

chemical shift tensors we have obtained the following information:

1. For the  $\text{PHO}_3^{2-}$  anion the PH bond distance is 1.47 Å,  $\sigma_{\parallel}^{\text{P}} = 325.4$  ppm,  $\sigma_{\perp}^{\text{P}} = 437.9$  ppm,  $\Delta\sigma^{\text{P}} = -112.5$  ppm.  $\sigma_{\parallel}^{\text{H}} = 56.1$  ppm,  $\sigma_{\perp}^{\text{H}} = 34.9$  ppm, and  $\Delta\sigma^{\text{H}} = 21.2$  ppm.

2. The components of the proton and phosphorus chemical shift tensors are relatively insensitive to changes in the PH bond distance. Consequently, the temperature dependence of these chemical tensors should be very small.

3. For the phosphorus chemical shift tensor only  $\sigma_{\perp}$  changes significantly as a function of temperature; therefore, the CSA and isotropic chemical shift change by approximately the same amount and with the same slope.

4. The PH bond distance becomes shorter by about 5 pm for each proton added to the  $\text{PHO}_3^{2-}$  anion.

5. The deuterium quadrupole coupling constant increases with decreasing pH.

6. Accurate information about bond distances, bond angles, and charge distribution may be obtained at the 6-31G\* level. Valence double-zeta plus polarization (4-31G\*) was not adequate

to describe how the chemical shift tensor changes as a function of bond distance, however, and the 6-311G\*\* basis set must be used for accurate results. By accurate we mean that the values obtained from ab initio calculations agree with the experimental values obtained from solid-state NMR measurements, solution-state NMR experiments, and/or X-ray and neutron diffraction measurements. For quadrupole coupling constant calculations, the 6-31G\* and 6-311G\*\* seemed to give equivalent results.

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## Quantitative Magnetic Circular Dichroism Spectroscopy

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Some of the experimental problems associated with the quantitative measurement of the magnetic circular dichroism spectra of solid samples are discussed. In particular, it is shown that the loss of circularly polarized intensity by scattering and depolarization may be allowed for quantitatively in a simple way. The effect of slit width upon the measurement of the differential absorbance is found to be much less significant than it is in the case of conventional electronic spectroscopy.

### Introduction

The rapid modern development of magnetic circular dichroism (MCD) spectroscopy dates from the seminal reassessment of the theoretical foundations of the experiment by Buckingham and Stephens in 1966.<sup>1</sup> Though it was realized at an early stage of this development that accurate quantitative measurements would enable the extraction from the spectra of many interesting parameters,<sup>2</sup> the majority of the MCD work published prior to 1980 laid rather small emphasis upon quantitative results. The major reason for this is the fact that the measurements for which accurate quantitative results are most valuable are measurements made at very low temperatures. Since these measurements are performed made on solid samples, problems additional to those encountered with room temperature solution samples arise. Thus, over and above the requirement for an accurate measurement of the dichroism, the magnetic field, and the temperature, problems peculiar to low-temperature solid samples must be faced. Here we address two such problems: the effect upon the measured dichroism of the scattering and depolarizing centers, which are always present in a solid sample, and of bandwidth which is well-known to be important in the quantitative measurement of electronic absorption spectra. These problems are of an essentially practical nature. For some types of experiment, in particular those outside the linear limit of the MCD theory,<sup>3</sup> there are also theoretical considerations which bear upon the quantitative appli-

cations of the experimental data and which do not appear to have been investigated to date. One of these, the question of origin dependence, will be discussed in a forthcoming paper.<sup>4</sup>

The type of quantitative MCD experiments which we have in mind are those in which the substance of interest is doped into a crystal<sup>5</sup> or polymer host,<sup>6</sup> frozen in a glass,<sup>7</sup> or isolated in a noble-gas matrix.<sup>8</sup> The MCD experiments which may be performed upon such samples are the measurements of moments<sup>3,9</sup> or, in the case of paramagnetic samples, the study of their magnetization or saturation behavior.<sup>10</sup> References 5-10 emphasize the early pioneering work in this field. For more recent examples of quantitative MCD spectroscopy see refs 11-13.

### Discussion

**1. Scattering and Depolarizing Samples.** It is clear that samples which scatter and/or depolarize the light incident upon them, as solid samples always do to some extent, may render the

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measurement of dichroism,  $\Delta A$ , inaccurate. However, in what follows we shall show that, within certain reasonable limits to be detailed, the scattering does not affect the measured MCD, while the effect of the depolarization can be readily and quantitatively allowed for.

If  $I_0$  and  $I'$  are respectively the intensities of light incident upon and transmitted by a sample, then the decadic absorbance,  $A_{10}$ , of the sample is defined to be

$$A_{10} = \log(I_0/I') \quad (1a)$$

$A_{10}$  is proportional to the path length,  $L$ , of the light through the sample and to the concentration,  $C$ , of absorbing species in the sample. The constant of proportionality is  $E_{10}$ , the decadic extinction coefficient, i.e.

$$A_{10} = E_{10}CL \quad (2a)$$

Absorbance and extinction coefficient are usually reported in the literature as values of  $A_{10}$  and  $E_{10}$ . However, for the purposes of the present discussion it is much more convenient to use the quantities  $A_e$  and  $E_e$  corresponding to  $A_{10}$  and  $E_{10}$  but based upon natural logarithms, i.e.

$$A_e = \log_e(I_0/I') = 2.3026A_{10} \quad (1b)$$

$$A_e = E_eCL \quad (2b)$$

Thus, in the following we shall deal solely with absorbance and extinction coefficients as defined by eq 1b and 2b, leaving to the very end the trivial matter of conversion to the common forms  $A_{10}$  and  $E_{10}$ . In addition, since no confusion can arise, we shall drop the subscript  $e$  in order to simplify the notation.

Circular dichroism, natural or magnetic, is the differential absorption,  $\Delta A$ , of right (RCP) and left (LCP) circularly polarized light, which we denote by means of the subscripts R and L, respectively. Following Stephens,<sup>9</sup> we define

$$\Delta A = A_L - A_R \quad (3a)$$

$$\Delta E = E_L - E_R \quad (3b)$$

$$A = (A_L + A_R)/2 \quad (4a)$$

$$E = (E_L + E_R)/2 \quad (4b)$$

In the case of materials which are not naturally optically active,  $\Delta A$  and  $\Delta E$  are zero, except in the presence of a magnetic field directed along the direction of propagation of the light, under which conditions they measure the magnetic circular dichroism of the material.

We now imagine that a light-absorbing material, M, which is not naturally optically active, is dispersed in a nonabsorbing medium which also contains scattering centers, S, and depolarizing centers, D. The scattering and depolarizing centers may, of course, be one and the same. All incident light, LCP, RCP, and unpolarized, is assumed to be equally affected by the scattering and depolarizing centers, except insofar as unpolarized light cannot be depolarized, and the effect of these centers is further assumed to be independent of the strength of the magnetic field.

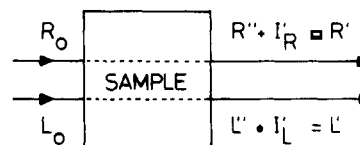
Now, if  $R$  is the intensity of RCP light, then, in the presence of a magnetic field, the decrease in  $R$ ,  $-dR$ , as the light propagates a distance of  $dl$  through the medium is given by eq 5.  $C_M$ ,  $C_D$ ,

$$-dR/dl = E_R C_M R + E_D C_D R + E_S C_S R \quad (5)$$

and  $C_S$  are respectively the concentrations of the absorbing material and the depolarizing and scattering centers.  $E_R$ ,  $E_D$ , and  $E_S$  are the corresponding extinction coefficients for RCP light, and also for LCP in the case of  $E_D$  and  $E_S$  as assumed above. Equation 5 implies that RCP light lost by scattering or depolarization may be formally viewed in the same way as light lost by absorption. For LCP light we have the corresponding equation

$$-dL/dl = E_L C_M L + E_D C_D L + E_S C_S L \quad (6)$$

The depolarization process produces randomly polarized light which can also be absorbed or scattered. The change in intensity,  $I_R$ , of the depolarized light when the sample is illuminated with



**Figure 1.** The fate of circularly polarized light traversing a sample which absorbs, scatters, and depolarizes the light.  $R_0$  ( $L_0$ ) is the intensity of the incident RCP (LCP) light.  $R''$  ( $L''$ ) is the intensity of the transmitted RCP (LCP) light.  $I'_R$  ( $I'_L$ ) is the intensity of the transmitted, randomly polarized light.  $R'$  ( $L'$ ) is the total intensity of transmitted light.

RCP light is given by eq 7. Equation 8 describes the corresponding situation for illumination with LCP light. Integration of eq 5

$$-(dR/dl) = -E_D C_D R + E_C M R + E_S C_S R \quad (7)$$

$$-(dL/dl) = E_D C_D L + E_C M L + E_S C_S L \quad (8)$$

from  $l = 0$  to  $L$  gives eq 9, in which  $R_0$  is the incident intensity

$$R = R_0 \exp[-(E_R C_M + E_D C_D + E_S C_S)L] \quad (9)$$

of RCP light. Integration of eq 6 results in a corresponding equation for LCP light. Substitution of eq 9 into (7) gives

$$-(dI_R/dl) = E_C M I_R + E_S C_S I_R - E_D C_D R_0 \exp[-(E_R C_M + E_D C_D + E_S C_S)L] \quad (10)$$

Integration of eq 10 gives<sup>14</sup>

$$I_R = [E_D C_D R_0 / \{C_M(E - E_R) - E_D C_D\}] \times [\exp\{-(E_R C_M + E_D C_D + E_S C_S)L\} - \exp\{-(E_C M + E_S C_S)L\}] \quad (11)$$

Equations 9 and 11, together with the corresponding results for LCP light, give us the intensities of circularly and randomly polarized light emerging from a medium which absorbs, scatters, and depolarizes a proportion of the circularly polarized light passing through it. The situation is illustrated diagrammatically in Figure 1.

In the absence of a magnetic field then, provided that  $R_0 = L_0$ ,  $R'' = L''$ ,  $I'_R = I'_L$  and consequently,  $R' = L'$ . In the presence of a magnetic field, and at absorbed wavelengths, only the first equality holds and the observed MCD of the sample,  $\Delta A_{\text{obs}}$ , is

$$\Delta A_{\text{obs}} = A_L - A_R$$

$$= \log_e(L_0/L') - \log_e(R_0/R')$$

$$= \log_e\{(R'' + I'_R)/(L'' + I'_L)\} \quad \text{because } R_0 = L_0$$

$$= \log_e\{[R_0 \exp(-A_R - A_D - A_S) + A_R\{\exp(-A_R - A_D - A_S) - \exp(-A - A_S)\}]/[L_0 \exp(-A_L - A_D - A_S) + A_L\{\exp(-A_L - A_D - A_S) - \exp(-A - A_S)\}]\}$$

where  $R = A_D R_0/(-A_R + A - A_D)$  and  $A_L = A_D L_0/(-A_L + A - A_D)$ . Using eq 3a and 4a, together with the fact that  $R_0 = L_0$ , the above expression for  $\Delta A_{\text{obs}}$  can be reduced to

$$\Delta A_{\text{obs}} = \log_e\{([\Delta A \exp(\Delta A/2 - A_D) - 2A_D]/[-2A_D + \Delta A])/[\Delta A \exp(\Delta A/2 - A_D) + 2A_D]/[2A_D + \Delta A]\} \quad (12)$$

Equation 12 gives the observed MCD,  $\Delta A_{\text{obs}}$ , in terms of the true MCD,  $\Delta A$ . We note that the effects of scattering do not enter into this relationship from which the true MCD can be determined if  $A_D$  is known.

In order to find  $A_D$  we first determine the connection between  $A_D$  and the degree of depolarization of the light passing through the medium in the absence of a magnetic field. Under this condition, and with the assumptions outlined above,  $I'_R = I'_L$  and  $R'' = L''$  (Figure 1). Then, according to eq 11

$$I' = I'_L = I'_R = R_0 \exp[-(E_C M + E_S C_S)L][\exp(-E_D C_D L) - 1]$$

and from eq 9

$$I' = L'' = R'' = R_0 \exp[-(E_C M + E_S C_S)L] \exp(-E_D C_D L)$$

(14) Benson, S. W. *The Foundations of Chemical Kinetics*; McGraw-Hill: New York, 1960.

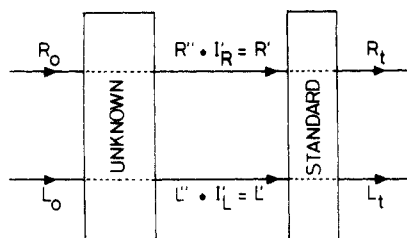


Figure 2. The fate of circularly polarized light traversing a sample which absorbs, scatters, and depolarizes the light, followed by passage through a naturally optically active standard.

Thus, the degree of depolarization of the circularly polarized incident light,  $I''/I'$ , is found to be

$$I''/I' = [-\exp(-E_D C_D L) + 1] / \exp(-E_D C_D L) \\ = [1 - \exp(-A_D)] / \exp(-A_D)$$

or

$$A_D = \log_e [(I''/I') + 1] \quad (13)$$

To proceed further we now allow the light emerging from the medium discussed above, in the *absence* of a magnetic field, to traverse a standard sample of a naturally optical material of known dichroism,  $\Delta a$ . The absorbances for LCP, RCP, and their average for this standard sample are  $a_L$ ,  $a_R$ , and  $a$ , respectively. The procedure is illustrated diagrammatically in Figure 2.  $R_t$  and  $L_t$  are the total transmitted intensities, of both polarized and unpolarized light, after passing through the unknown and the standard. They are given by eq 14 and 15. Therefore, the

$$R_t = R'' \exp(-a_R) + I'_R \exp(-a) \quad (14)$$

$$L_t = L'' \exp(-a_L) + I'_L \exp(-a) \quad (15)$$

observed circular dichroism of the standard,  $\Delta a_{\text{obs}}$ , is given by

$$\Delta a_{\text{obs}} = \log_e \left\{ \frac{R'' \exp(-a_R) + I'_R \exp(-a)}{L'' \exp(-a_L) + I'_L \exp(-a)} \right\} \\ = \log_e \left\{ \frac{I'' \exp(-a_R) + I' \exp(-a)}{I'' \exp(-a_L) + I' \exp(-a)} \right\} \quad (16)$$

where  $I''$  and  $I'$  are respectively the intensities of circularly polarized and randomly polarized light transmitted by the unknown. Using eq 4a to simplify 16, we obtain

$$\Delta a_{\text{obs}} = \log_e \left\{ \frac{\exp(\Delta a/2) + I''/I'}{\exp(-\Delta a/2) + I''/I'} \right\} \quad (17)$$

Thus the degree of depolarization of the light,  $I''/I'$ , can be determined from the observed,  $\Delta a_{\text{obs}}$ , and true,  $\Delta a$ , circular dichroism of the standard by using eq 17. By means of eq 13 we can then obtain  $A_D$  from which, using eq 12,  $\Delta A$  may be determined from  $\Delta A_{\text{obs}}$ . For the great majority of cases of practical interest the process is very simple as the data in Tables I and II show. Note that these data have been calculated by using decadic logarithms so that the circular dichroism values given are in the normal units for these quantities,  $\Delta a_{10}$  and  $\Delta A_{10}$ , in the notation used here.

Table I records the effect, calculated by means of eq 17, of using partially depolarized light to measure the circular dichroism of a sample of known  $\Delta a_{10}$ . We see that for true  $\Delta a_{10}$  values up to 0.01 the percentage decrease in measured circular dichroism is exactly equal to the percentage depolarization of the light. For  $\Delta a_{10}$  values below 0.5 the two percentages differ, but by an amount which would be very difficult to detect experimentally. Only for very high  $\Delta a_{10}$  values do significant deviations occur, and such values are rather rare in practice. It is clearly a very simple matter to choose a standard such that the measured  $100(\Delta a_{\text{obs}}/\Delta a_{\text{true}})$  gives the percentage depolarization of the light directly.

TABLE I: The Dependence, As Calculated According to Eq 17, of the Observed Circular Dichroism,  $\Delta a_{\text{obs}}$ , of a Standard upon Its True Dichroism,  $\Delta a_{\text{true}}$ , and the Percentage Depolarization of the Circularly Polarized Light Incident upon It

$100I''/(I'$ + $I'')^a$	$100(\Delta a_{\text{obs}}/\Delta a_{\text{true}})$					
	$\Delta a_{10}^b =$ 0.01	0.10	0.50	1.00	5.00	10.00
0.0	100.00	100.00	100.00	100.00	100.00	100.00
5.0	95.00	94.99	94.76	94.03	75.07	62.79
10.0	90.00	89.98	89.60	88.42	68.84	59.54
15.0	85.00	84.98	84.51	83.10	64.92	57.53
20.0	80.00	79.98	79.48	78.01	61.94	56.02
25.0	75.00	74.98	74.49	73.09	59.47	54.77
30.0	70.00	69.98	69.55	68.32	57.31	53.68
35.0	65.00	64.99	64.63	63.65	55.34	52.69
40.0	60.00	59.99	59.74	59.06	53.50	51.76
45.0	55.00	54.99	54.87	54.52	51.73	50.87
50.0	50.00	50.00	50.00	50.00	50.00	50.00

<sup>a</sup> Percentage depolarization. <sup>b</sup> Decadic circular dichroism.

TABLE II: The Relationship between the Observed Circular Dichroism,  $\Delta a_{\text{obs}}$ , of a Depolarizing Sample, Its True  $\Delta A$ ,  $\Delta A_{\text{true}}$ , and the Percentage Depolarization of the Radiation Transmitted by It, Calculated by Using Eqs 12 and 13

$100I''/(I' + I'')^a$	$100(\Delta a_{\text{obs}}/\Delta A_{\text{true}})$	
	$\Delta A_{10}^b = 10^{-5}-0.10$	$\Delta A_{10} = 1.00$
0.0	100.00	100.00
5.0	97.50	97.20
10.0	94.90	94.40
15.0	92.30	91.70
20.0	89.60	88.90
25.0	86.90	86.10
30.0	84.10	83.30
35.0	81.20	80.40
40.0	78.30	77.50
45.0	75.30	74.50
50.0	72.10	71.50

<sup>a</sup> Percentage depolarization. <sup>b</sup> Decadic circular dichroism.

Table II shows that for  $\Delta A_{10}$  values up to 0.1 and depolarizations of 20% or less a very simple rule holds:

$$\% \text{ decrease in } \Delta A = (\% \text{ depolarization}) / 2 \quad (18)$$

For example, if we look at the figure for 20% depolarization, we may imagine that the magnetically optically active material throughout the depolarizing sample is illuminated by polarized light which has a mean depolarization of 10%: 0% on entry to the sample and 20% on leaving it. Clearly, corrections can be made for higher depolarization and higher  $\Delta A_{10}$  values, but it seems unlikely that these, particularly the latter, will be required in practice.

One useful practical point should be noted in Table II. Even at 50% depolarization, the  $100(\Delta a_{\text{obs}}/\Delta A)$  value is constant up to  $\Delta A_{10} = 0.1$ . This is important in that it means that, whatever the correction to be applied, it can be applied with equal accuracy to both the maxima and the minima of  $|\Delta A|$ , throughout the MCD spectrum.

2. *The Effect of Spectral Bandwidth.* In some respects it is preferable to make fixed wavelength magnetization measurements with a somewhat wider spectral bandwidth than is usual for recording spectra. If the distribution of frequencies in the incident light is wide, it is to be expected that the intensity of the observed MCD will be comparatively insensitive to small field-dependent changes in the MCD line shape and the observed signal will be, in some sense, an integral over a portion of the band. Clearly, some signal intensity is lost by this procedure, but this is to some extent offset by a decrease in noise and can often be tolerated. However, it is well-known that for absorption spectra the use of excessively large spectral bandwidths leads to a loss of the linear dependence of the observed absorption on the true extinction coefficient, and it seems pertinent to enquire if this effect might

also distort measured MCD magnetization curves.

We start by considering the case for absorption. Let the intensity per unit frequency of light incident upon the sample be represented as a function of frequency by  $I_0(|w - w_0|)$ , where it is assumed that the distribution is symmetrical about the monochromator setting,  $w_0$ . Likewise, let the absorption line shape be  $A(|w - w_0|)$ . Then the transmitted intensity per unit frequency is given by

$$I'(|w - w_0|) = I_0 \exp[-A(|w - w_0|)] \quad (19)$$

and the observed absorbance  $A_{\text{obs}}(w_0)$  is given by

$$A_{\text{obs}}(w_0) = \log_e \left[ \int I_0(|w - w_0|) dw / \int I'(|w - w_0|) dw \right] \quad (20)$$

where the integrations are over the range of  $w$  for which  $I_0(|w - w_0|)$  is greater than zero. If we now assume a triangular slit function

$$I_0(|w - w_0|) = I_m[(w_m - w)/(w_m - w_0)] \quad (w_0 < w < w_m) \quad (21)$$

and a Gaussian absorption

$$A(|w - w_0|) = A_m \exp[-(w - w_0)^2/s^2] \quad (22)$$

we have

$$A_{\text{obs}}(w_0) = \log_e \left\{ \frac{(w_m - w_0)^2}{\int 2(w_m - w) \exp[-A_m \exp[-(w - w_0)^2/s^2]] dw} \right\} \quad (23)$$

The results of simple trapezium-rule quadratures of eq 23 for various values of  $x = s/(w_m - w_0)$  are presented in Figure 3. The expected, deviation from linearity is clear.

Turning to the MCD we have

$$\Delta A_{\text{obs}}(w_0) = \log_e (I'_L/I'_R) \quad (24)$$

The expression corresponding to eq 23 is

$$\Delta A_{\text{obs}}(w_0) = \log_e \left[ \frac{\int (w_m - w) \exp[-A_L \exp[-(w - w_0)^2/s^2]] dw}{\int (w_m - w) \exp[-A_R \exp[-(w - w_0)^2/s^2]] dw} \right] \quad (25)$$

This expression is plotted as a function of  $\Delta A_{\text{true}}$  for various values of  $s/(w_m - w_0)$  in Figure 4, the value of the total absorption being chosen to lie in the region where the nonlinearity in Figure 3 is most noticeable. Surprisingly, the MCD shows no appreciable departure from linearity in the range investigated. This is confirmed by examination of the numerical data.

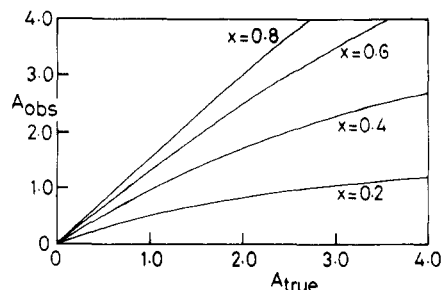


Figure 3. Values of observed absorbance,  $A_{\text{obs}}$ , calculated by using eq 23, plotted against the true absorbance,  $A_{\text{true}}$ , for various values of the parameter  $x = s/(w_m - w_0)$ .

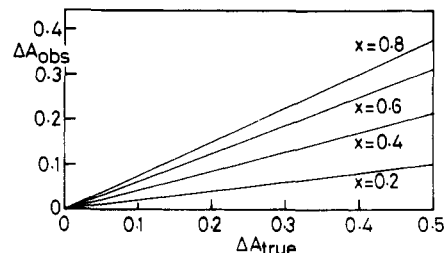


Figure 4. Values of observed differential absorbance,  $\Delta A_{\text{obs}}$ , calculated by using eq 25, plotted against the true differential absorbance,  $\Delta A_{\text{true}}$ , for various values of the parameter  $x = s/(w_m - w_0)$ .

Because this result is somewhat unexpected, it is interesting to see how it might arise. If we write

$$A_{\text{obs}} = f(A_{\text{true}}) \quad (26)$$

then

$$\Delta A_{\text{obs}} = f(A_{L,\text{true}}) - f(A_{R,\text{true}}) \quad (27)$$

or equivalently

$$\Delta A_{\text{obs}} = f(A_{\text{true}}/2 + \Delta A_{\text{true}}/2) - f(A_{\text{true}}/2 - \Delta A_{\text{true}}/2) \quad (28)$$

Expanding  $\Delta A_{\text{obs}}$  as a Taylor series about  $A_{\text{true}}/2$  we obtain

$$\Delta A_{\text{obs}} = \Delta A_{\text{true}} f'(A_{\text{true}}/2) + (1/24)(\Delta A_{\text{true}})^3 f'''(A_{\text{true}}/2) + \dots \quad (29)$$

We see that the condition for  $\Delta A_{\text{obs}}$  to be linear in  $A_{\text{true}}$  is that the third and higher odd order derivatives of  $A_{\text{true}}$  with respect to  $A_{\text{obs}}$  disappear. This would be true if  $A_{\text{true}}$  could be adequately represented by a quadratic function of  $A_{\text{obs}}$  in the range of interest. The form of Figure 3 makes this appear eminently reasonable.

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