Use of the TRAF function in Electron Spin Resonance Signal Processing

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Abstract

In this paper the application of the TRAF function to Electron Spin Resonance (ESR) spectra is reported. The TRAF function is a window function made to amplify signal low frequencies while decreasing noise high frequencies. This was done by designing and using a program to graph the original spectrum, transform it from the time domain to the frequency domain, multiply the original spectrum in the frequency domain together with a TRAF function that the user can vary, transforming the edited spectrum back to the time domain. The program allows measuring the signal to noise ratio (S/N) and observing the resolution changes. The TRAF function proved an effective alternative to typically used methods of increasing S/N and/or resolution in ESR spectra.

Introduction

ESR spectroscopy can be used to determine an abundance of information about a free radical. Some of this information includes the hyperfine splitting, the ‘g’ value, the number of hydrogen environments, and the number of degenerate hydrogens in each environment.[1]

The ESR spectrometer uses a microwave cavity that is highly resonant to increase sensitivity to detect signals, but this makes the spectra prone to noise. This fact makes post signal processing extremely valuable in ESR specroscopy.[2]

Post signal processing requires the manipulation of large amounts of data, making computer programs extremely valuable and necessary. The programming language used in this project was Python. Python was chosen because of its user-friendly interface and pre existing modules that pertain to post signal processing. The program used can be explained by figure one.

A fast fourier transform is an approximation of the fourier transform, which is a complex integral that is used to transform spectra from the time domain to the frequency domain. This is especially useful in signal processing because it separates noise high frequencies from signal frequencies.[2]

Window functions are typically multiplied together with the FFT to amplify signal and/or reduce noise. Some common window functions are a square wave and an exponential decay function.[3]

A window function commonly used in Nuclear Magnetic Resonance (NMR) spectroscopy, but not previously used in ESR spectroscopy is the TRAF function. The TRAF function is used on Free Induction Decay diagrams in NMR spectroscopy. The formula for this function is $\frac{E}{E^2+e^2}$, where $E = exp(\frac{-t}{LB})$and $e = exp(-\frac{AQ-t}{LB})$, and t=time, LB=Line broadening constant, and AQ=total acquisition time. This type of function has a shape resembling an exponential decay function with a bump in the beginning to boost low signal frequencies more than a normal exponential decay window function, while cutting off high noise frequencies (Fig. 2).[4] This function is particularly useful in FID diagrams because noise typically appears at higher frequencies and signal typically appears at lower frequencies. For the same reasons, this function is also theoretically useful for ESR spectra.

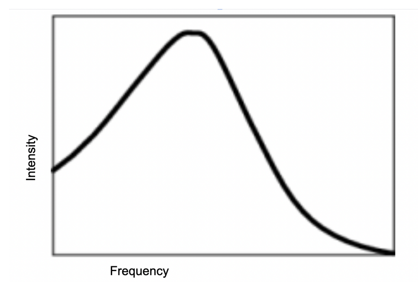

Fig. 2: TRAF Function[3]

Methods

The Python program uses an ESR text file with all of the ESR data points, the sweep width, the center field, and the number of data points to graph the ESR spectrum.

The program performs a Fast Fourier Transform (FFT) on the ESR spectrum in order to transform the spectrum from the time domain to the frequency domain.

A TRAF function is then multiplied to the positive and negative frequencies of the ESR FFT evenly. Sliders allow users of the program to manually change where the TRAF function is applied on the ESR FFT and change the line broadening constant in the TRAF function. The shift slider moves the two TRAF functions that are applied equally to the positive and negative frequencies of the FFT of the original spectrum toward and away from each other, thus changing where the TRAF function is applied. Moving the shift slider in the negative direction moves the two traf functions away from each other and moving the shift slider in the positive direction moves the two TRAF functions toward each other.

The edited ESR FFT is inverse fast fourier transformed in order to return it to the time domain. The user selects a peak in the recovered spectrum. The program measures the difference in the magnetic sweep between the two peaks in both the original and recovered spectra in order to approximate resolution change. The program also measures the signal to noise ratio in the original and recovered spectra by automatically selecting the maximum signal point and dividing that by the standard deviation of the noise in a region that is selected by the user.

The program displays the recovered spectrum, original spectrum, signal to noise ratio improvement, original resolution, and recovered resolution so that the user can see how changing the line broadening in the TRAF function, changing where the TRAF function is applied (the shift value), and changing the noise range affects them in real time.

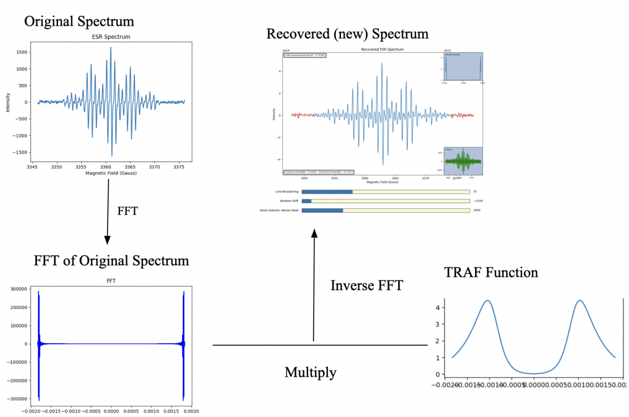

Fig. 3: Windowing Explanation

In order to record results, sliders were changed one at a time and S/N and resolution were recorded. Additionally, the slider settings were also recorded for each S/N and resolution value. Three different spectra were observed. These spectra include a noisey biphenylene spectrum, a clean biphenylene spectrum, and a tempo spectrum.

Results and Discussion

Three different spectra were observed, they include a noisey Tempo spectrum, a noisey biphenylene spectrum, and a clean biphenylene spectrum. All three spectra showed different results when the TRAF function was applied. One artifact that appeared in all of the spectra was non-signal peaks that appeared in between every signal peak when the TRAF function was applied with a low line broadening constant (Fig.4).

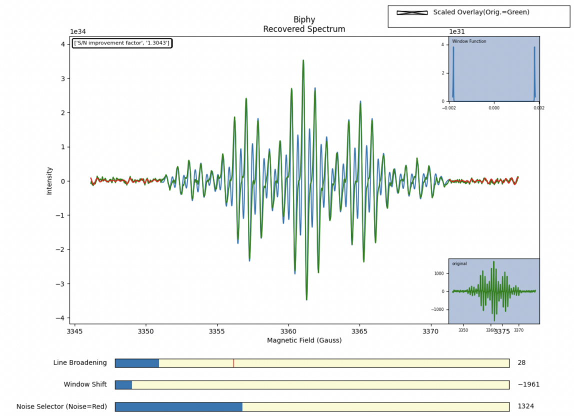

Fig. 4: Recovered spectrum with artifact present is blue and the scaled original spectrum is green

These lines were taller at lower line broadening constants and became smaller as the line broadening constant was increased. In each spectrum the non-signal peaks disappeared at different line broadening constants. In each spectrum the highest S/N and resolution enhancement tended to appear in spectra where the non-signal peaks were present. Recovered spectra with the artifact are usable, but for the purpose of this paper, these spectra will be discussed separately from the recovered spectra without the artifact.

The noisey Tempo spectrum had a high S/N improvement with the artifact present (LB range of 0-25) in the recovered spectrum at 238% maximum S/N enhancement and 7.32% resolution enhancement at these settings. The maximum resolution enhancement with the artifact present was 28.8%, but the S/N was decreased by 3.08%. The maximum S/N improvement without the artifact present was 194%, but the resolution was only increased by 1.95%. The maximum resolution enhancement without the artifact present was 14.0%, but the S/N improvement was 87%. The resolution enhancement tended to decrease more than the S/N when the line broadening constant was increased in order to eliminate the artifact.

Line Broadening	Shift Value	Recovered Linewidth (original linewidth=1.489)	S/N improvement factor
10.8	-1993	1.18	0.3619
10.8	-1998	1.12	0.4784
10.8	-2006	1.06	0.9692
10.8	-2013	1.12	1.6861

10.8	-2018	1.17	1.9023
10.8	-2023	1.42	2.86
10.8	-2030	1.62	2.6696
20.4	-1998	1.21	1.2292
20.4	-2003	1.21	1.5396
20.4	-2008	1.22	1.8796
20.4	-2016	1.27	2.33
20.4	-2023	1.38	3.0044
20.4	-2028	1.50	3.38
20.4	-2033	1.64	3.37
20.4	-2035	1.75	3.066
30.6	-1996	1.28	1.504
30.6	-2003	1.28	1.8755
30.6	-2011	1.31	2.2032
30.6	-2020	1.39	2.7687
30.6	-2025	1.46	2.9426
30.6	-2033	1.56	2.8780
40.3	-1996	1.31	1.7394
40.3	-2008	1.34	2.2056
40.3	-2016	1.37	2.4388
40.3	-2028	1.47	2.70
40.3	-2023	1.55	2.51
50.5	-1996	1.35	1.8697
50.5	-1998	1.35	1.9578
50.5	-2008	1.37	2.2188
50.5	-2013	1.38	2.34
50.5	-2018	1.40	2.4275
50.5	-2025	1.45	2.50304
50.5	-2038	1.52	2.3995
60.7	-1993	1.37	1.9046
60.7	-2001	1.37	2.0346
60.7	-2011	1.39	2.2289
60.7	-2020	1.42	2.3879
74.8	-1961	1.42	1.4588
74.8	-1976	1.40	1.6768
74.8	-1988	1.39	1.8685
74.8	-1993	1.39	1.9455
74.8	-2003	1.40	2.0942
74.8	-2013	1.41	2.2218
100	-2017	1.44	1.1105
100	-1934	1.43	1.3015
100	-1949	1.42	1.4487
100	-1956	1.42	1.5401
100	-1969	1.42	1.6659
100	-1976	1.41	1.7602
100	-1988	1.41	1.8964
100	-1996	1.41	1.9637
100	-2003	1.41	2.0452
150.2	-1801	1.45	0.6854
150.2	-1882	1.44	1.0824
150.2	-1912	1.44	1.2897
150.2	-1929	1.44	1.4207
150.2	-1951	1.44	1.5911
150.2	-1977	1.43	1.7716

Table 1: Noisey Tempo Spectrum Results

The noisey biphenylene spectrum showed similar results for S/N enhancement, but less promising results for resolution enhancement. The artifact also stayed in the noisey biphenylene for a much longer range of LB values. The artifact was minimal at a LB value around 100 and appeared to be eliminated at an LB value around 175. With the artifact present the highest S/N enhancement was 187%, but resolution dropped by 25.6%. The highest resolution enhancement value gathered with the artifact present was 5.18%, with a corresponding S/N enhancement of 25%. With the artifact minimized the highest S/N enhancement was 171%, but resolution dropped by 28.2%. The highest resolution enhancement attained with the artifact minimized was 7.7%, but resolution dropped 8%. With the artifact eliminated the highest S/N enhancement was 138%, but resolution dropped 20.5%. The highest resolution enhancement with the artifact eliminated was 2.6% with a S/N enhancement of 40%.

Line Broadening	Shift value	Recovered Linewidth (original linewidth=0.1428)	S/N improvement factor
12	-2019	0.4504	1.13
12	-2000	0.3881	2.35
12	-1942	0.1538	3.06
12	-1971	0.2087	1.73
19	-1913	0.1354	1.25
19	-1923	0.1428	1.75
19	-1942	0.1611	2.23
19	-1971	0.2160	2.75
19	-1990	0.3039	1.84
29	-1913	0.1391	1.82
29	-1923	0.1464	2.22
29	-1942	0.1684	2.62
29	-1971	0.2197	2.68
29	-1990	0.2856	2.19
41	-1913	0.1464	2.23
41	-1923	0.1538	2.51
41	-1942	0.1757	2.80
41	-1971	0.2197	2.69
41	-1990	0.2709	2.35
50	-1913	0.1538	2.41
50	-1923	0.1611	2.61
50	-1942	0.1794	2.83
50	-1971	0.2197	2.69
50	-1990	0.2563	2.40
60	-1913	0.1538	2.51
60	-1942	0.1794	2.83
60	-1971	0.2160	2.68
60	-2000	0.2673	2.28
72	-1907	0.1538	2.52
72	-1921.3	0.1647	2.73
72	-1932.3	0.1721	2.83
72	-1940.4	0.1794	2.87
72	-1951.4	0.1897	2.85
72	-1972.1	0.2124	2.71
72	-2000.4	0.2490	2.35
82	-1911.	0.1611	2.51
82	-1921	0.1647	2.62
82	-1932	0.1721	2.71
82	-1944.4	0.1831	2.75
82	-1960.4	0.1940	2.71
82	-1980.2	0.2160	2.55
94	-1902.2	0.1574	2.43

94	-1910.5	0.1611	2.52
94	-1925	0.1684	2.64
94	-1934.3	0.1757	2.69
94	-1945.4	0.1831	2.71
94	-1957.2	0.1940	2.69
94	-1971	0.2014	2.62
94	-1989	0.2197	2.45
151	-1700	0.1318	.92
151	-1802.2	0.1464	1.64
151	-1835.5	0.1501	1.93
151	-1854.4	0.1538	2.09
151	-1903.2	0.1647	2.44
151	-1923.4	0.1721	2.53
151	-2008.4	0.2050	2.36
269	-1700	0.1391	1.40
269	-1761.4	0.1464	1.687
269	-1811	0.1501	1.93
269	-1842.2	0.1574	2.08
269	-1910.3	0.1647	2.32
269	-1938	0.1721	2.38

Table 2: Noisey Biphenylene Spectrum Results

The clean biphenylene spectrum showed much smaller values for S/N and resolution improvement than the noisey Tempo spectrum and the noisey biphenylene spectrum. The artifact became negligible at a line broadening constant of around 45 before being eliminated altogether at a line broadening constant of around 100. The maximum S/N improvement with the artifact present was 105%, but resolution was decreased by 41.3%. The maximum resolution improvement with the artifact present was 14.0%, but S/N was improved by 4.81%. The maximum S/N improvement with the artifact minimized was 28.24% and the corresponding resolution was decreased 1.58%. The maximum resolution enhancement with the artifact minimized was 12.5% with a corresponding S/N improvement of 6.91%. The maximum S/N improvement with the artifact eliminated altogether was 19.8% with a resolution decrease of 2.99%. The maximum resolution enhancement with the artifact eliminated altogether was 4.69% with a S/N decrease of 3.43%.

Line Broadening	Shift Value	Recovered Linewidth (original=0.2343)	S/N improvement factor
9.3	-1976	0.2160	0.3867
9.3	-1993	0.3735	0.8034
9.3	-1998	0.3808	1.4293
9.3	-2006	0.3991	2.0508
9.3	-2011	0.4138	1.8203
20.4	-1951	0.2014	1.0481
20.4	-1959	0.2124	1.1640
20.4	-1976	0.2343	1.0801
20.4	-1988	0.3076	1.1198
30.3	-1947	0.2050	1.0691
30.3	-1954	0.2160	1.1961
30.3	-1964	0.2270	1.2614
30.3	-1976	0.2490	1.2162
30.3	-1986	0.2783	1.2244
40	-1934	0.2050	0.9998
40	-1945	0.2160	1.1586
40	-1964	0.2343	1.2801
40	-1986	0.2785	1.2711
50.2	-1912	0.2050	0.8309
50.2	-1939	0.2160	1.1388
50.2	-1951	0.2270	1.2419
50.2	-1964	0.2380	1.2824
50.2	-1976	0.2600	1.2790

60.7	-1910	0.2087	0.8983
60.7	-1944	0.2233	1.1994
60.7	-1956	0.2343	1.2547
60.7	-1976	0.2563	1.2659
75.1	-1890	0.2160	0.8739
75.1	-1929	0.2233	1.1239
75.1	-1944	0.2307	1.2008
75.1	-1956	0.2308	1.2384
75.1	-1988	0.2743	1.2067
102.5	-1882	0.2233	0.9657
102.5	-1912	0.2270	1.0803
102.5	-1927	0.2307	1.1370
102.5	-1942	0.2343	1.1764
102.5	-1951	0.2413	1.1978
102.5	-1971	0.2526	1.2034
125	-1863	0.2233	0.9572
125	-1924	0.2343	1.1306
125	-1947	0.2416	1.1696
125	-1983	0.2600	1.1608
149.6	-1870	0.2307	1.0169
149.6	-1897	0.2307	1.0752
149.6	-1932	0.2380	1.1362
149.6	-1969	0.2400	1.1560

Table 3: Clean Biphenylene Spectrum Results

Conclusion

The use of the TRAF function in ESR spectrometry shows serious promise. In various pieces of data the TRAF function improved resolution and S/N significantly. Examples of this can be seen clearly in the data gathered for the noisey tempo spectrum. The TRAF function regularly outperformed the exponential decay window function, which is commonly used for ESR post processing and improves S/N by around 100% in noisy spectra and typically decreased resolution5. These differences became especially prominent in the noisey biphenylene and noisey Tempo spectra.

The artifact does seem to limit the function of the TRAF function because the highest S/N and resolution improvement can be found at lower values of the line broadening constant, at which the artifact is present in the recovered spectra. Even so, the TRAF function outperformed the commonly used exponential decay window function, especially in S/N improvement. Again, the strengths of the TRAF function can be most clearly seen in the data for the noisey biphenylene spectrum and the noisey Tempo spectrum. Additionally, the recovered noisey Tempo spectrum showed the resolution enhancement capabilities of the TRAF function, where other window functions seem to fall short.

Moving forward, it would be worthwhile to investigate which frequencies are being amplified by the TRAF function to cause the artifact to occur in the recovered spectrum.

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