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Correcting Nonlinear Response of Mercury Cadmium Telluride Detectors in Open Path Fourier Transform Infrared Spectrometry

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The effect of a nonlinear response of mercury cadmium telluride (MCT) detectors to photon flux is to cause a large offset and a slow variation in the zero-line of single-beam Fourier transform infrared (FT-IR) spectra, which dramatically reduce the accuracy to which strongly absorbing bands or lines can be measured. We describe a noniterative numerical technique by which the baseline offset can be corrected by adjusting the values of the maximum point in the interferogram (the "centerburst") and the points on either side. The technique relies on the presence of three spectral regions at which the signal is known to be zero. Two of these are found in all spectra, namely, the region below the detector cutoff and the high-wavenumber region just below the Nyquist wavenumber where the interferogram has been electronically filtered. In open path FT-IR measurements there are several regions where atmospheric water vapor and CO_2 are totally opaque. We have selected the region around 3750 cm^{-1}. This algorithm is even shown to work well when the interferogram is clipped, i.e., the value at the centerburst exceeds the dynamic range of the analog-to-digital converter.

In Fourier transform infrared (FT-IR) spectrometry, it is well-known that the effect of a nonlinear response of a mercury cadmium telluride (MCT) detector is to produce a slowly varying offset in the calculated single-beam spectrum.[1] The effect of this nonlinearity is that the measured interferogram is no longer exactly proportional to the incident flux. Various mechanisms have been proposed to account for the nonlinear response of MCT detectors. Bartoli et al.[2] have demonstrated that photon fluxes in excess of 10^{19} photons$\cdot$cm$^{-2}\cdot$s^{-1} would cause significant nonlinearity. Although on the average half the source radiation is passed to the detector at all times during the measurement of interferograms, the photon flux increases significantly as the optical path difference passes through zero. Some investigations reveal other factors that cause a nonlinear response, including series resistance,[3–5] detector illumination,[4–6] the effect of the resistance of MCT elements, and the associated amplifiers.[6] For all mechanisms, the MCT detector and associated electronics (preamplifier and amplifier) introduce nonlinearity to the measured interferogram that should be corrected prior to any further analysis.

The cause of the baseline offset is readily understandable. Let us say that the only point in the interferogram to be affected by detector nonlinearity was at the centerburst maximum. The difference between the measured and true interferogram would only be nonzero at this point. The Fourier transform of this "error interferogram" is a constant, nonzero value at all wavenumbers in the spectrum. In practice, more than one point is affected, but as we will show, the error is largely restricted to the three largest points near the centerburst, which is why the baseline offset varies so slowly across the spectrum. This effect was reported by Chase,[7] who observed that detector nonlinearity resulted in a nonzero value in the single-beam spectrum below the detector cutoff. However, he did not explicitly consider the effect above the detector cutoff. Subsequently, the appearance of "nonphysical energy" in the single-beam spectrum below the detector cutoff has been suggested as a way of checking the photometric accuracy of FT-IR spectrometers.[1,8] Bowie and Griffiths proposed that the apparent transmittance at the peak of strong bands in the spectrum of poly(ethylene terephthalate) could be used to check this effect in regions above the detector cutoff.[9]

Ways to correct detector nonlinearity have been reported for many years. Some are based on hardware modifications. Guelachvili[10] developed a new method for removing nonlinearity from two-output Fourier transform spectrometers by combining the modulated outputs, which have the same amplitudes and opposite phases, in a manner in which the nonlinear signal cancels itself out. But this method is applicable only to dual-port interferometers. Schindler[3] proposed a nonlinearity-correction circuit for photoconductive detectors that compensated for series resistance, but the circuitry he proposed degrades the signal-to-noise ratio (S/N) significantly. Carter et al.[11] illustrated a reduced nonlinear response from MCT detectors by changing the detector biasing

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(1) Griffiths, P. R.; de Haseth, J. A. *Fourier Transform Infrared Spectrometry*, 2nd ed.; Wiley Interscience: Hoboken, NY, 2007; pp 187−191.

(2) Bartoli, F.; Allen, R.; Esterowitz, L.; Kruer, M. *J. Appl. Phys.* **1974**, *45*, 2150–2154.

(3) Schindler, R. A. *NASA Tech. Brief.* **1986**, *10*, 47.

(4) Keens, A.; Simon, A. Correction of non-linearities in detectors in Fourier transform spectroscopy. United States Patent 4927269, May 22, 1990.

(5) Alam, M. S.; Predian, J. P. *Opt. Eng.* **2003**, *42*, 3491–3497.

(6) Rahmelow, K. *Appl. Opt.* **1997**, *36*, 2123–2132.

(7) Chase, D. B. *Appl. Spectrosc.* **1984**, *38*, 491–494.

(8) American Society for Testing and Materials. *Standard Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One Tests*; E 1421-91, **1991**.

(9) Bowie, B. T.; Griffiths, P. R. *Appl. Spectrosc.* **2000**, *54*, 1192–1202.

(10) Guelachvili, G. *Appl. Opt.* **1986**, *25*, 4644–4648.

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from constant current to constant voltage, which significantly alters the detector response but does not further address the fundamental problem for constant current-biased detectors. In general, constant voltage biasing is more linear than constant current biasing but less tolerant of wire resistance contributions.[6] A patent[12] has been issued for a constant voltage-biased photoconductive MCT detector/preamplifier/amplifier combination where the photometric response is linearized by a circuit that is calibrated for the relationship between the signal input to a given detector/preamplifier/amplifier combination with an accurate output signal. This technique is adopted by Varian, but does not work if the detector is not completely illuminated.[5] Carangelo et al.[13] devised a preamplifier to correct for the nonlinear response of the detector. The error caused by the second-order interferogram can be corrected by adjusting a parameter until the values in the spectral region below the cutoff frequency are minimized. The problem with all these hardware implementations is that as the photon flux on the detector changes, some component usually has to be changed concomitantly. Thus, different settings are typically required for sample and background interferograms.

Several software solutions have been proposed as alternatives to hardware correction approaches. Many software corrections follow a similar pattern. First, nonlinearity is modeled, and then coefficients of the model are refined with an iterative procedure according to some criteria. Nonlinear models usually invoke either a presumed or empirical function and can be applied to the measured interferogram[14] or the corresponding single-beam spectrum.[15] One criterion is the minimization of the spectral artifacts that are believed to be due to nonlinearity.[14,16,17] This is sometimes called the “out-of-band method”. Another criterion is minimization of the difference between the retrieved quantity from the measurement, such as the detector response curve, absorbance, etc., and a reference measurement. The reference could be a standard blackbody measurement,[18–20] response curves from a transfer-standard detector and a laser source,[21] or the concentration of the molecule.[15] This is called “in-band method”.

In this paper, we present a simple method to correct the nonlinear response of MCT detector in open path Fourier transform infrared (OP/FT-IR) spectrometry. In this method, the correction is implemented by modifying the signal intensities of just three points on the affected interferogram. The three points are the centerburst and the two adjacent points. Since these points have larger values than all the remaining points, they are believed to be most affected by nonlinear detector response. Results showed significant effectiveness of this correction method, and the artifactual nonzero baseline in the single-beam spectrum of the affected interferogram was largely removed. This approach also features fast and automatic computation since an iterative process that is common to most nonlinearity-correction algorithms is not employed. It can, therefore, be applied in real time.

THEORY AND ALGORITHM

Several investigations have revealed that detector nonlinearity predominantly affects only a few points around the centerburst where the largest variations of incident photon flux occur.[14,16,17] On the basis of this fact, we have made the assumption that the observed nonlinearity is ascribed to the incorrectly recorded intensities of the centerburst (i.e., the maximum point in the interferogram) and its two adjacent points. Therefore, the difference between the measured interferogram, $\mathrm{IGM_M}$, and the true one, $\mathrm{IGM_T}$, is a zero signal except for three negative voltage values at the centerburst and its two adjacent points. In order to mathematically describe the relationship between $\mathrm{IGM_M}$ and $\mathrm{IGM_T}$, we employ the δ function

$$\delta(t) = \begin{cases} 1 & (t = 0) \\ 0 & (\text{otherwise}) \end{cases} \tag{1}$$

where t denotes the independent variable in the time domain. The difference between the sum of all points in the measured interferogram, $\mathrm{IGM_M}$, and the true interferogram, $\mathrm{IGM_T}$, is

$$\mathrm{IGM_M} - \mathrm{IGM_T} = -a\delta(t - C) - b\delta(t - C - \Delta) - b'\delta(t - C + \Delta) \tag{2}$$

where C is the centerburst position and Δ is the (constant) sampling interval of the interferogram. The coefficients a, b, and b' are the differences between the true and recorded intensities of the centerburst and the right and the left adjacent points, respectively.

The real part of the Fourier transform of eq 2 yields the relationship between the measured and true single-beam spectra,

$$\mathrm{SBS_M} - \mathrm{SBS_T} = -a - b\cos(2\pi\Delta\tilde{\nu}) - b'\cos(-2\pi\Delta\tilde{\nu}) \tag{3}$$

where $\tilde{\nu}$ is the wavenumber in the frequency domain, $0 \le \tilde{\nu} \le 1/(2\Delta)$. In our OP/FT-IR system, interferograms are sampled at every second zero-crossing of the interferogram of a helium−neon laser, so Δ equals the wavelength of the HeNe laser, λ_{HeNe}. Since the wavenumber of HeNe laser is 15802 $\mathrm{cm^{-1}}$, the upper limit of $\tilde{\nu}$ is 7901 $\mathrm{cm^{-1}}$.

In our OP/FT-IR system, the low-wavenumber cutoff of the MCT detector is about 700 $\mathrm{cm^{-1}}$; a low-pass filter on the amplifier cuts off all signals at frequencies higher than 7000 $\mathrm{cm^{-1}}$.[22] Thus, the true single-beam spectrum, $\mathrm{SBS_T}$, is approximately equal to zero below 700 $\mathrm{cm^{-1}}$ and above 7500 $\mathrm{cm^{-1}}$. In practice, we examine the spectrum at 500 $\mathrm{cm^{-1}}$ instead of 0 $\mathrm{cm^{-1}}$ because we

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(11) Carter, R. O., III; Lindsay, N. E.; Beduhn, D. *Appl. Spectrosc.* **1990**, *44*, 1147–1151.
(12) Curbelo, R. United States Patent 5262635, Nov 16, 1993.
(13) Carangelo, R. M.; Hamblen, D. G.; Brouillette, C. R. United States Patent 5136154, Aug 4, 1992.
(14) Abrams, M. C.; Toon, G. C.; Schindler, R. A. *Appl. Opt.* **1994**, *33*, 6307–6314.
(15) Richardson, R. L., Jr.; Yang, H.; Griffiths, P. R. *Appl. Spectrosc.* **1998**, *52*, 565–571.
(16) Jeseck, P.; Camy-Peyret, C.; Payan, S.; Hawat, T. *Appl. Opt.* **1998**, *37*, 6544–6549.
(17) Fiedler, L.; Newman, S.; Bakan, S. *Appl. Opt.* **2005**, *44*, 5332–5340.
(18) Lachance, R. L.; Rochette, L. Non-linearity correction of FTIR instruments. Presented at the Fifth Workshop of Infrared Emission Measurements by FTIR, ABB Bomem, Québec City, Canada, Feb 9−11, 2000.
(19) Knuteson, R. O.; Revercomb, H. E.; Best, F. A.; Ciganovich, N. C.; Dedecker, R. G.; Dirkx, T. P.; Ellington, S. C.; Feltz, W. F.; Garcia, R. K.; Howell, H. B.; Smith, W. L.; Short, J. F.; Tobin, D. C. *J. Atmos. Oceanic Technol.* **2004**, *21*, 1777–1789.
(20) Kleinert, A. *Appl. Opt.* **2006**, *45*, 425–431.
(21) Zhang, Z. M.; Zhu, C. J.; Hanssen, L. M. *Appl. Spectrosc.* **1997**, *51*, 576–579.
(22) Shao, L.; Pollard, M.; Griffiths, P. R.; Westermann, D. T.; Bjorneberg, D. L. *Vib. Spectrosc.* **2007**, *43*, 78–85.

found that near 0 cm^{-1} most OP/FT-IR single-beam spectra are seriously affected by $1/f$ noise. So we have

$$\text{SBS}_\text{T}(\tilde{\nu}=500)=0 \tag{4}$$

$$\text{SBS}_\text{T}(\tilde{\nu}=7901)=0 \tag{5}$$

Inserting eqs 4 and 5 into eq 3 yields

$$\begin{aligned}\text{SBS}_\text{M}(\tilde{\nu}=500) &= -a-b\cos(2\pi(500/15802))-b'\cos(-2\pi(500/15802)) \\ &= -a-0.98b-0.98b'\end{aligned} \tag{6}$$

$$\begin{aligned}\text{SBS}_\text{M}(\tilde{\nu}=7901) &= -a-b\cos(2\pi(7901/15802))-b'\cos(-2\pi(7901/15802)) \\ &= -a+b+b'\end{aligned} \tag{7}$$

From SBS_M, values at $\tilde{\nu}=500\ \text{cm}^{-1}$ and $\tilde{\nu}=7901\ \text{cm}^{-1}$ are readily obtained. However, these two equations are not sufficient to solve for the three coefficients, a, b, and b'.

In order to find the third equation, we turned to the imaginary part of the Fourier transform. For an ideal symmetrical interferogram, the imaginary part of its Fourier transform is zero. In practice, however, the phase error is approximately constant across the spectrum, so the imaginary part has a very similar shape to the real part, albeit with different amplitude and sign. Therefore, for a true interferogram without nonlinearity, the imaginary part of its Fourier transform exhibits the same spectral features as the corresponding single-beam spectrum, i.e., the real part, and should have zero values above 7000 cm^{-1} due to the low-pass filter mentioned above.

Taking the imaginary part of the Fourier transform of eq 2, we obtain the following relationship,

$$\text{IMAG}_\text{M}-\text{IMAG}_\text{T}=b\sin(2\pi\,\Delta\tilde{\nu})+b'\sin(-2\pi\Delta\tilde{\nu}) \tag{8}$$

where IMAG_M is the imaginary part of the Fourier transform of the measured interferogram; IMAG_T is that free of the effects of a nonlinear detector response. Note that $\delta(t-C)$ is an even function at the centerburst, and the imaginary part of its Fourier transform is zero. From the analysis in previous paragraph, at $\tilde{\nu}=7000\ \text{cm}^{-1}$, IMAG_T equals zero, and eq 8 gives,

$$\begin{aligned}\text{IMAG}_\text{M}(\tilde{\nu}=7000) &= b\sin(2\pi(7000/15802))+b'\sin(-2\pi(7000/15802)) \\ &= 0.351b-0.351b'\end{aligned} \tag{9}$$

$\text{IMAG}_\text{M}(\tilde{\nu}=7000)$ is available from the imaginary part of Fourier transform. Now solution of the three equations, eqs 6, 7, and 9, yields coefficients a, b, and b'. The effect of the nonlinear detector response is corrected by adding a, b, and b' to the measured intensities of the centerburst and to the right and the left adjacent points, respectively.

IMPLEMENTATION

To implement this correction, the Fourier transform of the measured interferogram is calculated. Then three values are obtained from the real part at $\tilde{\nu}=500\ \text{cm}^{-1}$ and $\tilde{\nu}=7901\ \text{cm}^{-1}$, respectively, and from the imaginary part at $\tilde{\nu}=7000\ \text{cm}^{-1}$. In practice, we used the mean value of 100 points around each of the three wavenumbers in order to reduce the effect of noise. Finally, coefficients a, b, and b' are solved from eqs 6, 7, and 9 and added to the measured intensities of the centerburst, the right, and the left adjacent points of the interferogram, respectively.

In corrections of OP/FT-IR spectroscopy, another wavenumber for eq 8 other than 7000 cm^{-1} is 3750 cm^{-1}. Because of strong absorption by atmospheric water vapor, both the single-beam (real) and the imaginary spectra have approximately zero values between about 3900 and 3400 cm^{-1}. In this case, eq 9 is changed into

$$\begin{aligned}\text{IMAG}_\text{M}(\tilde{\nu}=3750) &= b\sin(2\pi(3750/15802))+b'\sin(-2\pi(3750/15802)) \\ &= 0.997b-0.997b'\end{aligned} \tag{10}$$

Equation 10 is more reliable than eq 9 in practice, since IMAG_M ($\tilde{\nu}=3750$) is almost three times larger than IMAG_M ($\tilde{\nu}=7000$), and the estimated value is less affected by noise. However, eq 10 is only applicable to the correction of interferograms in OP/FT-IR spectroscopy or when a sample is available that is totally opaque in a given spectral region. For continuous process monitoring using an MCT detector, a notch filter where the transmittance is zero in a spectral region of no interest (e.g., 2400−2300 cm^{-1}) could be mounted in the beam.

EXPERIMENTAL SECTION

OP/FT-IR measurements were carried out in June and July 2004 and January, March, and June 2005, on and around animal farms in southern Idaho in a cooperative project for monitoring gaseous emissions with the Northwest Irrigation and Soil Research Laboratory of the United States Department of Agriculture. The OP/FT-IR spectrometer was manufactured by MDA Corp. (Atlanta, GA), and incorporated a Bomem Michelson 100 interferometer, a 31.5 cm telescope, a cube-corner array retroreflector, and a Sterling engine-cooled MCT detector. Every OP/FT-IR interferogram was measured by coadding 16 interferograms at a nominal resolution of 1 cm^{-1}. All spectra for the analysis were computed with a zero-filling factor of 8 and Norton−Beer “medium” apodization; Mertz phase-correction method was used with 512 points around centerburst. All manipulation of spectra and data processing was done using MATLAB 7.0.1 (The MathWorks Inc., Natick, MA) on the Windows XP operating system. Other details about the OP/FT-IR experiments and data processing can be found in refs 22–24.

RESULTS AND DISCUSSION

In continuous atmospheric monitoring, the effect of wind can sometimes actually improve the optical alignment slightly; as a result, the centerburst intensities of some measured interferograms are very high. This condition provides us quite a few interferograms with excessively high centerburst intensities to test the correction performance of our method.

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(23) Shao, L.; Griffiths, P. R. *Anal. Chem.* **2007**, *79*, 2118–2124.

(24) Shao, L.; Griffiths, P. R. *Environ. Sci. Technol.* **2007**, *41*, 7054–7059.

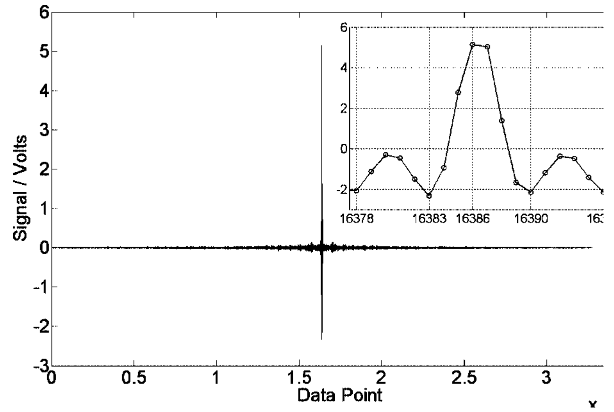

Figure 1. Measured OP/FT-IR interferogram with the centerburst located at point 16386; circles in the inset indicate the measured data points.

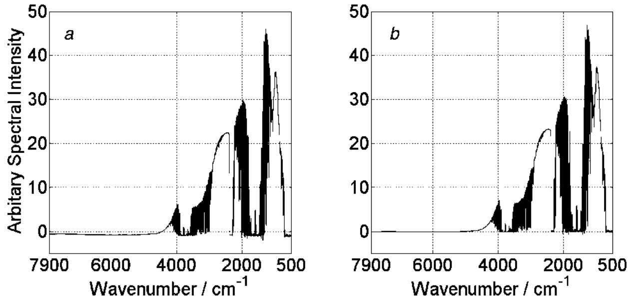

Figure 2. Real parts of the Fourier transforms of the (a) raw and (b) corrected interferograms.

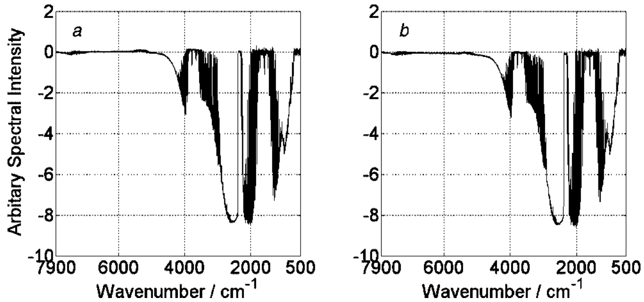

Figure 3. Imaginary parts of the Fourier transforms of the (a) raw and (b) corrected interferograms.

Correction Performance. The OP/FT-IR interferogram shown in Figure 1 was selected to test the correction method. It can be seen from the inset of Figure 1 that the centerburst and its two adjacent points are located at 16386, 16385, and 16387, respectively. Intensities of the three points were found to be 5.15, 2.77, and 5.04. The measured intensities of points 16386 and 16387 are quite close to the upper limit of the MCT detector in our OP/FT-IR system, and serious detector nonlinearity is expected. We performed Fourier transform to the raw interferogram and obtained the real and imaginary parts, as shown in Figures 2a and 3a. In both figures, one can observe obvious nonzero baselines. These baselines, according to above theoretical analysis, are caused by the nonlinear detector response.

When the raw interferogram was processed with our correction method, the intensities of the centerburst, and its left and right adjacent points were modified from 5.15, 2.77, and 5.04 to 5.92, 2.81, and 5.21, respectively. The accuracy to which the zero-energy level was calculated in the real and the imaginary parts of Fourier transform was substantially improved, as shown in Figures 2b and 3b. To evaluate the performance of this technique, single-beam spectra were calculated from the raw and the corrected interferograms. As noted above, in OP/FT-IR spectroscopy, the intensities in the single-beam spectrum at 3750, 2350, and 500 cm^{-1} should be very close to zero because of strong absorption by water vapor, carbon dioxide, and the detector response characteristics combined with the high-pass filter, respectively. In the uncorrected single-beam spectrum shown in Figure 4a, the spectral intensities at 3750, 2350, and 500 cm^{-1} are seen to be about 0.8 and 0.8 and 0.9 We therefore estimated the amplitude of the baseline error introduced by detector nonlinearity into the single-beam spectrum as about −0.8. It should be noted that the phase-correction algorithm has the effect of switching the sign of the intensity values in regions where the signal is very low. After nonlinearity correction, as shown in Figure 4b, spectral intensities at these wavenumbers were found to be 0.1, −0.1, and 0.0, and the amplitude of the residual baseline was about 0.1. Therefore, in this case, our correction method removed about 90% of the effect of nonlinearity. When the two single-beam spectra in Figure 4 are compared, the residual baseline is seen to be very small so that the error in the absorbance of strongly absorbing molecules is greatly diminished.

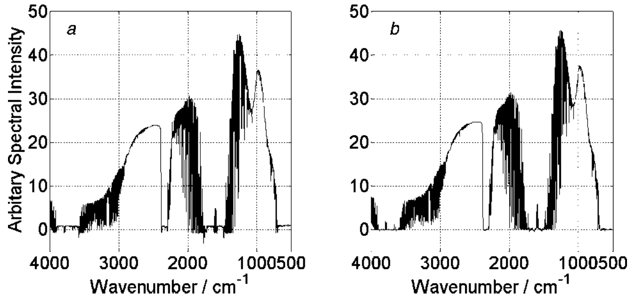

Figure 4. Single-beam spectra calculated from the (a) raw and (b) corrected interferograms.

To further evaluate the correction performance, we processed other OP/FT-IR interferograms with excessively high centerburst intensity. Those interferograms were measured in July, 2004 and January and June, 2005 on and around a dairy farm in southern Idaho; the meteorological conditions (wind and temperature) varied significantly both between and during these measurements. Average values of the single-beam spectrum in various regions before and after nonlinearity correction were calculated, and the baseline information was estimated and listed in Table 1. The data listed in this table confirm the effectiveness of the correction method. All nonzero baseline errors caused by detector nonlinearity were greatly reduced, especially those at 500 cm^{-1}. The fact that they were not completely eliminated indicated that some other points around the centerburst were also affected by the nonlinear detector response, but to nowhere near the same extent as the three largest points. For each single-beam spectrum in Table 1, the intensity changes made by the correction are different at different wavenumbers. This is because the baseline offset caused by detector nonlinearity is not constant, as suggested by eq 3. The data in Table 1 show the baselines in single-beam spectra were greatly, but not completely, reduced. Higher order

Table 1. Baseline Estimates of Single-Beam Spectra (a) before and (b) after Nonlinear Detector Response Correction

	intensities (a/b) at different wavenumber (cm^{-1})			
interferogram[a]	3750	2350	500	WNB[b]
no. 1	−0.62/−0.30	−0.45/−0.12	−0.70/0.00	38.6/39.2
no. 2	−0.78/−0.20	−0.66/−0.12	−0.91/0.00	33.7/34.6
no. 3	−0.30/−0.11	−0.19/−0.15	−0.42/0.00	35.6/36.0
no. 4	−0.41/−0.11	−0.30/−0.14	−0.53/0.00	36.0/36.5
no. 5	−1.34/−0.10	−1.34/−0.17	−1.68/0.00	46.3/47.9
no. 6	−0.73/−0.08	−0.73/−0.06	−0.84/0.00	38.8/39.6

[a] The interferograms are processed with high-pass filtering with a cutoff of ~480 cm^{-1} to remove the dc offset in the interferogram. [b] Intensities of the single-beam spectrum at wavenumbers where the maximum value of the single-beam spectrum occurs.

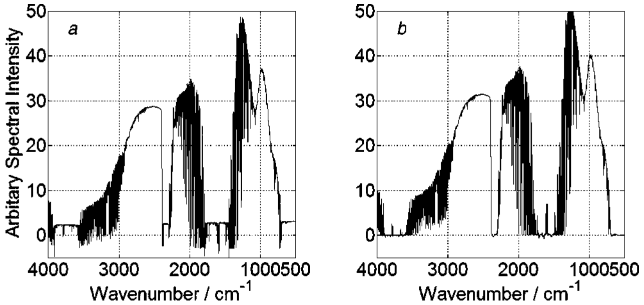

Figure 5. Single-beam spectra calculated from the raw (a) and the corrected (b) interferograms with clipped centerburst intensity.

nonlinearity might be present in the corresponding interferograms, and our method does not correct this type of nonlinearity.

In unattended OP/FT-IR monitoring sessions made on windy days, the optical alignment was occasionally greatly improved, presumably by the effect of wind, with the result that the intensities in the region of the centerburst of a few interferograms exceeded the dynamic range of MCT detector, i.e., the interferogram was "clipped". The approach described above appears to work equally well for clipped interferograms. We chose one such interferogram to illustrate the applicability of the correction method to such case. Of the points in the raw interferogram, the intensities of the centerburst and its left and right adjacent points were 5.28, 3.11, and 5.28, respectively, where 5.28 represents the maximum output of the analog-to-digital converter (ADC). The corresponding single-beam spectrum is shown in Figure 5a. As expected, there was a serious nonzero baseline, estimated to be at about −2.5. As a result, some strong lines in the spectrum of atmospheric water vapor give rise to negative values in the region of their maximum absorption, which leads to an invalid absorbance ($A_{peak} > \infty$). Thus, the determination of any analyte in a spectral region containing strongly absorbing water lines will be incorrect, even though the S/N may be fairly high. After nonlinearity correction, the intensities of the incorrect data points were modified to 7.21, 3.17, and 6.41, respectively. The residual baseline in the single-beam spectrum, shown in Figure 5b, was estimated as 0.2. In this case, the correction method described in this paper removed more than 90% of the effect of the error and no negative intensity values were recorded in the region of strong water lines.

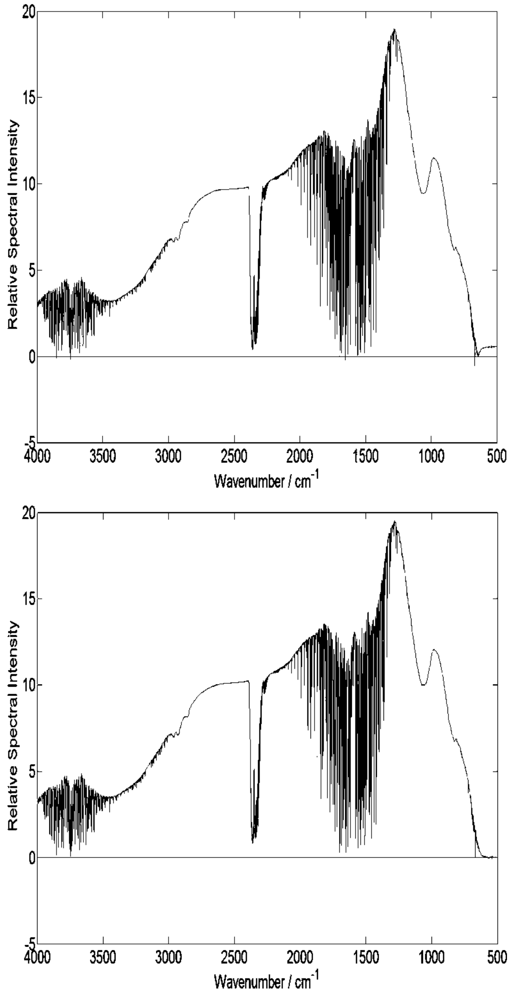

Figure 6. Short-path background spectrum (top) before and (bottom) after correction.

Nonlinearity Effects on Absorbance Spectrum. In most spectroscopic applications, the ultimate goal is to retrieve information for qualitative and quantitative analysis; to achieve this end, an accurate representation of the absorbance spectrum of each analyte and atmospheric interference must be obtained. In this section we evaluate the effect of detector nonlinearity on the accuracy to which absorbance may be measured in OP/FT-IR spectrometry where the spectral information is only useful in the so-called atmospheric windows, i.e., those spectral regions in which absorption by water vapor and carbon dioxide is weak. Absorbance spectra were calculated before and after correction for the nonlinear detector response. In all cases, a long path-length spectrum was ratioed against a short path-length background and converted to absorbance. The path-length for the background spectrum was so short that even the stronger lines in the spectrum of atmospheric water vapor do not absorb completely. Thus, to compensate for the effect of detector nonlinearity, we were forced to use another frequency where the signal should be zero, namely, at 7000 cm^{-1}, rather than 3750 cm^{-1}. The fact that 7000 cm^{-1} is close to one of the other frequencies that we use (7901 cm^{-1}) could mean that the correction would be less accurate than for the long-path spectra. However, the result appears to work well, as shown in Figure 6.

When a long-path spectrum is ratioed against a short-path spectrum, the effect of variations in the single-beam spectrum should be compensated, while the absorption spectra of water and

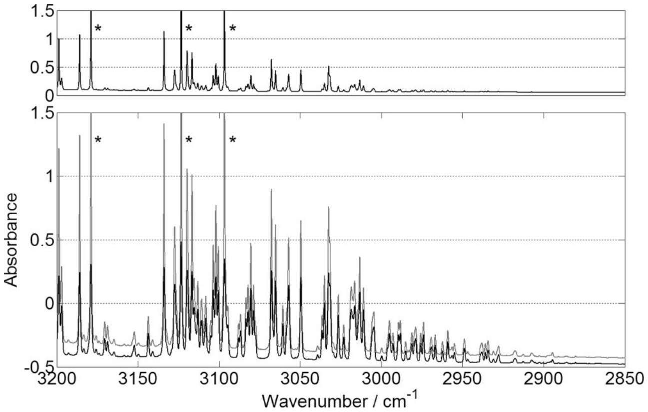

Figure 7. Absorbance spectra in atmospheric window of 3200−2850 cm^{-1} without (gray trace) and with (dark trace) nonlinear detector response correction. The trace in the upper axes is the difference between these two spectra. The absorbance values at 3179, 3124, and 3097 cm^{-1} on the gray trace (marked by asterisks) are meaningless because the corresponding single-beam spectral values are negative because of the effect of detector nonlinearity.

CO_2 still contribute strongly to the spectrum.[25] The fact that these spectra are often measured at different amplifier gains means that the baseline will generally not be at zero but the offset should be constant. However, differences in instrument alignment between the two measurements sometimes lead to an undulating baseline.

Absorbance spectra in the region between 2850 and 3200 cm^{-1} that were calculated by ratioing single-beam spectra of the type shown in Figure 5, parts a and b, against the corresponding corrected short-path background spectrum shown in Figure 6, bottom, are plotted in Figure 7. From the difference between the peak absorbance of water lines measured before and after correction for detector nonlinearity, one can see that the intensities of strong lines are changed significantly by the nonzero baseline. The more intense is a given water line, i.e., the closer the transmittance is to zero, the greater is the error introduced by detector nonlinearity. Thus, weak spectral features are less subject to the effect of detector nonlinearity than stronger features. However, the weaker is a given vibrational band or rotational line, the lower is the S/N at which it can be measured.

Even when an effective baseline removal method such as the application of wavelet transforms[24] is employed, the effect of detector nonlinearity will still lead to incorrect relative intensities and hence errors in quantification when strongly absorbing water vapor absorption lines are in the spectral region that is being examined. This statement is true no matter whether classical least-squares (CLS) or partial least-squares (PLS) regression is being used to retrieve quantitative information from OP/FT-IR spectra, although in practice the effect of detector response is even more critical for CLS as Beer's law must be strictly obeyed in this case. When PLS is applied, nonlinear Beer's law behavior may be partially compensated by the use of additional factors. For measurements made by our group, PLS regression has been the method of choice. For the spectral region shown in Figure 7, however, PLS regression cannot be carried out on the absorbance spectrum shown by the gray line, even though the S/N is high. The maxima of lines that are marked by asterisks, at 3179, 3124, and 3097 cm^{-1} on the gray trace are meaningless because corresponding single-beam spectral values are negative due to the effect of detector nonlinearity. After correction for the nonlinear detector response, however, the transmittance of all water lines is positive, and the spectrum appears to be of high quality.

CONCLUSION

In our investigation, all corrections were carried out completely automatically and noniteratively and yielded satisfactory results in all cases. The results are also consistent with our theoretical analysis of nonlinearity effects, i.e., incorrect intensities of the centerburst and its two adjacent points account for most of the effect of the nonlinear response of MCT detectors, and correcting the intensities of these three points removes most of the effects of nonlinearity.

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(25) Hart, B. K.; Berry, R. J.; Griffiths, P. R. *Environ. Sci. Technol.* **2000**, *34*, 1346–1351.