Uncertainty of oscillator strengths derived from lifetimes and branching fractions


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Abstract

A widely used method for determination of transition probabilities and oscillator strengths is based on measurements of branching fractions and radiative lifetimes. In the present work the different sources of uncertainty in branching fraction measurements using Fourier transform spectroscopy and lifetime measurements using laser induced fluorescence are discussed. A detailed description is presented of how the uncertainties should be combined to provide a well-defined uncertainty of the derived quantity. Finally, an example shows how the individual uncertainties can be presented in an “uncertainty budget”. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Determination of transition probabilities and oscillator strengths through measurements of lifetimes and branching fractions has been a standard method for many years, and large amounts of data have been published. A study of the literature shows that the stated relative uncertainty of the measurements varies from a few percent up to 50%, but the method for estimating the uncertainty is generally mentioned only briefly or—in many cases—not at all.
Because the uncertainty is crucial for the users of the data, and because several sources of uncertainty are involved in the transition probability measurements, we have considered it worthwhile to investigate the problem in some detail. This has resulted in a well-defined procedure for deriving uncertainties that we intend to use in our future work. The method is based on the concept of uncertainty as discussed in “Guidelines for evaluating and expressing the uncertainty of NIST measurement results” [1], which is based on “Guide to the expression of uncertainty in measurement” from BIPM, Bureau International des Poids et Mesures [2].

2. Basic relations

The transition probability $A_k$ of an emission line from a given upper level to a lower level $k$ can be derived from the radiative lifetime $\tau$ of the upper level and the branching fraction $(BF)_k$ of the line, where the lifetime and the branching fraction are given by

$$\tau = \frac{1}{\sum_{j=1}^{n} A_j},$$  \hspace{1cm} (1)

$$(BF)_k = A_k / \sum_{j=1}^{n} A_j.$$

(2)

The sum includes all radiative transitions from the same upper level, see e.g. [3]. We can also write

$$(BF)_k = \frac{I_k}{\tau} = \sum_{j=1}^{n} c_j I'_j,$$

(3)

where $I_j$ is the number of transitions per second in line $i$ from the given upper level, $I'_j$ is the observed intensity of the line, measured as photons per second, and $c_j$ is the calibration factor related to the wavelength dependent response of the spectrometer system. Combining Eqs. (1)–(3) we obtain the basic relation

$$A_k = \frac{(BF)_k}{\tau} = \frac{I_k \sum_{j=1}^{n} c_j I'_j}{\tau \sum_{j=1}^{n} I_j},$$

(4)

We can thus write

$$A_k = f(I_1, I_2, \ldots I_n, \tau).$$

Assuming that the uncertainties of $I_i$ and $\tau$ are uncorrelated, we can apply the law of propagation of uncertainty in the form

$$u_c^2(A_k) = \sum_{j=1}^{n} \left( \frac{\partial A_k}{\partial I_j} \right)^2 u^2(I_j) + \left( \frac{\partial A_k}{\partial \tau} \right)^2 u^2(\tau),$$

(5)

where $u_c$ is the combined standard uncertainty of $A_k$ and $u(I_j)$ and $u(\tau)$ are the standard uncertainties of the measured quantities. The term standard uncertainty is used according to the definition in the NIST report [1], i.e. “equal to the positive square root of the estimated variance $u^2$”. Evaluating the
derivatives of Eq. (5) we obtain the following relation for the combined relative standard uncertainty $u_{c,r}$ of $A_k$:

$$
(u_{c,r}(A_k))^2 = \left( \frac{u_c(A_k)}{A_k} \right)^2 = (1 - (BF)_k)^2 \left( \frac{u(I_k)}{I_k} \right)^2
$$

$$
+ \sum_{j \neq k}^n (BF)_j^2 \left( \frac{u(I_j)}{I_j} \right)^2 + \left( \frac{u(\tau)}{\tau} \right)^2,
$$

which also can be written as

$$
(u_{c,r}(A_k))^2 = \left( \frac{u_c(A_k)}{A_k} \right)^2 = (1 - 2(BF)_k) \left( \frac{u(I_k)}{I_k} \right)^2
$$

$$
+ \sum_{j=1}^n (BF)_j^2 \left( \frac{u(I_j)}{I_j} \right)^2 + \left( \frac{u(\tau)}{\tau} \right)^2.
$$

Application of this formula requires knowledge of the standard uncertainties $u(I)$ related to the branching fraction measurements and the uncertainty $u(\tau)$ of the lifetime measurement. The minus sign in the first term of these two forms of the equation is caused by the fact that the intensity $I_k$ of line $k$ is present both in the numerator and in the sum in the denominator of the definition of $BF$ in Eq. (3). It is thus taking care of the covariance of $I_k$ and $\sum I_j$.

### 3. Uncertainty of branching fractions

The uncertainties $u(I)$ related to the branching fractions in Eq. (6) are determined by the uncertainties of the observed intensities $I'$ and the calibration factors $c$. As the measurement of the line intensity and the determination of the calibration factor are uncorrelated, we can derive the combined relative uncertainty from

$$
\left( \frac{u(I)}{I} \right)^2 = \left( \frac{u(I')}{I'} \right)^2 + \left( \frac{u(c)}{c} \right)^2.
$$

#### 3.1. Fitted line profiles

In Fourier transform spectroscopy (FTS) the recorded spectral lines are generally completely resolved, i.e. the instrumental line width is smaller than the width of the lines emitted from the light source. We restrict the discussion to symmetrical lines with profiles unaffected by blends or unresolved fine, hyperfine or isotope structures. The position and intensity of a line are then generally determined by fitting a function describing the line profile to the observed feature, generally a Voigt function. The algorithm used for the fitting may provide some estimate of the uncertainty of the fitted parameters, that could be used as $u(I')$. To obtain a deeper understanding of the uncertainty inherent in such a fitting procedure we have undertaken a systematic study of how the uncertainty is affected by different parameters.
The method of this study consists of generating a synthetic spectral feature consisting of a line with a known shape, Gaussian or Lorentzian, plus added random noise. A function of the same shape as the original line was then fitted to the noisy feature. The position—the center of the function—and the intensity—the area under the function—of the fitted line were compared to the corresponding quantities used for generating the original line. By repeating this for the same parameter combination but with different noise, the uncertainty of the line position and intensity could be estimated as the standard deviation of the individual determinations. By performing this for a large number of different combinations of parameters it was possible to parametrize the uncertainty as an analytical function of the signal-to-noise ratio (SNR), the full width at half maximum of the line (FWHM), and the resolution interval (the distance between the measured points). A comprehensive description of the procedure and the computer code used for the simulations is available in Ref. [4].

The result of the study, based on a large number of simulations, is that the standard deviation $s(\sigma)$ of the line position $\sigma$ can be written as

$$s(\sigma) = \frac{\sqrt{\text{d}x}}{S} \sqrt{\frac{w}{w}} = \frac{\sqrt{\text{d}x}}{S} \sqrt{\frac{w}{n}},$$

where $S$ is the SNR of the line, i.e. the ratio of the maximum value of the spectral feature to the rms value of the noise, $\text{d}x$ is the resolution interval, and $w$ is the FWHM. The number of points $n$ in the line width is given by $n = \frac{w}{\text{d}x}$. The value of the numerical constant $\alpha_\sigma$ is $0.69 \pm 0.02$ for a Gaussian profile and $0.80 \pm 0.13$ for a Lorentzian. Both the analytical form of expression (9) and the values of $\alpha_\sigma$ are in perfect agreement with the corresponding quantities theoretically derived and reported by Brault [5] ($\alpha_\sigma = 0.693$ for a Gaussian and $\alpha_\sigma = 0.798$ for a Lorentzian).

The analysis of the area $Y$ under the fitted function gives a standard deviation $s(Y)$, that can be written as

$$s(Y) = \frac{\sqrt{\text{d}x}}{S} \sqrt{\frac{1}{w}} = \frac{\sqrt{\text{d}x}}{S} \sqrt{\frac{1}{n}},$$

where $\alpha_Y$ is the derived from the analysis is $1.41 \pm 0.04$ for a Gaussian profile and $1.60 \pm 0.04$ for a Lorentzian. It seems reasonable to assume that $\alpha_Y = 2 \times \alpha_\sigma$.

To conclude, we can use the value $s(Y)/Y$ calculated by means of Eq. (10) as an estimate of the relative uncertainties $u(I'/I')$ in Eq. (8). A typical value at FTS recordings is $n = 4$, which means that the relative uncertainty for Gaussian lines with $S = 10$ is 7%, whereas it is well below 1% for lines with $S > 100$.

### 3.2. Spectrometer efficiency calibration

The calibration factors $c$ in Eq. (3) describe the wavelength (or wavenumber) dependent response of the spectrometer system, which is determined by means of light sources with known relative spectral radiance. Both continuous spectra and line spectra may be used for this calibration.

#### 3.2.1. Calibration with a continuous spectrum

Various types of continuous emitters are available and can be calibrated at standard laboratories. Deuterium discharge lamps [6] are commonly used in the region 1650–3600 Å, while tungsten strip
lamps are useful at longer wavelengths. The data from the calibration laboratory may be reported either as absolute spectral radiance in units of power per unit projected area, unit solid angle and unit wavelength interval, or as relative spectral radiance in relative power units. In both cases the spectral bandwidth or resolution used for the comparison with a primary standard source is specified.

The output from an FTS recording is produced on a wavenumber scale in relative units of photons per wavenumber interval. The calibration data are therefore converted from power per wavelength interval to photons per wavenumber interval. The recorded spectrum emitted from the calibrated lamp has to be transformed to a wavelength scale and to the same spectral resolution as the calibration data. The transformed spectrum is divided by the converted calibration data to produce the response function, which is then transformed back to the original wavenumber scale. This (normalized) response function \( R(\sigma) \) then gives the calibration factors of Eq. (3) as \( c = 1/R(\sigma) \).

The uncertainty \( u(c) \) to be used in Eq. (7) should include the uncertainty of the calibration data, reported from the standard laboratory. The uncertainty for the lamps available to us expressed as one standard deviation is of the order 3–5%.

The comparison between the recorded spectrum and the calibration lamp may, however, introduce an uncertainty that is larger than the uncertainty of the calibration data. This is due to the fact that the light entering the spectrometer may be emitted from a region of the lamp that differs from that investigated at the standard laboratory. For instance, the temperature and thus the spectral radiance, varies along the strip of a tungsten strip lamp. A variation may also occur between different radiating parts of a deuterium lamp. We have tested such variations by slightly changing the lateral position of the lamp and by changing the imaging onto the spectrometer entrance aperture. With reasonable changes, i.e. when alignment and focusing are judged by the eye to be good, the recorded spectra are reproduced within \( \pm 5\% \) over the widest regions we use for our recordings. We use the NIST guidelines (Section 4.6) to estimate the standard relative uncertainty at this rectangular probability distribution as \( 2 \times 5/\sqrt{3} = 5.8\% \). Adding this in quadrature to the uncertainty from the calibration laboratory gives a total calibration uncertainty of 6.5–7.7%.

This total uncertainty may, however, overestimate the uncertainty of the observed intensities. The spectral radiance of the calibrated lamps we use can be safely assumed to vary smoothly with the wavenumber, as a tungsten strip lamp is approximately a black body radiator and a deuterium lamp spectrum is continuous over the region 1800–3600 Å. As the uncertainty reported from the calibration laboratory concerns any point in the calibrated region, the intensity ratio of two lines separated by a small distance should be less uncertain due to this smoothness than a ratio involving two widely separated lines. The change of a lamp spectrum caused by a misalignment, as discussed in the previous paragraph, appears as a shift of the recorded spectrum, that is still smooth. Also in this case the relative intensities will be less affected for close lines. We therefore consider it reasonable to correct the total uncertainties by \( \Delta \sigma/W_\sigma \), where \( \Delta \sigma \) is the distance between the two lines with the highest and the lowest wavenumber in \( \sum I_j \) of Eq. (3), and \( W_\sigma \) is the full width over which the standard lamp was calibrated with the rated uncertainty.

In this discussion, we have to mention two potential sources of error, that must be duly considered and eliminated. One is caused by the fact that a deuterium lamp is ageing, i.e. its spectral radiance is slowly changing with the total operating time [7]. This means that the calibrated lamp should only be used for initial calibration and for regular checking of secondary standards that are used in the daily work. Another source of error is specific to the FTS method, where the usually applied
method of undersampling may cause a continuum from a neighboring alias to be folded into the alias containing the spectrum being investigated. This error has to be eliminated by proper optical filtering. A corresponding but perhaps more obvious source of error in grating spectrometers is the influence of scattered light.

3.2.2. Line spectra

The standard sources discussed in the previous section are external in the sense that the spectra are produced by another source than the line spectra being investigated. Any difference in the optical path may introduce an error, the minimum difference being that necessarily introduced by the different windows of the sources. An internal standard source would therefore be a great advantage. Such standards are in fact available in the shape of sets of carefully measured intensity ratios of lines, normally emitted by the carrier gas in the light source. The main requirement for each set of lines is that the lines are emitted at transitions from a common upper level, thereby eliminating the influence of the excitation conditions in the source.

Such branching ratios have been measured at several laboratories, and a comprehensive critical compilation of ArI and ArII data covering the region 2100–4591 Å has been published by Whaling et al. [8]. The measurements were partly based on calibration of the used instruments by the method discussed in the previous section, i.e. by comparison with continuous sources with a known spectral radiance, partly on comparisons with other known branching ratios. The uncertainties are given as standard deviations derived from the scatter of the different measurements, except for one line, usually the strongest one, from the common upper level in each set of lines, where the branching ratio is by definition set to unity. Application of this method is based on interpolation of a preliminary response curve between the lines in a set, and manually fitting as many overlapping sets as possible to produce a smooth curve.

A certain amount of ambiguity is inherent in this method, and according to our experience the spread of the points finally defining a curve over a wide range may give a too large uncertainty to make it useful. Over a limited region, with several overlapping sets of lines, the uncertainty may, however, be sufficiently low, and the method is then convenient as no separate recording of a standard spectrum is needed. It is also useful in combination with a response curve from a standard source to check for systematic errors caused by e.g. a folded-in ghost continuum or a contaminated window at the light source. Another case where internal standards are necessary is recordings including the near vacuum ultraviolet region, where the light path between the source and the spectrometer input is kept as short as possible and purged with nitrogen to reduce the absorption. Even a small difference in path length between the line source and an external standard source might then lead to an erroneous response curve. Several sets of ArII lines extending from 2200 Å into the vacuum ultraviolet region [9] are particularly useful in this case.

Used in this way over limited regions we estimate the standard uncertainty of this calibration method to be of the same order as the total uncertainty by calibration with a continuous source.

3.2.3. Calibration uncertainty

The calibration concerns the relative spectral radiance, and therefore it will add a relative uncertainty to the intensity of all lines relative to the intensity of the line we are investigating. The calibration uncertainty \( u(c) \) should therefore be added to all lines, except line \( k \) in Eqs. (6) and (7).
Eq. (6) should therefore, with the help of Eq. (8) be re-written as

\[(u_{c,r}(A_k))^2 = (1 - (BF)_k)^2 \left( \frac{u(I'_k)}{I'_k} \right)^2 + \sum_{j \neq k} \frac{(BF)_j^2}{(BF)_{in\ P}} \left( \left( \frac{u(I'_j)}{I'_j} \right)^2 + \left( \frac{u(c_j)}{c_j} \right)^2 \right) + \left( \frac{u(\tau)}{\tau} \right)^2 \]  

(11)

3.2.4. Connecting spectral regions

In many cases it may be impossible to include all lines in the sum in Eq. (3), i.e. all lines from a common upper level, in one recording, due to limitations set by detector sensitivity or FTS alias width. The different recordings then have to overlap to such an extent that at least one line is present in both recordings. Ideally this line should belong to the group of lines with a common upper level for which the BF’s are being studied. If the light source is run under identical conditions, any line in the overlap region could, however, be used. A normalization factor is determined as the ratio of the observed intensities of this line from the two recordings and used for putting the two recordings on the same relative intensity scale. This normalization introduces a new uncertainty, which can be estimated from the normalization factors derived from the different sets of lines.

This additional calibration uncertainty will only affect lines which are not in the same spectral region as the line \(k\) itself. An extra term in Eq. (8) should be added to those lines, and the equation should be written as

\[\left( \frac{u(I)}{I} \right)^2 = \left( \frac{u(I')}{I'} \right)^2 + \left( \frac{u(c)}{c} \right)^2 + \left( \frac{u(nf)}{nf} \right)^2, \]

(12)

where \(u(nf)\) is the uncertainty in the normalization factor, \(nf\). In the case of only two spectral regions, \(P\) and \(Q\), with the line \(k\) in spectral region \(P\), Eq. (11) should be written as

\[(u_{c,r}(A_k))^2 = (1 - (BF)_k)^2 \left( \frac{u(I'_k)}{I'_k} \right)^2 + \sum_{j \neq k (in \ P)} \frac{(BF)_j^2}{(BF)_{in\ P}} \left( \left( \frac{u(I'_j)}{I'_j} \right)^2 + \left( \frac{u(c_j)}{c_j} \right)^2 \right) + \sum_{j (in \ Q)} \frac{(BF)_j^2}{(BF)_{in\ Q}} \left( \left( \frac{u(I'_j)}{I'_j} \right)^2 + \left( \frac{u(c_j)}{c_j} \right)^2 + \left( \frac{u(nf)}{nf} \right)^2 \right) + \left( \frac{u(\tau)}{\tau} \right)^2. \]

(13)

In the case of only one spectral region, Eq. (13) reduces to Eq. (11), as expected.
3.3. Missing lines

The sum in Eq. (3) is supposed to include all transitions from the common upper level. In a complex spectrum a number of the possible transitions may be too weak to be detected above the noise level. One or more of the transitions may also appear in a region that is not accessible due to experimental limitations. If the sum of the intensities of all these lines is not negligible, its omission will introduce a systematic error in the transition probabilities.

The sum of the missing intensities can be estimated by theoretical methods, e.g. a calculation with the Cowan code [10], and if it is small, say a branching fraction below 10%, then this estimate is good enough to be used as a correction added to \( \sum I_j \). The relative uncertainty of this correction has to be included in Eq. (6) as an extra term in \( \sum (BF)^2 (u(I)/I)^2 \). Even if the relative uncertainty \( u(I)/I \) of the correction is large, say 50%, its influence on the uncertainties of the measured lines is small due to the small value of the \( BF \).

3.4. Self-absorption

Photons emitted in transitions to long-lived strongly populated lower levels may be reabsorbed inside the emitting plasma, if the atom or ion density is high enough. The observed intensity of the line, and thus the derived transition probability, will then be too low.

As the probability for this self absorption depends on the absorption coefficient, it is strongest at the center of a line, thereby affecting the line profile. It can therefore be checked at FTS recordings, where the profiles are fully resolved. It reveals itself as an increase of the width of the self-absorbed line, and if a Voigt function is fitted to the line profile, the residual shows a typical double hump pattern [11]. This pattern may, however, be difficult to distinguish at low SNR.

As the amount of self absorption depends on the plasma density, it can also be checked by studying the intensity ratio of two lines from the same upper level as a function of current in the light source. If this ratio is constant, then neither of the lines is affected by self absorption. If the ratio is not constant, it may be extrapolated to zero current and thus to zero plasma density, as shown in Fig. 1. This figure is based on the results of a recent investigation of self absorption in Fe I and Fe II in a hollow cathode plasma [12], and it shows how intensity ratios in a Fe I multiplet as a function of the current can be extrapolated to zero current. The points at zero current represent the ratios derived from Blackwell’s highly accurate oscillator strengths [13] from absorption measurements. It can be seen that the extrapolated ratios will agree closely with Blackwell’s values.

Another method to correct for self absorption, derived by Kock and collaborators [14–16], is based on the increased width of a self-absorbed line. This width, compared to the width of an unaffected line, is used for deriving the optical depth at the center of the line, which is then used for correcting the intensity. Fig. 2 contains the same data as Fig. 1, but it shows the intensity ratios when the intensities are corrected by this method. Obviously, the correction to a great extent reduces the influence of self absorption, but it is not quite sufficient when the absorption is large.

When the SNR is large, extrapolation in the way shown in Fig. 1 should not increase the uncertainty of a line intensity. In many cases the situation is less clear, and the uncertainty of the correction factor should be added in quadrature to the total relative uncertainty of the intensity in Eq. (7). The uncertainty of the correction can be estimated from the width \( \Delta \gamma \) of the interval where an extrapolated curve may hit the ordinate axis in a diagram like that in Fig. 1. If the probability
distribution is supposed to be rectangular, the estimated standard uncertainty of the correction is \( \Delta y/\sqrt{3} \).

4. Uncertainty of lifetimes

In lifetime measurements using the laser-induced-fluorescence (LIF) method ions are transferred from a ground or metastable level to the level under investigation by a wavelength-tuned laser pulse. The fluorescent light released at the subsequent decay of the level is then captured using fast detection equipment. The recorded light will, in an ideal case, show an exponential decay and the inverted decay constant is the natural radiative lifetime. Although the method generally is considered as one of the most reliable for measuring lifetimes, there are a number of effects that contribute to the uncertainty of an experimental lifetime value. The contributions can be divided into statistical uncertainty, physical effects within the sample of ions and effects due to imperfections or limitations in experimental equipment. The magnitude of the different contributions vary from case to case and may eventually lead to a situation where a lifetime cannot be measured.
The discussion of uncertainties below is related to an experimental situation where the ions are produced by focusing a pulsed laser beam onto a target of the element to be studied [17]. A small plasma, containing electrons, atoms and ions in ground and metastable states, is then formed and expands out from the target. Pulses from a tuneable laser excite the atoms or ions to the level under investigation. The excitation laser pulse has a duration of about 1 ns with a pulse-to-pulse fluctuation of typically 20%. Fluorescence light released at the decay of a level is recorded using a photomultiplier tube and a sampling oscilloscope.

4.1. Statistical uncertainty

Typical lifetimes for ionic levels are a few ns and this means that most of the fluorescence occurs during the fall time of the laser pulse. In the measurements laser pulses and fluorescence signals are therefore recorded alternately and the lifetime values are obtained by fitting a convolution of the recorded laser pulse and an exponential to the observed decay curve. The statistical uncertainty that can be calculated from the spread of data points around the fitted curve is usually negligibly small. A more important uncertainty is due to the fact that the laser pulse and fluorescence are not recorded simultaneously. The fluctuations in duration of the laser pulse, although averaged, will cause a scattering in the lifetime values when different pulse recordings are applied to one fluorescence signal in the evaluation procedure.
The recorded laser pulse shows a duration of 1.5 ns. The deviation from the true duration of 1 ns is due to the limited bandwidth of the detection system. The observed fluorescence is affected by a similar broadening. The evaluation procedure, however, takes the limited time response into account since the recorded pulse and fluorescence are affected by the same response function. Therefore the limited bandwidth should in principle not introduce any error. However, when the width of the recorded fluorescence approaches the width of the laser pulse, the statistical uncertainty of the fit will increase significantly. For a lifetime of 2 ns, the spread in the derived lifetimes for curves with a sufficient SNR taken at similar conditions is smaller than 0.1 ns. Usually, the presented lifetime is an average of 10–20 curves. Previous experiments have given a total statistical uncertainty of 4% (one standard deviation).

4.2. Uncertainties due to physical effects

The laser-produced plasma is a versatile ion source, which can been utilized for atoms and ions in a large number of elements. The source has the advantage of high particle densities and the possibility of using populated metastable levels as a starting point for laser excitation. One major drawback, however, is the high ion velocity. During a few lifetimes, when the ions emit light, they might fly out of the detected region. This will cause an apparent non-exponential decay, but this is not evident from the fit if the effect is small. An estimate of the uncertainty introduced by this effect can be obtained by moving the detector, and thereby measuring the light-in- or light-out-of-view effect. The influence on the fluorescence curve is most severe for long-lived levels and sets a limit for how long lifetimes it is meaningful to measure using this method.

Multiple scattering, which is basically the same effect as self absorption discussed in Section 3.4 in this paper, is due to recapture of emitted photons and increases the observed lifetime. The effect is most marked when levels that combine with the ground level are studied. A worst case is when the laser pulse energy is low and this has to be compensated for by using a high ion density. The effect is checked by recording decay curves at decreasing signals, to lower the effect of self-absorption, until the derived lifetime reaches a constant value.

An opposite experimental situation compared to the above is when the ion density, for example in a particular metastable level, is low. To obtain a reasonable signal, the excitation pulse energy may have to be increased and there is a risk that the laser pulse saturates the transition. This will not affect the decay curve when the laser pulse is off, but when a convolution is made, a strong saturation will cause a poor fit. Reducing the laser power to vanishing signal can test the effect.

Collisions mean that ions in the studied level, instead of decaying to a lower level by emitting a photon, decay through a radiationless transition. Just like multiple scattering the effect will not show up in a poor fit in the evaluation procedure, as the decay is still exponential. This effect is most severe when hot plasmas are used, i.e. when a high metastable level is used as starting point for excitation and only few particle are in that metastable level compared to the total number of particles, electrons ions and atoms in various levels. The effect is tested by reducing the particle density to vanishing signal or by measurements on a long-lived level under similar conditions.

The four effects, flight-out-of-view, multiple scattering, saturation and collisions are not present at the same time. Due to this, it is possible to check for each effect one at a time. Suitable measurement conditions are assumed to exist in a region where none of the four effects can be detected. For
lifetimes between 2 and 30 ns, and when carefully checked for, their contribution to a final uncertainty are found to be $< 6\%$.

5. Uncertainty budget

The combined relative uncertainty of a measured quantity can be presented as an uncertainty budget according to the recommendations in “Guidelines for evaluating and expressing the uncertainty of NIST measurement results” [1]. As an example, we have chosen a resonance line from the level $z^6P_{5/2}$ in Mo II included in a recent measurement of transition probabilities [18]. The results of the measurements are presented in Table 1. Virtually all of the sources of uncertainties discussed in this paper are present in the measurements, which included intensity measurements of spectral line profiles, radiometric calibration of spectra, connecting spectral regions, self absorption correction, a calculated residual and measured radiative lifetimes. In this table the resonance line at 2015 Å is the line $k$ in the nomenclature used earlier in this paper. The column “Theory” contains the branching fractions from a calculation with the Cowan code. It is included here to show how the residual $BF$, i.e. the sum of the intensities of the lines not observed, can be estimated.

The uncertainty budget is presented in Table 2. The relative standard uncertainties are calculated according to the principles discussed above. The lines $k$, 1, 2 and 3 were measured in one recording, and 3–7 in another. The normalization factor was derived from the two observations of line 3, appearing in the overlap region. The sensitivity factors are the coefficients of the relative uncertainties in Eq. (13), i.e. $(1 - (BF)_k)$ and $(BF)_j$. The combined relative standard uncertainty $u_{c,r}(A_k)$ is found to be 14%.

In the published paper on Mo II [18], the uncertainty of the line $k$ is given as 23%. That figure was based on a conservative estimate, made before the method discussed here was fully implemented. The discrepancy is mainly due to an overestimated influence of the uncertainty from the self-absorption correction and from the combination of spectral regions in [18].

Table 1
Experimental branching fractions ($BF$) and $gf$-values for the upper level $z^6P_{5/2}$ in Mo II ($\tau_{exp} = 2.9(2)$ ns) [18]. The derived oscillator strength for the line $k$ is $gf = 0.320$

<table>
<thead>
<tr>
<th>Line</th>
<th>Lower level</th>
<th>$\lambda_{air}$ (Å)</th>
<th>$\sigma$ (cm$^{-1}$)</th>
<th>$BF$ (Exp.)</th>
<th>$BF$ (Theory)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>$d^3 a^6S_{5/2}$</td>
<td>2015.109</td>
<td>49609.08</td>
<td>0.254</td>
<td>0.236</td>
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<td>1</td>
<td>$d^35s a^6D_{3/2}$</td>
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<td>37574.66</td>
<td>0.332</td>
<td>0.383</td>
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<td>37191.45</td>
<td>0.304</td>
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<td>32662.00</td>
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<tr>
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<td>24496.53</td>
<td>0.006</td>
<td>0.004</td>
</tr>
<tr>
<td>7</td>
<td>$d^35s b^4D_{7/2}$</td>
<td>4119.628</td>
<td>24267.19</td>
<td>0.014</td>
<td>0.012</td>
</tr>
<tr>
<td>$r$</td>
<td>Residual</td>
<td></td>
<td></td>
<td>0.009</td>
<td></td>
</tr>
</tbody>
</table>
Table 2
Uncertainty budget in the resonance line at 2015.109 Å, which is referred to as line k

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>Line</th>
<th>Relative standard uncertainty (%)</th>
<th>Sensitivity factor</th>
<th>BF and τ unc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity measurement</td>
<td>k</td>
<td>2</td>
<td>0.746</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–2</td>
<td>1</td>
<td>0.304–0.332</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3–7</td>
<td>5</td>
<td>0.006–0.030</td>
<td></td>
</tr>
<tr>
<td>Calibration</td>
<td>1–2</td>
<td>7</td>
<td>0.304–0.332</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3–5</td>
<td>7</td>
<td>0.025–0.030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6–7</td>
<td>4</td>
<td>0.006–0.014</td>
<td></td>
</tr>
<tr>
<td>Normalization factor</td>
<td>3–7</td>
<td>8</td>
<td>0.006–0.030</td>
<td></td>
</tr>
<tr>
<td>Self absorption</td>
<td>k</td>
<td>10</td>
<td>0.746</td>
<td></td>
</tr>
<tr>
<td>correction</td>
<td>1–2</td>
<td>&lt; 1</td>
<td>0.304–0.332</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>r</td>
<td>50</td>
<td>0.009</td>
<td>BF :12.3</td>
</tr>
<tr>
<td>Radiative lifetime</td>
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<td></td>
</tr>
<tr>
<td>Statistical</td>
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<td></td>
</tr>
<tr>
<td>Systematic</td>
<td></td>
<td>6</td>
<td>1.0</td>
<td>τ:6.7</td>
</tr>
</tbody>
</table>

Combined relative standard uncertainty in $A_k$: 14%

6. Conclusions

The procedures described in this paper can be used for establishing a well-defined and reproducible method for ascribing uncertainties to measured transition probabilities and oscillator strengths. We intend to use this method in our future work in this field, using $u_{e,r}(A_k)$ as the stated uncertainty. This will correspond to a level of confidence of approximately 68% of a Gaussian distribution.

We hope that the procedures described in this paper will be used also by other groups working in this field of research, as this would make it easier to compare data from different laboratories. An error budget as shown in Table 2 will also help to reveal the main source of uncertainty in a measurement, and could thus act as a guideline for improving the accuracy. The most convenient way to apply the method is to use a spreadsheet program, which performs the operations included in Eq. (13). A file which can be used as a template for calculations with Microsoft Excel can be obtained from the authors on request.

Acknowledgements

We are grateful for extensive help and advice from Dr. Anne P. Thorne, Imperial College, London, concerning the procedures for spectrometer efficiency calibration.
References

[10] Cowan RD. The theory of atomic structure and spectra. Berkeley: University of California Press, 1981. (The Cowan code is available at different Web sites, e.g. (http://plasma-gate.weizmann.ac.il), where a version modified for PC by Ralchenko and Kramida can be found).