Theoretical Signal-to-noise Ratio and Resolution in Ion-cyclotron-resonance Spectroscopy

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A comparison is made theoretically of the signal-to-noise (S/N) ratio between the usual slow-sweep or the continuous-wave method and the pulsed Fourier-transform (FT) method in ion-cyclotron-resonance spectroscopy. Expressions of the maximum S/N ratio, as characterized by experimental parameters, are given in concrete form for both methods. Based on these expressions, it is shown that the FT method has a Fellgett S/N advantage when the resolution of a measurement is selected so as to be nearly equal to the true linewidth. A tradeoff between the S/N ratio and the resolution is discussed, and a possible reconciliation is suggested of inconsistent statements on a relation between the S/N and the resolution in the literature.

A physical system of spectroscopic interest can be considered to be an example of linear systems when the amplitude of excitation is small. According to the theory of linear systems, a spectrum of spectroscopy corresponds to what is called either a "system function" or "frequency response". There are several methods to obtain the system function.[1,2] One of them is the continuous-wave (CW) method, in which the amplitude and phase of a response are measured by sweeping frequencies of excitation. The name "frequency response" arose from this. Another one is the impulse-excitation method, in which the system function is obtained through the Fourier transformation of the response to a unit impulse excitation. The stochastic excitation method has also been proposed; in it the system function is evaluated through the Fourier transformation of the cross-correlation function of excitation and responce.

Of the many branches of spectroscopy, nuclear magnetic resonance (NMR), more specifically high-resolution NMR, which is a part of radio-frequency spectroscopy, is one of the most suitable for testing above ideas. This might be partly due to its spectroscopic characteristic that whole resonance lines concentrate within a narrow frequency range compared to the carrier frequencies, thus making it feasible to excite and detect a number of resonance lines at once. In NMR, of course, the CW method was employed first. Long after that, the impulse excitation method was applied by Ernst and Anderson, who noted that the method had an S/N advantage over the usual CW method.[3] An S/N gain of about one order was observed within a given experimental time. Spectrometers based on this principle are called "pulsed Fourier-transform spectrometers", and, because of their essential high sensitivity, they are now widely adopted in chemical and biological measurements. Soon after the advent of the FT method, the stochastic excitation method was also introduced; with pseudo-noise excitation, a similar S/N gain was obtained.[4,5] Meanwhile, in biological measurements a technique was required with which any portion of the whole spectrum could be excited and, at the same time, the S/N was high. The rapid scan or the correlation method was such a technique, in which excitation frequencies are swept fast linearly to time.[6,7] This may be considered to be another form of excitation for acquiring the system function.

The three relatively new methods have the common advantages over the CW method of a short observation time and, in consequence, a high sensitivity. These advantages essentially constitute a Fellgett advantage, which results from the simultaneous excitation and simultaneous detection of all spectral elements.[8] The Fellgett advantage may be described as follows. In spectroscopy, the frequency and amplitude of each frequency component are measured with a certain accuracy. The accuracy in frequency measurement defines the resolution. It is evident that it takes about $1/\Delta f$ to measure the frequency of a wave with an accuracy of Δf. This is a manifestation of the uncertainty principle between energy and time.[9] Thus, it takes $1/\Delta f$ to record one element of a spectrum with a resolution width of Δf. In the CW method, all the spectral elements are measured one by one, while in the other three methods they are obtained all at once. The former is a sequential method, while the latter three are simultaneous methods. The number of elements is $F/\Delta f$, where F is the whole spectral range of interest. Therefore, for the sequential method, the time required to record the whole spectrum is $F/(\Delta f)^2$. The band-width of noise superimposed on a spectral element is given by Δf. For the simultaneous method, on the other hand, the measurement time is only $1/\Delta f$, which is shorter by a factor of $(F/\Delta f)^{-1}$ than that for the sequential method. The band-width of noise is given again by Δf, though the band-width of the physical filter actually employed is F. Thus, S/N ratios are identical for the two methods if the magnitudes of the signals are assumed to be the same. Since S/N is improved as a square root of the measurement time[10], it is now evident that a Fellgett S/N gain of $(F/\Delta f)^{1/2}$ is obtained by the use of the simultaneous method. For radio-frequency spectroscopy, in which a coherent monochromatic excitation source is easily available, it is unclear why the sequential method is inefficient for utilizing signal energy, while it is evident for the infrared spectroscopy, in which only a small portion of the signal energy is utilized at one time by the use of a monochromator, the other big portion being wasted on the jaws of a slit, as Fellgett himself noted.

The pulsed-FT and rapid-scan methods have, in recent years, also been applied to ion cyclotron resonance (ICR), one branch of radio-frequency spectroscopy.[11,12] Besides the Fellgett advantage, the FT method as applied to ICR has an additional advantage of high resolution, which results essentially from the long observing time made possible by the use of ion-trapping cells.[13,14] Partly, however, it results from the characteristic of the FT method that the excitation period of ion motion is short; theoretically, high resolution may also be feasible for the CW method but experimentally it would be difficult since a very small amplitude of excitation is required. It was discussed by Marshall and Comisarow, by the use of analogy to optical multichannel spectrometers, how FT ICR has the Fellgett advantage.[15] There remains, however, some features to be clarified. First, in order to obtain the full Fellgett S/N gain it is necessary that the magnitude of a free decaying signal be the same as the signal magnitude for the CW method. This is not obvious, since the FT method utilizes transient responses, while the CW method treats steady-state responses. The second problem concerns noise levels. In the FT method, the band-width of a physical filter allowed is F, far broader than the band-width of the low-pass filter employed in the CW method. This may lead to an S/N disadvantage. Since a spectrum is obtained through the Fourier transformation of a time-domain signal, noise is also subjected to transformation, thus causing a frequency-domain noise. Third, it was stated by Marshall that there is a trade-off between the S/N and the resolution in the FT method.[16] More recently, however, a manuscript reporting contrary results has appeared.[14] In view of this situations, the present author felt that it was necessary to discuss S/N and resolution for the FT and the CW methods on a general basis. The ambiguities mentioned above will be made clear in this manuscript by evaluating S/N ratios at several stages involved in actual experiments.

Theoretical

We shall first describe some experimental conditions. The frequency range of a spectrum of interest is denoted by F. The resolution width of a measurement has the usual meaning that the width of a resonance line with a true width narrower than the resolution width may become widened through the measurement to the apparent magnitude of the resolution width; it is denoted by Δf. For the CW method, it is the reciprocal of the time spent to measure one frequency channel, and at the same time it is channel width. By using the scanning time, T_s, it is given thus;

$$\Delta f_{\mathrm{CW}} = (F/T_s)^{1/2}. \quad (1)$$

For the FT method, on the other hand, it is given by the reciprocal of the sampling time, T_0, of free decaying (FD) signals:

$$\Delta f_{\mathrm{FT}} = 1/T_0 \quad (2)$$

In order to obtain true line shapes determined by physical conditions, the resolution width of a measurement should be much narrower than the width of a resonance curve, $\Delta f_{1/2}$; *i.e.*

$$\Delta f \ll \Delta f_{1/2} \quad (3)$$

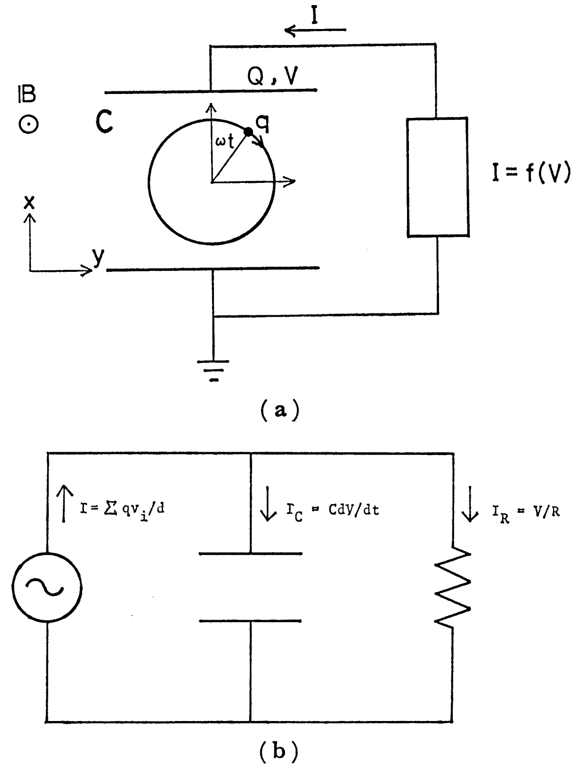
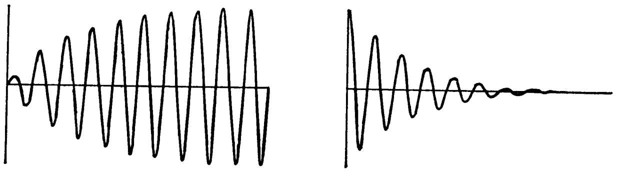


Fig. 1. (a): Moving ions in an ICR cell whose top and bottom plates form a capacitor C. The plates are connected with an outer circuit satisfying a current-voltage relation $I=f(V)$. Magnetic field is along z-axis, (b): current source equivalent to moving ions in a capacitor.

For the FT method, this is equivalent to a condition that the sampling time, T_0, should be much longer than the relaxation time. It should be noted that a so-called high resolution corresponds to a small resolution width in the present paper. The total experimental time is denoted by T_t. We assume ion-trapping cells,[17] since usual FT ICR experiments are done with such cells. With ion-drift cells, FT ICR experiments may be equally feasible, though greater experimental skill would be required. With a short burst of ionizing electrons, N numbers of ions are produced in a cell. If the trapping of ions is perfect, then only one burst of electrons will be sufficient for the whole experiment. Actually, however, the loss of ions from a cell can be significant after some time. Therefore, in order to enhance the S/N ratio through ensemble averaging, N ions must be produced afresh at every cycle after ejecting the ions of the previous cycle. For the CW and FT experiments, we assume a common detector which is equivalent to a pure resistance. It is realized either by the use of a parallel resonant circuit or by the use of a parallel CR combination when the circuit is essentially resistive, *i.e.*, $R \ll 1/j\omega C$. For the sake of simplicity, we shall limit considerations to a situation where only one resonance line is present in the whole spectrum range of interest. However, the following considerations may be easily extended to the case of N resonance lines.

Next, let us evaluate the maximum signal voltage obtained at a detector circuit. According to the signal



(a) (b)

Fig. 2. (a): Velocity component vertical to cell plates of an ion just at resonance condition for the initial condition $v=0$ at $t=0$ which is subjected to radio-frequency electric field with constant amplitude, (b): velocity component vertical to cell plates of an ion executing free decaying motion under no electric field after irradiation with a radio-frequency pulse.

theory,[18,19] moving ions are equivalent to a constant-current-source shunt across a cell whose top and bottom plates form a capacitor. This situation is illustrated in Fig. 1. There, the strength of the current source is:

$$I = \sum_{i=1}^{N} q_i v_i / d, \tag{4}$$

where q_i is the charge; v_i, a velocity component vertical to the plates and d, the distance between the two plates, and where summation is taken over the N ions in the cell. The velocity of the ion is given by the equation of motion for an average ion:

$$m d\boldsymbol{v}/dt = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}) - mc\boldsymbol{v}, \tag{5}$$

where $\boldsymbol{E}$ is, as usual, the electric field; $\boldsymbol{B}$, the magnetic field, and c in the last term, a damping constant attributable to collisions with neutral atoms and molecules, which is usually called the reduced collision frequency.[20,21] Equations 4 and 5 form a pair of basic equations describing ICR phenomena. Equation 5 can be shown to be equivalent to the equation of motion for a harmonic oscillator with a friction. Thus, solutions of the latter problem are useful in ICR. Let us consider the ion motion under the condition of CW experiments in which ions are subjected to a radio-frequency electric field with a constant amplitude. The velocity of the ion at just the resonance for the initial condition, $v=0$ at $t=0$, is given by the form that increases with a time constant, $1/c$, and becomes nearly constant after some multiples of the time constant. This is shown in Fig. 2(a). The constant value depends on the amplitude of the rf electric field and on the collision frequency. The radius, r, of the ion orbit is limited within $d/2$ by the finite dimensions of a cell. Thus, when $r=d/2$, the ion velocity given by the $v=r\omega_c$ formula has as its maximum value $d\omega_c/2$, where ω_c is the cyclotron angular frequency. Since all ions subjected to an rf electric field rotate with the same radii and phases, Eq. 4 leads to:

$$I_{\mathrm{CW}} = Nq\omega_c/2. \tag{6}$$

As we have assumed a pure resistance, R, for a detector, the maximum voltage is given simply as:

$$V_{\mathrm{CW}} = Nq\omega_c R/2. \tag{7}$$

For FT experiments, on the other hand, ions are accelerated with a short *rf* pulse. The velocity of the ions quickly reaches its maximum value, $d\omega_c/2$, and thereafter decays exponentially with a time constant, $1/c$, under no external electric field. This free decaying motion is shown in Fig. 2(b). The maximum amplitude of the FD signal is again given by:

$$V_{\mathrm{FT}} = Nq\omega_c/2. \tag{8}$$

It is evident that the maximum signal voltage for the FT method is the same as that for the CW method. We shall henceforth use V_m to denote it. It is worth noting that, for the latter, V_m corresponds to the peak value of a spectrum, while for the former it does not. For the FT method, the peak value of a spectrum is obtained after the Fourier transformation of an FD signal and it is given by the average amplitude of the FD signal. The FD signal decays exponentially with the time, as is illustrated in Fig. 2(b), so that the average amplitude over the sampling time decreases as the sampling time increases. We will see later that this feature leads to a serious tradeoff between the S/N and the resolution.

We shall next evaluate the maximum S/N ratio obtained for the CW method. Among various types of noise, we assume only thermal noise which appears across a resistor in a detector circuit. This is the so-called "detector limited-noise case". Thermal noise has a white power spectrum, and its rms voltage is:

$$\overline{(v_t^2)}^{1/2} = (4kTRf)^{1/2}, \tag{9}$$

where f is the band-width in which noise is measured. This form shows that, in order to get better S/N, the band-width should be made as narrow as possible by the use of a filter. However, the minimum width of a filter employed is determined by the condition that a measurement is carried out with a certain resolution. Considering a measurement by a point-by-point spectrometer, a predecessor of CW spectrometers, we see that the minimum width of a filter is equal to the resolution width, Δf. Then, the rms value of the noise voltage becomes $(4kTR\Delta f)^{1/2}$. In that condition, the signal of amplitude, V_m, can pass through the filter without appreciable decrease. Hence, the maximum S/N ratio for the CW method with the resolution width, Δf, is now obtained thus:

$$(S/N)_{\mathrm{CW}} = V_m/(4kTR\Delta f)^{1/2}. \tag{10}$$

It is worth noting that S/N increases in proportion to the square root of the magnitude of resistance, R, since V_m in Eq. 10 is actually proportional to R, as can be seen in Eq. 7. The scanning time for the experiment is evidently given be:

$$T_s = F/(\Delta f)^2. \tag{11}$$

The result of Eq. 10, which has been obtained rather intuitively, can be obtained in a more rigorous fashion by the theory of the matched filter. This approach is the same as Ernst employed in the S/N analysis of FT NMR.[3] The matched filter may be defined to be a filter such as can give the maximum S/N ratio for a signal pulse superimposed with noise.[1] According to the theory of the matched filter, the muximum S/N ratio obtained by the use of the filter is given in the frequency domain as:

$$(S/N)^2 = (1/2\pi)\int_{-\infty}^{\infty} |S(\omega)|^2/N(\omega)d\omega, \quad (12)$$

where $S(\omega)$ is the Fourier transform of a time-domain signal, $s(t)$, and where $N(\omega)$ is power spectrum of the noise. For the white noise assumed here, $N(\omega)=$ const, which we denote by W. Equation 12 then reduces to:

$$(S/N)^2 = (1/2\pi W)\int_{-\infty}^{\infty} |S(\omega)|^2 d\omega. \quad (13)$$

Using Parceval's theorem:

$$(1/2\pi)\int_{-\infty}^{\infty} |S(\omega)|^2 d\omega = \int_{-\infty}^{\infty} s(t)^2 dt, \quad (14)$$

we move to a more convenient time-domain description to obtain:

$$(S/N)^2 = (1/W)\int_{-\infty}^{\infty} s(t)^2 dt. \quad (15)$$

Here, the term $\int_{-\infty}^{\infty} s(t)^2\, dt$ stands for the total energy of a signal, $s(t)$, and W stands for the noise energy per unit of time and unit angular frequency. Since we measure signals over the resistance, R, we must replace Eq. 15 with

$$(S/N)^2 = (1/WR)\int_{-\infty}^{\infty} V_s(t)^2 dt, \quad (16)$$

where $V_s(t)$ is the signal voltage measured over the resistance, R. By specifying the functional form of $V_s(t)$, S/N can thus be evaluated. The signal pulse corresponding to the ICR absorption may be described by the Lorentzian form:

$$V_s(t) = V_m c^2/\{(at - \omega_c)^2 + c^2\}, \quad (17)$$

where a is the scanning rate and is equal to $2\pi F/T_s$. The peak value of this signal is V_m, and the width is $2c$. Although the evaluation of Eq. 16 with this form is possible, we can employ an alternative form without introducing much error since we are deriving general results which depend not on the details of the line shape, but on the width:

$$V_s(t) = \begin{cases} 0 \text{ for } t < (\omega_c - c)/a \\ V_m \text{ for } (\omega_c - c)/a \leqq t \leqq (\omega_c + c)/a \\ 0 \text{ for } (\omega_c + c)/a < t. \end{cases} \quad (18)$$

This is a rectangular pulse with the same height and width as the Lorentzian pulse. The evaluation of Eq. 16 with this form easily gives:

$$(S/N)^2 = V_m^2/4kTR(a/2c). \quad (19)$$

Here, the relation $W=4kT$ has been used. By using $a=2\pi F/T_s$ and $T_s=F/(\Delta f)^2$, Eq. 19 is rewritten to

$$(S/N) = V_m/(4kTR\Delta f')^{1/2}, \quad (20)$$

$$\Delta f' = \pi(\Delta f)^2/c. \quad (21)$$

Here, $\Delta f'$ is the effective band-width of noise, which is determined by the band-width of the matched filter. As we are considering an experiment with a resolution of Δf, we must put the linewidth equal to the resolution width, *i.e.*, $c/\pi=\Delta f$. Then, the band-width of the matched filter also becomes equal to the resolution width. Moreover, S/N is again given by Eq. 10. The band-width of the matched filter and, in consequence, the effective band-width of noise have the following simple meanings. Note that the frequency components of a signal pulse with a certain duration, Δt, are contained mainly in a band-width of about $1/\Delta t$. Therefore, the minimum width of a filter which let pass through the main frequency components of the signal and, at the same time, reject noise is evidently $1/\Delta t$. By applying this result to the signal pulse with a duration of $2c/a$ considered above, the width of the filter is found to be $\pi(\Delta f)^2/c$, which agrees with Eq. 21.

Now let us evaluate the maximum S/N ratio for the FT method. For this case, the band-width of a filter applicable to FD signals is not Δf, but F. Actually, the filter is necessary only to guarantee that FD signals can be sampled at the Nyquist rate. Since usually $F \gg \Delta f$, the S/N of one FD transient is much worth than that of a spectrum of the CW method. As we have denoted the maximum amplitude of an FD signal by V_m, the S/N for one transient is:

$$(S/N)_{1\mathrm{FT}} = V_m/(4kTRF)^{1/2}. \quad (22)$$

By requiring the resolution width of a spectrum to be Δf, the measurement time of the FD signals is set as $1/\Delta f$. This is equal to the measurement time of one frequency channel for the CW method with the same resolution width. Let us now consider the Fourier transformation of FD signals and noise. The FD signal is generally described by:

$$V_s(t) = V_m \cos(\omega_c t) \exp(-ct). \quad (23)$$

Assuming a finite sampling time, T_o, we may expand this in a Fourier series:

$$V_s(t) = \sum_{n=0}^{\infty} \{\alpha_n \cos(\omega_n t) + \beta_n \sin(\omega_n t)\}, \quad (24)$$

where $\omega_n=2\pi n/T_o$ and where n is an integer.[22] The Fourier coefficients α_n and β_n are given as usual:

$$\alpha_n = (2/T_o)\int_0^{T_o} V_s(t) \cos(\omega_n t) dt, \quad (25a)$$

$$\beta_n = (2/T_o)\int_0^{T_o} V_s(t) \sin(\omega_n t) dt. \quad (25b)$$

By substituting Eq. 23 into these forms, the absorption component, α_n, and the dispersion component, β_n, are obtained. The absorption gives the Lorentzian line shape of Eq. 17, and its peak amplitude is:

$$\alpha_n(\omega_n = \omega_c) = (V_m/cT_o)\{(1 - \exp(-cT_o))\}. \quad (26)$$

This expression quantitatively describes how the peak amplitude varies with the sampling time: The amplitude decreases as the sampling time increases. The Fourier coefficients of noise are similarly obtained by substituting a random variable, $V_n(t)$, into Eq. 25. Then, α_n and β_n also become random variables; their dispersions are given by:

$$\overline{\alpha_n^2} = \overline{\beta_n^2} = N(f_n)/T_o, \quad (27)$$

where $N(f_n)$ is the power spectrum of the noise. This result can be directly derived from the definition of Eq. 25 by assuming that the correlation time of the noise is shorter than the sampling time, T_o.[10] Equation 27 shows that, through Fourier transformation, the band-width of the noise is reduced from F to Δf and that the rms value of the noise decreases with the square root of the reciprocal of the sampling time.

By combining Eqs. 26 and 27, the S/N ratio of a spectrum of the FT method is found to be:

$$(S/N)_{1\mathrm{FT}} = (V_{\mathrm{m}}/cT_{\mathrm{o}})\{1-\exp(-cT_{\mathrm{o}})\}/(4kTR)^{1/2}. \qquad (28)$$

When the resolution of a measurement is nearly equal to the true width of a resonance line, *i.e.*, $1/T_{\mathrm{o}} \sim c$, this reduces to:

$$(S/N)_{1\mathrm{FT}} \simeq V_{\mathrm{m}}/(4kTR\Delta f)^{1/2}.$$

This is the same form as Eq. 10 for the CW method. Therefore, when the resolution width of a measurement is nearly equal to the true linewidth, time is saved with the FT method by a factor of $\Delta f/F$. Through ensemble averaging of the coherent addition of $(F/\Delta f)$ samples which are obtained in the time equal to one scanning time, T_{s}, for the CW method, the S/N ratio can be enhanced by the factor of $(F/\Delta f)^{1/2}$. This is the Fellgett S/N gain. It should be noted, however, that the full Fellgett S/N gain can be obtained only if the condition $\Delta f \simeq c/\pi$ is satisfied. For usual experiments in which an accurate peak amplitude or linewidth is needed, the resolution width should be selected to be much smaller than the linewidth, *i.e.*, $\Delta f \ll c/\pi$. Therefore, the parameter of S/N enhancement is $(F\Delta f)^{1/2}/c$ rather than the Fellgett value $(F/\Delta f)^{1/2}$.

Finally, let us summarize the relations among the S/N, the resolution, the scanning time, and the total experimental time. For the CW method, the S/N and the resolution width are given in terms of the total spectral range of interest, F, and the scanning time, T_{s}:

$$S/N = V_{\mathrm{m}}/(4kTR\Delta f)^{1/2} = V_{\mathrm{m}}T_{\mathrm{s}}^{1/4}/(4kTR)^{1/2}F^{1/4},$$
$$\Delta f = (F/T_{\mathrm{s}})^{1/2}.$$

When F is constant, these forms indicate that the S/N increases as the fourth root of the scanning time and that the so-called resolution appropriately given by $1/\Delta f$ also increases in accordance with the square root of the scanning time. Thus, there is no tradeoff between the S/N and the resolution. The fourth root law of the S/N seems curious, since it is inconsistent with the well-known fact that the accuracy of a measurement (S/N) increases with the square root of the measurement time.[10] Note, however, that, for the CW method, the increase in the scanning time inevitably results in an increase in the resolution. If an experiment in which the resolution is kept constant is considered, it can be shown that the usual square-root dependence of the S/N on the total time holds: by assuming a fixed resolution of Δf, the scanning time becomes $F/(\Delta f)^2$ and S/N is given by $\alpha T_{\mathrm{s}}^{1/4}F^{-1/4}$, where α is a constant and is equal to $V_{\mathrm{m}}/(4kTR)^{1/2}$. Consider the total experimental time, T_{t}, which is much longer than T_{s}. In that time, $(T_{\mathrm{t}}/T_{\mathrm{s}})$ times of scans are carried out. Through the ensemble averaging of the scans, the S/N can be enhanced by a factor of $(T_{\mathrm{t}}/T_{\mathrm{s}})^{1/2}$, and the overall S/N ratio becomes $\alpha T_{\mathrm{t}}^{1/2}T_{\mathrm{s}}^{-1/4}F^{-1/4}$. By the use of the $T_{\mathrm{s}}=F/(\Delta f)^2$ relation, this is rewritten to a convenient form:

$$(S/N)_{\mathrm{nCW}} = \alpha T_{\mathrm{t}}^{1/2}(\Delta f)^{1/2}F^{-1/2}, \qquad (29)$$

where the subscript n stands for the number of scans and is equal to $T_{\mathrm{t}}/T_{\mathrm{s}}$. This shows the usual square root dependence of S/N ratio on the measurement time. It is also evident that in a given time, T_{t}, the tradeoff between the S/N and the resolution exists. This is the usual meaning of the tradeoff. For the FT method, on the other hand, the S/N and the resolution width are geven in terms of only the sampling time, T_{o}:

$$S/N = (V_{\mathrm{m}}/cT_{\mathrm{o}}^{1/2})\{1-\exp(-cT_{\mathrm{o}})\}/(4kTR)^{1/2},$$
$$\Delta f = 1/T_0.$$

These forms show that, as T_{o} increases, the resolution increases and the S/N decreases. This behavior is different from that in the case of the CW method, where both the S/N and the resolution increases with the scanning time. Consider also an experiment in this time where the resolution is held constant. In a given total experimental time, T_{t}, which is much longer than T_{o}, $(T_{\mathrm{t}}/T_{\mathrm{o}})$ times of FD signals are obtained, so that the S/N can be enhanced by a factor of $(T_{\mathrm{t}}/T_{\mathrm{o}})^{1/2}$. Then, the overall S/N ratio becomes:

$$(S/N)_{\mathrm{nFT}} = (V_{\mathrm{m}}T_{\mathrm{t}}^{1/2}\Delta f)\{1-\exp(-cT_{\mathrm{o}})\}/c(4kTR)^{1/2}, \qquad (30)$$

where the subscript n is again the number of transients and is equal to $T_{\mathrm{t}}/T_{\mathrm{o}}$. This form again indicates the usual square root dependence of the S/N ratio on the total time and the tradeoff between the S/N and the resolution. However, the S/N is proportional to Δf for the FT method, so the tradeoff is more marked than for the CW method, where the S/N is proportional to the square root of Δf.

Discussion

We have shown in the previous section that the tradeoff between the S/N and the resolution is marked for the FT method. Marshall also discussed the tradeoff by considering the FD signals and the noise averaged over the sampling time, though he did not explicitly treat the Fourier transformation of the noise.[16] He obtained an expression describing the behavior of the relative S/N ratio vs. the sampling time, which is essentially the same as Eq. 30 in the present manuscript. More recently, however, a paper has appeared which reported that the tradeoff was not observed and that the S/N and the resolution simultaneously increased with the FT ICR.[14] Note that the simultaneous increase in the S/N and the resolution was obtained by lowering the sample pressure in that paper. The tradeoff should be referred to the method of measurements when the physical states of systems, for example, the sample pressure, are kept constant. It seems misleading to say that the S/N and the resolution simultaneously increase without the tradeoff, since the tradeoff between the S/N and the resolution has wide acceptance in physical measurements.

We shall next consider the so-called exponential filter. The operation of multiplying free-induction decay signals by an exponential function is called either "the exponential filter" or "the matched filter".[3,23,24] It seems inappropriate, however, to call such an operation a "filter" at all, since a filter is what carries out a convolution operation on time-domain signals to lower noise levels. Convolution in the time domain corresponds to multiplication in the frequency domain. As we have seen in the previous section, through Fourier transformation the effective band-width of noise is reduced to a resolution width which is usually very narrow compared to the original band-width of noise in the time domain, so that the noise level is reduced. The so-called exponential filter carries out, on signals in each domain, the operation opposite to that of usual filters. It is evident that the convolution operation on a spectrum in which the noise level has already been reduced to a resolution width will not effectively improve the S/N ratio without leading to additional line-broadening.

Both ICR and NMR belong to radio-frequency spectroscopy, and there are many similarities between them. It would be useful to utilize such similarities. Among several techniques with the Fellgett advantage, the stochastic excitation method has not yet been applied to ICR. This method was, however, applied to NMR by Ernst, and thereby it was noted that it has a unique feature that the S/N and the resolution can be separately optimized.[4)] Since the tradeoff between the S/N and the resolution seems general, however, it would be necessary to examine this method closely. The analysis of the S/N and the resolution in the present paper is general, and it can also be applied to NMR with a little modification. The Fellgett advantage can be obtained in various branches of spectroscopy, since it results essentially from the simultaneous excitation and simultaneous observation of all frequency channels.[25)]

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