titration to assess the amount of water in BMIM PF_6. After applying stringent drying conditions (*in vacuo,* at 75 °C for 24 h), they report that the Karl–Fisher analysis indicated the water content to be ~0.015 M (or ~0.02% w/w). They found that sequential drying of BMIM PF_6 did not change their estimated $E_T(30)$ values considerably. Using three of the solvatochromic probes used in the present studies, Reichardt's dye, 1-pyrenecarboxaldehyde, and 1,3-*bis*-(1-pyrenyl)propane, ~0.1% w/w water within BMIM PF_6 can be readily detected and quantified.

CONCLUSION

We have clearly demonstrated the effect of the presence of small amounts of water within a popular RTIL, BMIM PF_6, on solvatochromic probe molecules possessing different chemical functionalities: pyrene, Reichardt's betaine dye, 1-pyrenecarboxaldehyde, and 1,3-*bis*-(1-pyrenyl)propane at ambient conditions. The solvatochromic probe nature of each of these four compounds is represented via a different spectroscopic parameter (i.e., I_I/I_{III} for pyrene, $\lambda_{max}^{absorbance}$ for Reichardt's betaine dye, $\lambda_{max}^{fluorescence}$ for 1-pyrenecarboxaldehyde, and I_E/I_M for 1,3-*bis*-(1-pyrenyl)propane). The presence of water has a profound effect on the latter three, whereas I_I/I_{III} for pyrene is unaffected. Changes in the cybotactic regions of probes with different functionalities due to the presence of trace amounts of water within BMIM PF_6 provides information about the interaction of a particular probe moiety with water in the immediate solubilizing micro-environment. Also, our results can be used effectively to detect and quantify water within BMIM PF_6 and other RTILs.

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Assessment of Detector Nonlinearity in Fourier Transform Spectroscopy

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INTRODUCTION

In Fourier transform spectroscopy (FTS), nonlinearity amplitude distortions in the interferograms are mainly due to the detector. In the case of photoconductive detectors, for example, the semiconductor MCT (Mercury-Cadmium-Telluride) detector, which is most frequently used for high-performance infrared measurements, the nonlinearities have been discussed in the literature (e.g., Ref. 1). For other infrared detectors, such as bolometers, the effect has not been studied with equal attention although some nonlinearity is expected to be present. Amplitude distortions in the interferogram induce, through Fourier transform (FT), radiometric errors in the acquired spectra.

In order to eliminate radiometric errors, the interferograms must be corrected before Fourier transformation by using either a measurement[2] or a model[3,4] of the real response of the acquisition system. An assessment of nonlinearity errors in FTS can also be made after Fourier transformation using the harmonic features that are introduced in the measured spectra by the nonlinear response. In Ref. 5 nonlinearity was detected by looking for a nonzero signal in the low-frequency region of the spectrum, where the spectral response should be equal to zero. This procedure

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may be difficult in the presence of 1/f noise, which prevents an accurate identification of the low frequency feature.

In this paper, a method for the detection and characterization of small nonlinearity effects by way of an analysis of the amplitude of the second harmonic feature in the acquired spectral distribution is presented and discussed. The method is applied to real measurements obtained from a far-infrared (FIR) interferometer with a ^{3}He cooled bolometric detector.

MODEL OF DETECTOR RESPONSIVITY

In an interferometer the output optical signal is given by a constant component plus a modulated component, i.e., the optical interferogram $I(x)$, where x is the optical path difference. The acquired interferogram signal $V(x)$ is obtained by taking the modulated component at the output of an AC-coupled preamplifier. In the case of nonlinear response, the acquired signal can be expanded into a power series of $I(x)$. The series expansion yields

$$V(x) = r_0[1 + \alpha I(x) + \beta I^2(x) + \cdots]I(x) \qquad (1)$$

where the coefficients of the power expansion, α and β, are in general dependent on the operating point, which is determined by the unmodulated optical signal. The frequency-dependent linear response of the acquisition system is assumed to be constant and equal to r_0. Both the detector and the electronics may contribute to the nonlinearities of the interferogram, but usually the effects of the latter can be made significantly smaller than those of the former. Therefore, we can assume that only detector nonlinearities contribute to Eq. 1.

Nonlinearity has different effects on acquired interferograms depending on the number of outputs used for the signal acquisition and processing. With a single output, both in rapid scanning or signal modulation techniques, the signal $V(x)$ includes all the terms of the series expansion; alternately, if the difference signal between the two output ports is used, the even terms cancel out and only the odd order terms in Eq. 1 are different from zero.[6] In this paper, we analyze Eq. 1 for a single output acquisition.

The measured spectrum $S(\sigma)$ is given by the FT of Eq. 1:

$$S(\sigma) = r_0[B(\sigma) + \alpha B(\sigma)*B(\sigma) + \beta B(\sigma)*B(\sigma)*B(\sigma) + \cdots] \qquad (2)$$

The first term $B(\sigma)$ is the detected spectral radiance, which is equal to the product of the input spectral radiance and the optical response of the interferometer. The other terms are convolutions of increasing order, which cause the generation of features at multiple frequencies (harmonics) of the original spectral distribution. The symbol * indicates the operation of convolution. In particular, the second term, corresponding to the autocorrelation of $B(\sigma)$, produces a feature centered at zero and a second harmonic feature, whereas the third term produces a first harmonic feature (that is superimposed to $B(\sigma)$) and a third harmonic feature.

In general, even terms of the series expansion of Eq. 1 give even harmonics in Eq. 2, and odd terms give odd harmonics. The maximum order of the harmonics produced by each term is equal to the order of the term. Usually, as the order of the term increases, its amplitude decreases. However, while this rule reliably applies within the subsets of the odd and the even terms, no general rule applies regarding the relative amplitudes of odd and even terms, which depend, respectively, on symmetric and antisymmetric distortions. The odd terms in general, and in particular the third term, which is the first and largest odd term, always contribute to some error at the frequencies in which $B(\sigma)$ is located (in-band distortion). The even terms in general, and in particular the second term, which is the largest even term, introduce some error into the measured spectrum only if the bandwidth of $B(\sigma)$ spans more than one octave.

Therefore, if the bandwidth of $B(\sigma)$ spans less than one octave, not only does the second term of nonlinear distortion not effect the wanted measured spectrum, but its presence can easily be observed and its amplitude can be determined. In this case, if a reliable model of the detector properties can be used to assess the relative amplitude of odd and even terms, the knowledge of the second term provides a useful means for estimating the in-band nonlinear distortions caused by the third term as well.

In the case of cryogenic bolometric detectors, nonlinearity in the responsivity depends on the nonlinear relation between the temperature variation, which is induced by the external photon flux, and the bolometer resistance. For semiconductor bolometers at temperatures below 1 K, the resistance R can be described as a function of temperature T by the parametric relation:[7]

$$R(T) = R_\infty e^{(\delta/T)^n} \qquad (3)$$

where R_∞ is equal to the asymptotic value of resistance for $T \gg \delta$, δ is equal to about 10–20 K depending on the material, and $n = 0.25$, 0.5, or 1 depending on the doping and temperature range.

Equation 3 can be used to assess the relative amplitude of odd and even terms of the nonlinear distortion. For this purpose, it can be expanded in a power series as a function of T around the operating point at $T = T_0$. For the sake of simplicity, $n = 1$ is considered.

$$\Delta R \approx R(T_0)\left\{-\frac{\delta}{T_0^2}\Delta T + \left[\frac{\delta}{T_0^3} + \frac{1}{2}\left(\frac{\delta}{T_0^2}\right)^2\right]\Delta T^2 - \left[\frac{\delta}{T_0^4} + \frac{\delta^2}{T_0^5} + \frac{1}{6}\left(\frac{\delta}{T_0^2}\right)^3\right]\Delta T^3\right\} \qquad (4)$$

For cryogenic bolometers with $T_0 \ll \delta$, the ratio between the third and second term of Eq. 4 turns out to have the same order of magnitude as the ratio between the second and the first term. Equation 4 can be compared with Eq. 1, assuming that $\Delta R \propto V$ and $\Delta T \propto I$. The comparison shows that the relative third-order nonlinear distortion βI^2 is about equal to $(\alpha I)^2$, and can be determined by measuring αI. The same result is also obtained for a general value of n and in the case of MCT detectors, where the responsivity is considered proportional to the cube root of the input power.[8]

NONLINEAR CHARACTERIZATION

In this section, we describe a procedure for the characterization of the nonlinear response in the case of a spectrum with a bandwidth smaller than one octave. In this case, the second harmonic distortion is not superimposed

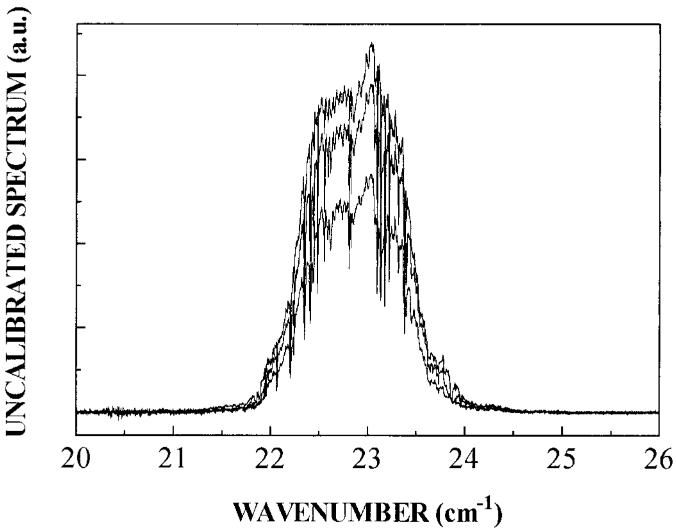

FIG. 1. Uncalibrated spectra in arbitrary units (a.u.) observed at 17 km flight altitude for zenith-angle views of 80°, 90°, and 92°, from top to bottom, respectively; (SAFIRE-A, APE-GAIA Campaign, 12 October 1999).

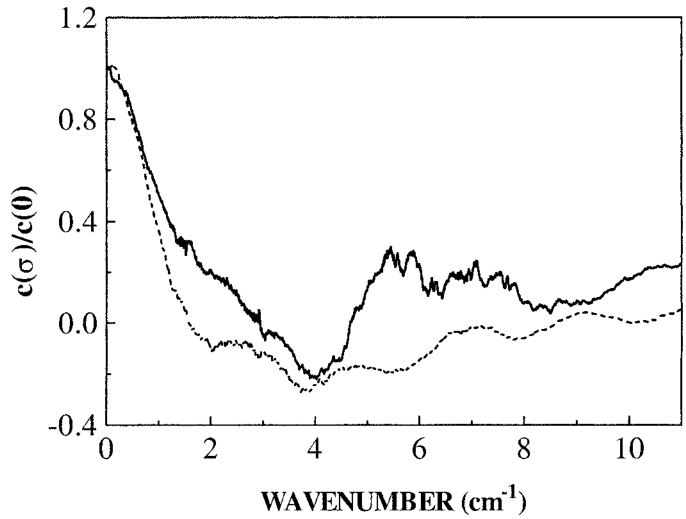

FIG. 2. Normalized second-order spectral correlation $c(\sigma)/c(0)$ against wave number for 80° zenith angle view (space view), calculated for the case of SAFIRE-A, APE-GAIA Campaign, 23 September 1999 flight (solid line) and 12 October 1999 flight (dashed line).

on the bandwidth of the spectrum. The procedure is based on the calculation of the spectral convolution $c(\sigma)$ between the overall measured spectrum $S(\sigma)$, given by Eq. 2, and the autocorrelation of $S_b(\sigma)$, where $S_b(\sigma) = F_b(\sigma) \cdot S(\sigma)$ is the measured spectrum in the desired spectral bandwidth (in-band spectrum) and $F_b(\sigma)$ is a filter that selects this bandwidth. In practice, in order to avoid 1/f noise in the autocorrelation term $S_b(\sigma) * S_b(\sigma)$, we limited our analysis to the second harmonic region, obtaining

$$c(\sigma) = S(\sigma) * \left\{ F_b\left(\frac{\sigma}{2}\right) \cdot [S_b(\sigma) * S_b(\sigma)] \right\} \quad (5)$$

$c(\sigma)$ has a peak at $\sigma = 0$, with a width on the order of twice the spectral bandwidth. In a first approximation, the amplitude of this peak can be calculated using $S(\sigma) \approx (\alpha/r_0) S_b(\sigma) * S_b(\sigma)$. In this case,

$$c(0) \approx \frac{\alpha}{r_0} \left\{ S_b(\sigma) * S_b(\sigma) * \left[F_b\left(\frac{\sigma}{2}\right) \cdot [S_b(\sigma) * S_b(\sigma)] \right] \right\}_{\sigma=0} \quad (6)$$

Since the term in curl braces is a constant that can be easily calculated, from the amplitude of the peak it is possible to determine the quantity α/r_0, which can be used in Eq. 1 to evaluate the distortion αI in the measured interferogram.

APPLICATION TO SAFIRE-A FAR INFRARED FT SPECTROMETER

Nonlinear characterization was applied to data acquired by the SAFIRE-A (Spectroscopy of the Atmosphere using Far InfraRed Emission—Airborne) instrument[9] during the APE-GAIA Antarctic campaign (Ushuaia, Argentina, September–October, 1999).[10] The instrument is an FIR-FT spectrometer that operated aboard the Russian M-55 Geophysica aircraft up to a maximum altitude of 21 km. SAFIRE-A provided limb sounding observations of atmospheric spectra, with a resolution of 0.004 cm^{-1} over two spectral channels: 22–23.5 cm^{-1} and 123–125 cm^{-1}, in which spectral features of O_3, ClO, N_2O, HNO_3, HCl, and H_2O, respectively are present. For the nonlinear assessment, we used data acquired from the first channel at 22–23.5 cm^{-1} with a photon noise limited bolometric detector operating at 0.3 K, which was developed at Queen Mary and Westfield College, London. Figure 1 shows, for example, typical uncalibrated spectra observed at different limb angles.

The normalized value of $c(\sigma)$ calculated with SAFIRE-A data is shown close to 0 cm^{-1} in Fig. 2 (continuous line for the 23 September 1999 flight and dashed line for the 12 October 1999 flight). The curves were obtained by taking the mean value over the whole flight (32 and 33 measurements, respectively) of $c(\sigma)$ for the 80° zenith angle view (space view) in which we measured the largest interferometric signal. A correlation peak is evident near 0 cm^{-1}, with a width equal to about 2 cm^{-1}, i.e., twice the optical bandwidth as expected. Consistent results were obtained for other zenith angle values in which the signal and, conse-

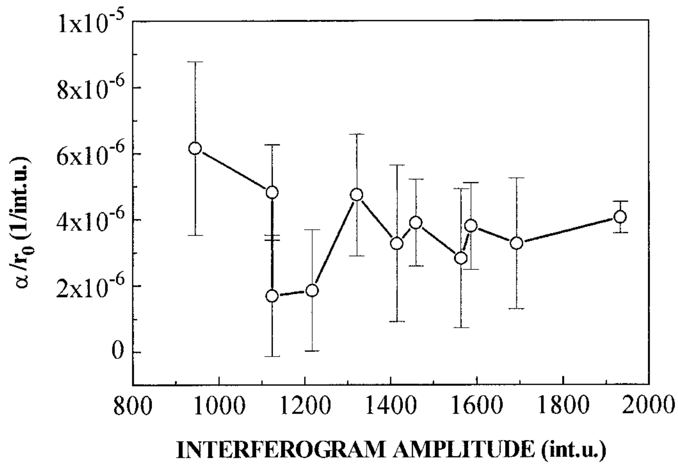

FIG. 3. Nonlinear parameter α/r_0 as a function of the signal amplitude expressed in terms of the number of interferogram units (int.u.) recorded at the maximum of the interferogram, for the SAFIRE-A, APE-GAIA Campaign, 12 October 1999.

quently, nonlinearity effects were lower. In this case, the correlation peak is measured with greater uncertainty.

In Fig. 3, the measured quantity α/r_0 is shown for the 12 October 1999 flight as a function of the interferogram amplitude obtained for different zenith angle values. The interferogram amplitude is expressed in terms of the number of interferogram units (int.u.) recorded at the maximum of the interferogram, and the quantity α/r_0 is expressed in terms of the inverse of int.u. The error bars were evaluated from the amplitude of the oscillations of $c(\sigma)$ around the correlation peak. The weighted mean value of α/r_0 is equal to $(3.8 \pm 1.6) \times 10^{-6}$ int.u.$^{-1}$. The value of the second-order component αI of the relative nonlinear distortion, which is approximately equal to the product $(\alpha/r_0)V$, can be obtained for each interferogram by multiplying the two parameters shown in Fig. 3. The maximum value of αI is equal to about 8 parts in 1,000, and it is reached in the case of the interferogram with the greatest amplitude. Within the measurement error, α/r_0 did not depend on the signal amplitude despite the fact that a different optical load of the detector, i.e., a different operating point, was known to be present for different signal amplitudes. The value of αI was obtained with a sensitivity of 0.001. Similar results were obtained from the measurements made during the other flights of the campaign.

The third-order component βI^2 of the relative nonlinear distortion, which is equal to about $(\alpha I)^2$ for bolometric and MCT detectors, turned out to have an upper limit of about 10^{-4}. This relative distortion, which directly introduces an error into the band of the measured spectrum (i.e., about 0.01% of the peak value), is negligible with respect to measurement error of the interferogram and does not pose a problem.

Nevertheless, if this detector had been used for measurements over a large spectral interval, so that the interferogram had a greater amplitude, this nonlinearity would have been a problem.

CONCLUSION

A procedure has been devised for the determination of the second-order component of nonlinear effects. This procedure can be used in the case of spectra that span less than one octave and that are derived from interferograms acquired from a single output of the interferometer. By starting from the knowledge of the second-order component, which affects the interferogram but does not introduce any error into the band of the measured spectrum, a suitable model of the detector response function can also provide the magnitude of the third-order component of nonlinearity. The third-order component also causes a distortion of the measured spectrum that cannot be directly determined from the measurement.

In the case of SAFIRE-A data, the measured second-order nonlinear term corresponds to a maximum relative error of 0.8% in the inteferogram amplitude, whereas the third-order term gives a maximum error of 0.01%, which causes a negligible distortion in the measured spectrum. The achieved sensitivity of about 1 part in 1,000 in the detection of the second harmonic distortion was high enough to make small nonlinear effects evident.

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