is $q = 1.78$, corresponding to a line-centre transmission of approximately 17%. This reduction in optimum q is principally due to the degraded irradiance SNR at the line centre giving rise to much more uncertainty in the corresponding recovered k values.

The simulation departs from the simple analysis for high absorber quantities: this is principally caused by the rapid increase in the uncertainty of k values recovered from small, noisy irradiances near the line centre. The lower part of Fig. 3 (in which fractional error in $\mathscr{S}$ is plotted against q) indicates that there is in addition a consistently positive bias associated with the recovered $\mathscr{S}$ value which increases at higher absorber quantities. This bias, which is a consequence of the non-linearity in the relation between irradiance and absorption coefficient, is swamped by the increased uncertainty in $\mathscr{S}$, hence the overall SNR reduces at high q. These points are discussed at greater length below.

The effects of increased damping were investigated under the same noise conditions; no significant shift in the optimum q values was observed, but the overall SNR is improved. This is a consequence of the fact that the wings of the line are more prominent than for a pure Gaussian profile, and therefore the inaccurate recovered k values from the line centre and far wings are relatively less important. It should be recalled that the $\mathscr{S}$ values were evaluated over a specified optical bandwidth; were this bandwidth to increase, the small but relatively uncertain k values from the wings of the line would make a larger contribution to the overall uncertainty, and the peak SNR would fall. The SNR scale is also affected by the absolute r.m.s. noise level, but as long as the assumption of "small noise" holds, the curve shapes are similar and the optimum q values remain essentially the same. Similar effects would be encountered when observing a line broadened by (perhaps unresolved) fine structure.

In some situations, the irradiance SNRs considered above may be unobtainable, and the "small noise" approximation is inappropriate. The increase in line strength uncertainty apparent at high absorber quantities eventually affects the optimum conditions as the spectral SNR degrades: this is shown in Fig. 4. Once again, a shot-limited CDS is most sensitive to spectral noise, showing a decrease in optimum absorber quantity for SNRs below about 50.

3.2. *Results for FTS*

The two noise regimes of an FTS are best treated separately. Detector noise limited operation is the simpler case since the r.m.s. noise is the same in each interferogram sample regardless of light input; after Fourier transformation, the noise contribution to each spectral sample is also uniform. For the purposes of comparison with the results for a CDS presented above, it will be assumed that a normalized detector noise r.m.s. level of 0.01 per spectral sample obtains (the interferogram r.m.s. noise would, of course, be smaller by a factor $\sqrt{N}$, there being N independent spectral samples).

The shot noise case is more problematic, since it requires assumptions to be made regarding the total bandwidth entering the FTS and the interferogram sampling; a large bandwidth brings with it a greater total shot noise contribution, and this noise is redistributed evenly amongst all the samples in the spectrum. In the shot-limited situation, the FTS does not show a significant advantage over an array-fitted CDS, and in order to avoid the specification of detailed experimental parameters, it will be assumed that the FTS is arranged so as to yield a normalized shot noise r.m.s. level of 0.01 per spectral sample when viewing the light source in the absence of absorption.

It was noted in the foregoing analysis that the FTS case resembles that of a detector noise limited conventional spectrometer because each spectral sample has a constant noise level; it is therefore not unexpected that the optimum absorber quantity is lower than that for a shot noise limited dispersive spectrometer. The dramatic effects of small admixtures of detector noise seen in the dispersive system are therefore absent in the FTS, as demonstrated in Fig. 5.

The absorber quantity giving largest SNR is approximately 1.85 for shot-limited operation and 1.78 for detector-limited operation, although minimum bias occurs for a value nearer 1.3. The SNR simulation departs from the first-order theory for high q in both regimes; this is to be expected since the irradiance SNR is relatively poorer near the line centre than for the CDS, and non-linearity becomes evident. The bias increases similarly in both cases. The use of a Voigt profile with higher damping was investigated, and there is very little effect on the optimum q (a marginal increase is observed). The overall SNR increases (as for the CDS) although the reasons are slightly different; in addition to the previous arguments, a broader line absorbs slightly more light from the total bandpass entering the FTS, and this helps to reduce the shot noise over the whole spectrum. This effect would only be significant when a very narrow pre-selecting filter is employed ahead of the FTS (as in this simulation).

The optimum absorber quantity required for an FTS reduces slightly as the noise levels increase beyond the "small" regime (refer back to Fig. 4). The shot noise limited case is less sensitive than for a CDS, and the reduction in optimum q in both shot and detector limited regimes is small.

4. DEFINING ERROR LIMITS ON $\mathscr{S}$

The dependence of both SNR and bias in measurements of $\mathscr{S}$ on absorber quantity q is attributable to the non-linear relationship between measured irradiances I_m and recovered spectral absorption coefficients k_σ; this is illustrated in Fig. 6. At any given optical frequency, the experimental I_m values have a Gaussian probability distribution; when values of (kq) are recovered from such noisy data, they will have a skewed distribution as indicated in Fig. 6 by reason of the finite curvature of the logarithmic transformation. This curvature (given by the second differential of the log function) increases as the irradiance decreases; it is especially important to note that the curvature remains finite around unit irradiance, so that the distribution of (kq) values recovered in the absence of absorber (or from line wings) is still skewed. Figure 7 shows the effect on the distribution of absorption coefficients of increasing q whilst measuring a unit k. For small absorber quantities, the distribution of k_σ is narrow and appears quite symmetric; as q is increased, the shape becomes more skew, with a long tail towards higher k values. Although the mode shifts towards smaller k, the mean in fact increases slightly. Two conclusions may be drawn from these curves: firstly, when working with large peak absorptions, the spread of k values increases greatly. This is the principal cause of the decrease in line strength signal-to-noise ratio at high q shown earlier (Figs. 3 and 5). Secondly, inherent positive bias in the distribution of k which is present even if there is no absorption explains the bias in line strength observed for low q values. The fact that, in recovering k, one has to divide by a small q value simply enhances this bias. This, combined with the possibility that the precise absorber quantity may be uncertain, argues that the experimenter should avoid working with small peak absorptions if at all possible.

In computing $\mathscr{S}$ across an absorption line, k_σ obviously varies according to the line profile, and the degree of skewness in its distribution will vary also. It is greatest when k_σ is largest, but it may still be significant for smaller values of k_σ if q is large enough. The only way to avoid these effects is to minimize the spread of measured irradiances at each frequency by obtaining the cleanest possible absorption spectrum prior to determining $\mathscr{S}$; this may be achieved in practice either by using more light or by extending the effective observation time in an effort to "beat down" the noise. The experimenter must then determine the uncertainty in the value of $\mathscr{S}$; it is to be expected that any error limits quoted will be asymmetric.

The problem reduces to that of determining the full probability density function (PDF) of $\mathscr{S}$ given the different distributions of absorption coefficient at each frequency across a given line profile, and a fixed absorber quantity. Since $\mathscr{S}$ can be considered as the sum of many independent

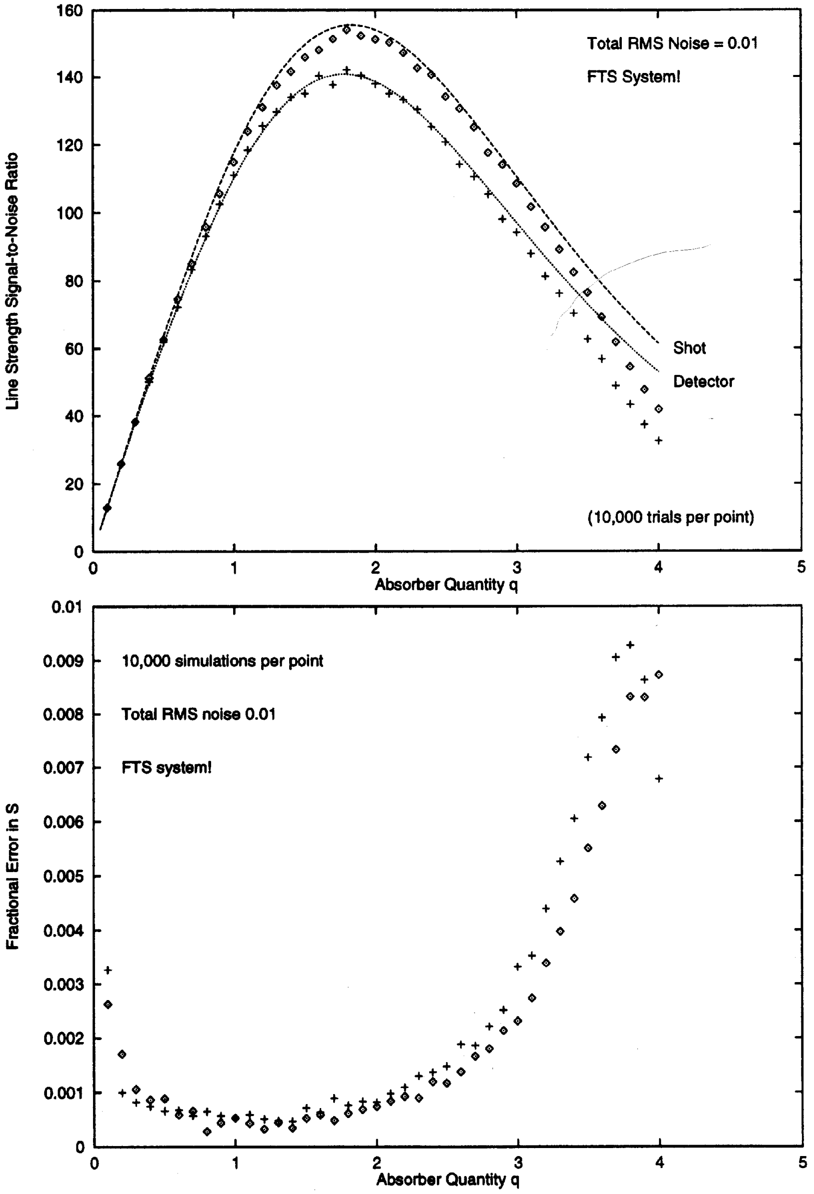

Fig. 5. A Gaussian line profile viewed by a FTS with a normalized r.m.s. noise level of 0.01 per spectral sample. Note the resemblance to detector-limited operation of a CDS.

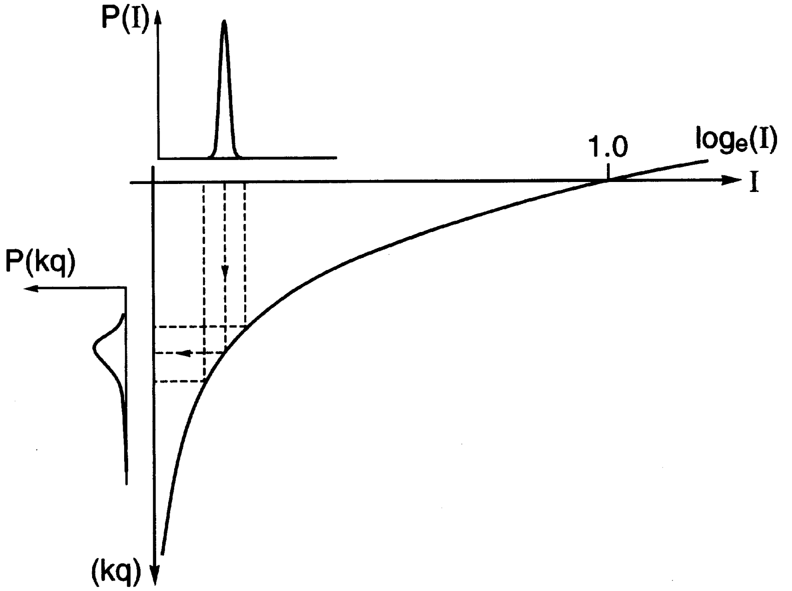

Fig. 6. The mapping between a noisy measurement of irradiance I and the corresponding value of (kq). The finite curvature of the logarithmic function causes a Gaussian irradiance noise distribution $P(I)$ to yield a skewed distribution of (kq), per Eq. (15).

random variables (the individual k_σ), the PDF of $\mathscr{S}$ may be calculated by convolving PDFs of all the constituent k_σ together.[10] This is simply a generalization of the simple error theory employed previously.

As noted at the outset, the measured irradiance I_m is related to the absorption coefficient k by Beer's law, which may be written briefly as $B(k, q)$. The PDF of each k value, $pk(_k)$ is related to that of the measured irradiances ($p_{I_m}(I)$, assumed to be a Normal distribution) by the following

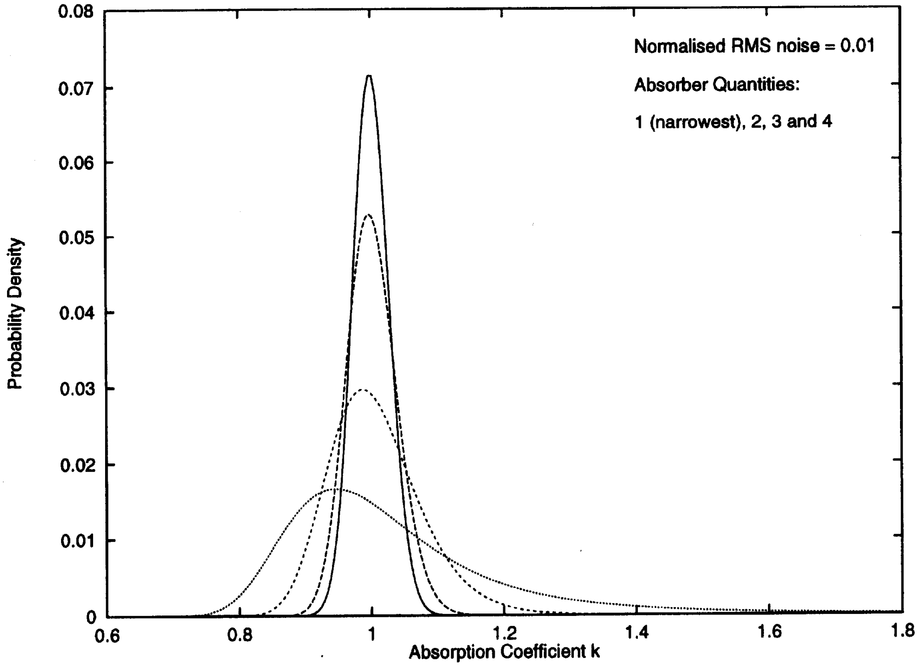

Fig. 7. Single-frequency spectral absorption coefficient probability density functions for various absorber quantities q. Constant Gaussian-distributed irradiance noise (0.01 normalized r.m.s.) is assumed.

transformation:[9]

$$p_k(k) = pI_m(I_m = B(k, q))\left|\frac{dI_m}{dk}\right|_{I_m = B(k,q)}. \tag{14}$$

Note that both the differential and the irradiance PDF are evaluated at the I_m corresponding to the particular k under consideration. If the explicit form of Beer's law is substituted into this equation, then

$$p_k(k) = qI_m p_{I_m}(I_m). \tag{15}$$

Having obtained a formula for the distribution of k_σ, the convolution was performed by generating a separate p_k for each frequency across a given line profile, given the prevailing irradiance noise parameters as before, and forming the cumulative product of their Fourier transforms. The final distribution of $\mathcal{S}$ was then obtained by reverse Fourier transformation of this product. The entire process was then repeated for different values of absorber quantity q and the resultant distributions were plotted. Due precautions were taken throughout to avoid sampling and wrap-around problems.

In order to determine error bars, the following procedure was adopted: for each absorber quantity q the cumulative distribution function (CDF) of the measured line strength was computed. A confidence level (between 0 and 100%) was then specified and error bars were set so as to enclose the appropriate fraction of the total distribution. In the results which follow, a 68% confidence interval was chosen, following standard "$\pm$ one-standard-deviation" practice as applied to Gaussian distributions. In the current situation this gives rise to asymmetric error bars, an effect which would be magnified were a larger confidence interval to be specified.

Figure 8 shows the results for a Gaussian line profile measured with both CDS and FTS systems in shot and detector noise limited regimes. It is apparent that a CDS operated in a shot noise limited regime yields the smallest uncertainty and bias, even for high absorber quantities. It is well, however, to recall the extreme sensitivity of such systems to detector noise before filling the gas cell, since this will introduce considerable bias (not to mention extra noise) for high q values as shown in the second plot. In addition, the throughput advantage of a FTS may in practice allow better spectra to be obtained in a given measurement period using a lower q. Note that the "true" $\mathcal{S}$ value is represented by the dotted horizontal line at zero fractional deviation. The error bars are plotted with respect to the (biased) experimentally-derived values of $\mathcal{S}$; when considered in relation to the true value their asymmetry is much more significant. The third plot refers to a FTS operated in a shot noise limited regime; the unconnected points (squares) indicate the detector noise limited situation, which is identical to that of a conventional spectrometer. The errors and the bias of the FTS are marginally smaller than for the conventional spectrometer, but the sensitivity to detector noise is much lower. Qualitatively similar results were obtained for damped Voigt profiles, although the uncertainties were reduced in comparison to the Gaussian case. For a damping factor of 10 the errors are approximately halved in magnitude, but the optimum q remains very similar.

5. EFFECTS OF REDUCED RESOLUTION

The resolution paradigm assumed above (about 20 samples per FWHM) is but rarely achieved in practice. Two distinct effects of reduced resolution must be accounted for: smoothing of the spectral profile and improvement in SNR due to greater available throughput. The latter point is often a forceful practical argument for not attempting the highest possible resolution.

Reduced resolution was simulated as follows: the original line profiles were used to generate synthetic absorption spectra as previously, but these were subjected to matched low-pass filtering and decimation prior to the addition of noise. Statistics were gathered as before using typically 10,000 simulations per absorber quantity. Beginning with approximately 20 samples per FWHM and a Gaussian profile, degradations by factors up to 10 were investigated. CDS and FTS instruments were considered in both shot and detector limited regimes, assuming a maximum normalized r.m.s. noise of 0.05 at full resolution (spectral SNR of 20). The noise contribution was then reduced as a function of the resolution degradation F according to the particular regime. For

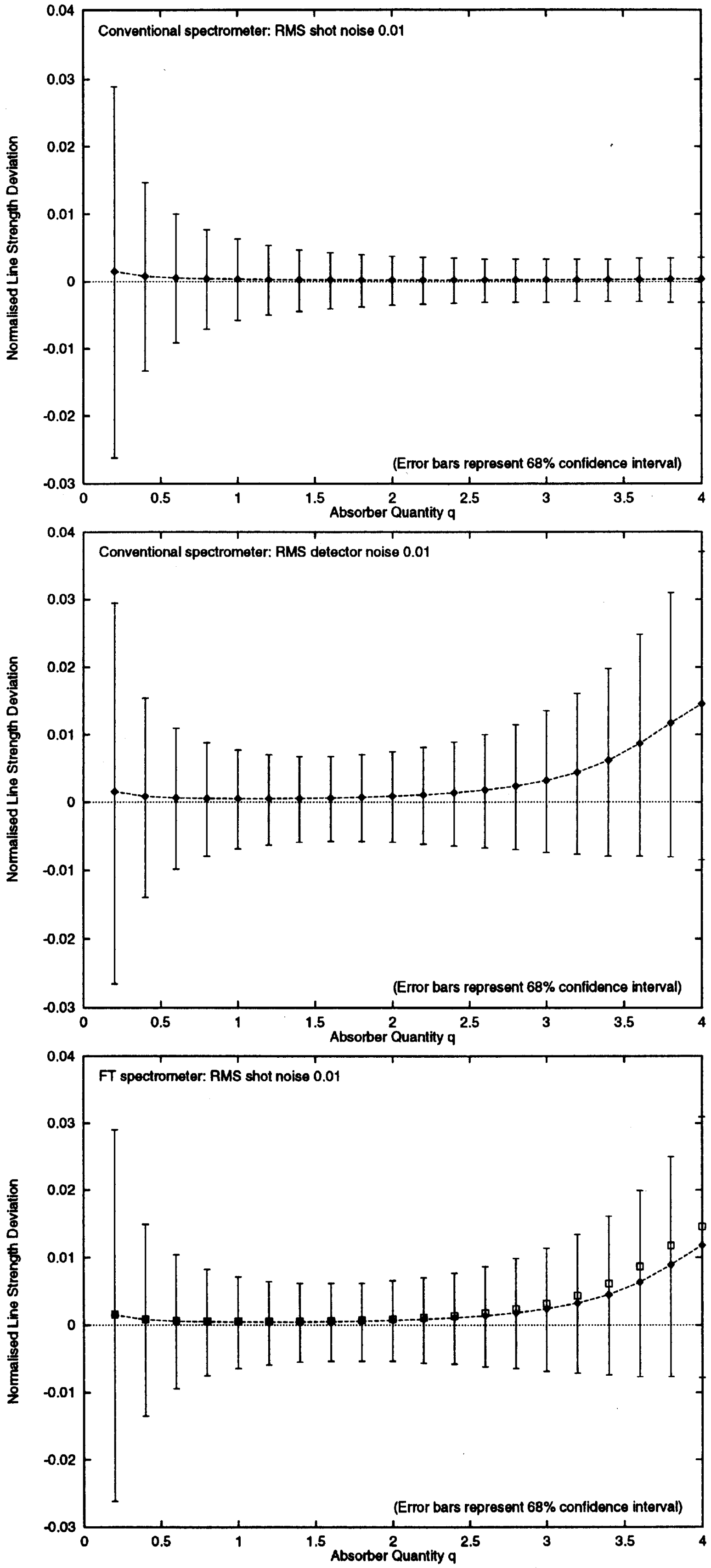

Fig. 8. Errors in $\mathscr{S}$ measurements for a Gaussian profile as a function of absorber quantity. Normalized r.m.s. noise is 0.01 in each case. Note that the detector noise limited FTS and CDS cases are identical. The true line strength is represented by the dotted horizontal line.

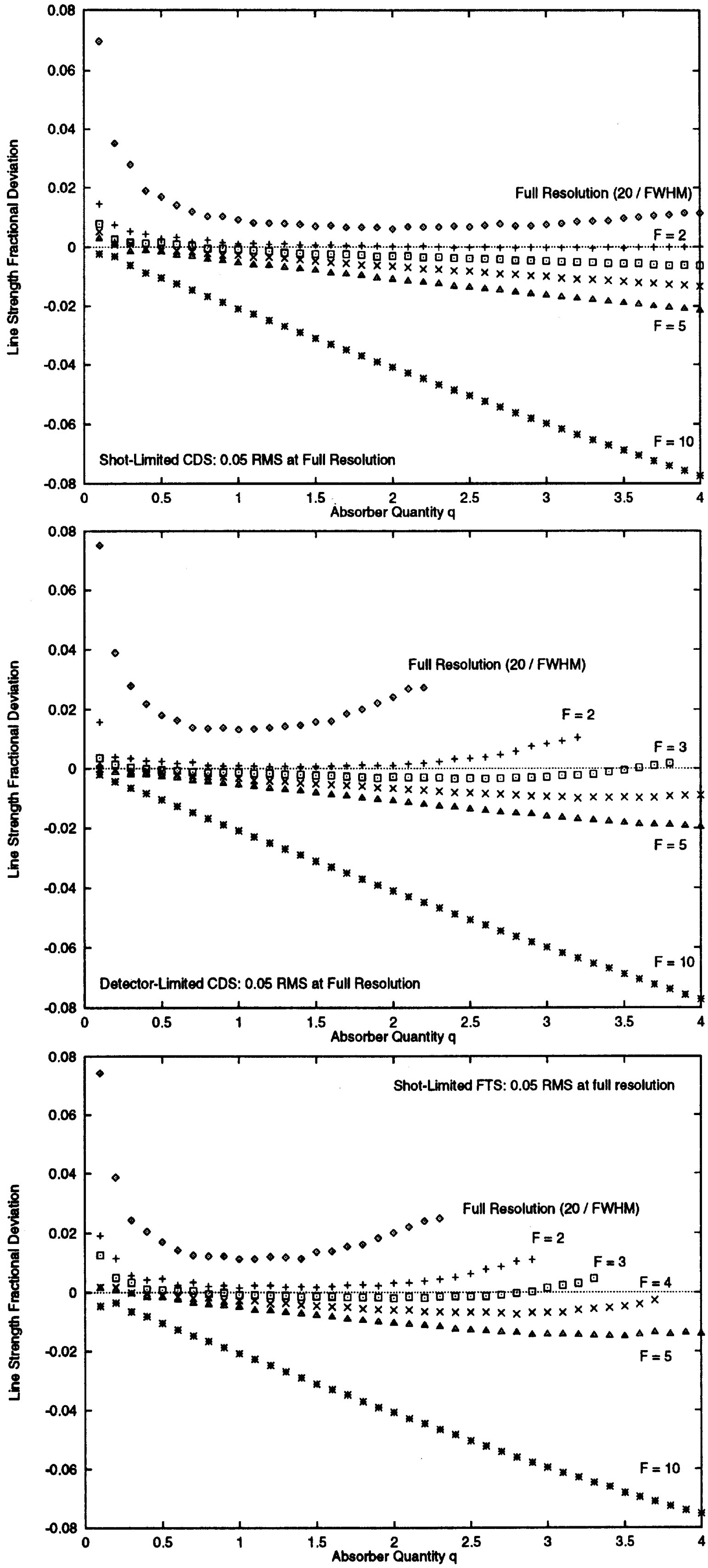

Fig. 9. Effect of degraded resolution on line strength bias. A Gaussian profile is assumed with normalized r.m.s. noise of 0.05 at full resolution (20 samples per FWHM). Degradations by factors F of 2, 3, 4, 5 and 10 (equivalent to 2 samples per FWHM) are shown.

a CDS with resolution element $\delta\lambda$ viewing a source for total time T, the SNR in shot and detector limited regimes scales as[11]

$$\mathrm{SNR}_{\mathrm{shot}} \propto \delta\lambda\sqrt{T} \tag{16}$$

$$\mathrm{SNR}_{\mathrm{detector}} \propto (\delta\lambda)^{3/2}\sqrt{T}. \tag{17}$$

The signal increases with $(\delta\lambda)^2$ whereas the detector noise drops by $\sqrt{\delta\lambda}$ due to larger array elements. The SNR for the FTS scales in exactly the same way with frequency interval $\delta\sigma$.

It was found that degraded resolution has no effect on the absorber quantity required for optimum line strength SNR other than the small shifts (noted above) incurred as a result of operation outside the "small noise" regime. This result holds in all cases even if the r.m.s. noise level is held constant as the resolution degrades. It is consistent with the observation that different line shapes have a similarly small effect on optimum q values. The peak SNR is, however, affected: in a shot-limited situation it improves with the square root of the resolution degradation factor F, whereas it scales linearly with F for detector-limited operation. These changes in SNR result from the opposition of two effects: the improvement in spectral SNR with degrading resolution is offset by a reduction in line strength SNR which results from the spectral smoothing.

There are significant effects upon the inherent bias in recovered line strengths as illustrated in Fig. 9. The simulation fails when the minimum transmission becomes similar to the noise level; some of the curves have been truncated for this reason. It is as well to recall the optimum absorber values for each situation when viewing these curves (around 1.8 for FTS and detector-limited CDS, and around 3.6 for shot-limited CDS).

The most obvious effect of degraded resolution is an increasingly negative bias (underestimation) on recovered line strengths, the bias being worst when resolution is smallest. It is tempting to back off resolution in an attempt to minimise bias, and such a strategy will improve signal-to-noise (a factor of 2 or 3 down from 20 samples per FWHM would suffice). Further gains in SNR may be had by degrading resolution further, but the bias would have to be compensated. Previous studies[12] have modeled the negative bias caused by poor resolution, but they have neglected the variable positive bias attributable to the non-linear transfer of irradiance noise.

The change in bias may be explained crudely as follows. As resolution is reduced, the measured irradiance profile becomes shallower; at the centre of the line, the absorption coefficient is underestimated, and this reduces the recovered line strength. The shallower measured absorption is less susceptible to the non-linear effects of noise, (being located on a less-curved portion of the logarithmic curve) so the variance of the recovered k's is reduced. The onset of nonlinearity is only delayed however; if the absorber quantity is increased so that the smoothed profile becomes saturated, the irradiance measured at the line centre will again contribute an over-estimated absorption coefficient to the line strength. Having increased the width of each spectral sample, the relative effect on the line strength of the irradiances measured at the line centre is greater, and the bias increases more strongly than in the full-resolution case. This is apparent in the curves of Fig. 9 given that the r.m.s. noise has been reduced for the lower resolution cases.

6. DISCUSSION AND CONCLUSIONS

It has been shown that, given a knowledge of the prevailing noise regime and of the system in use, it is possible to determine an optimum absorber quantity to use in the experimental system. This optimum quantity has been found in all cases to be well outside the so-called "linear region", and in some situations allows only a few percent transmission at the line centre. It has been shown additionally that these conditions hold for all noise levels that may be considered small (irradiance SNRs of 50 or better), and that only small reductions in optimum absorber quantity need be made for larger noise levels. The shot-limited CDS was found to be most vulnerable in this respect.

The calculations and simulations presented above have been applied to Gaussian and Voigt profiles; no significant changes to optimum absorber quantity were found as the line shape was varied, although better SNRs were obtained for more highly damped profiles. This fact suggests that the results are applicable to more complex absorption bands. No *a priori* assumptions have been made for this reason regarding the line profile: no knowledge of the correct damping factor is assumed. Were such information to be available, the experimenter could arrange to perform a least-squares fit of the spectra to a prototype profile and thereby derive a value for $\mathscr{S}$. Such a procedure should, in the limit of high resolution, yield similar results, but experience shows that fitting routines can run into trouble at low resolution in the presence of noise.

The inherently non-linear relationship between spectral irradiance and absorption coefficient gives rise to a bias in recovered line strengths which is positive in the well-resolved situation and not insignificant when the spectral SNR is poor. The most important consequence for experimental procedure stems from the fact that this bias cannot be reduced by averaging multiple measurements of line strength. The experimenter should concentrate instead on obtaining the best possible spectral profile (perhaps by averaging measured irradiances, or extending the measurement period) before computing a single line strength value. The errors on the final result may be estimated by the procedure explained above given a knowledge of the relative contributions of shot and detector noise. Previous treatments of the effects of under-resolution have suggested that the most accurate line strengths were to be obtained by using several small absorber quantities and extrapolating to $q = 0$ (see, for example, Ref. 12). The curves of Fig. 9 indicate that this is approximately the case for gross under-resolution (less than 2 samples per FWHM), but that significant errors might arise for higher resolutions. The non-linear behaviour of the bias as a function of q and the possibility of positive bias are absent from these treatments.

Recommending an optimum resolution is problematic: on one hand, improved resolution can reduce the under-estimation of line strengths and yield more precise values. Set against this is the increase in line strength uncertainty occasioned by the lower instrumental throughput and consequently poorer spectral SNR. It appears that a resolution equivalent to between 5 and 10 samples per FWHM is to be preferred for minimum bias, but the most important point is that the bias can be estimated and compensated in a lower resolution case.

The differing susceptibilities to noise of CDS and FTS instruments have been demonstrated; it has not been the purpose of this work to suggest which type of system is to be preferred—such a choice is highly complex and often driven by factors other than those considered herein. It can however be concluded that there is a need to characterize the noise sources carefully, especially if one is running a CDS in a potentially shot-limited regime. It was shown that even quite small admixtures of detector noise reduce the optimum absorber quantity significantly (from about 3.6 down to about 1.7 units). One could lose a factor of 4 in line-strength SNR by failing to consider this point.

The experimenter, armed with the foregoing results and methods, can estimate the optimum absorber quantity required for his particular system; there remains only the problem of checking that the correct conditions have indeed been achieved. This may be difficult if the line strength is not well known in advance and the instrument cannot resolve the line fully. In such situations, a measurement of the spectrum will not immediately show whether or not a line is saturated. Recourse may be made to measurements of the equivalent width of the line under scrutiny for different absorber quantities so that the curve of growth may be obtained. Accurate determination of q is especially important for weak absorptions as any errors affect the bias greatly.

In cases where the spectrum to be measured contains a large range of line strengths, it may be necessary to measure spectra for several different absorber quantities. This requirement can only be judged in the light of required error tolerances; the relative insensitivity of the FTS to changes in absorber quantity compared to the CDS may allow the number of measurements to be reduced.

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